QUANTITATIVE INORGANIC ANALYSIS
By the same author

ELEMENTARY PRACTICAL ORGANIC CHEMISTRY

Part I. Small Scale Preparations.
Part II. Qualitative Organic Analysis.
Part III. Quantitative Organic Analysis.

Available in parts as listed or as one complete volume.

A TEXT-BOOK OF PRACTICAL ORGANIC CHEMISTRY, INCLUDING QUALITATIVE ORGANIC ANALYSIS

Third edition, revised and enlarged.

"It can be said of the third edition, as it could of the text when it was originally published, that if a student could have only one reference book available in the organic laboratory, he would make no mistake in choosing Vogel's Practical Organic Chemistry. Furthermore, at its moderate price he can be certain that he is getting full value for his money."—Journal of the American Chemical Society.

A TEXT-BOOK OF MACRO AND SEMIMICRO QUALITATIVE INORGANIC ANALYSIS

Fourth edition (new and enlarged version of Qualitative Chemical Analysis).

"As a textbook for undergraduates, the treatise has already proved its value and as a book of reference it must find a place in every library."—Science Progress.
A TEXT-BOOK OF
QUANTITATIVE
INORGANIC ANALYSIS
THEORY AND PRACTICE

BY
ARTHUR I. VOGEL, D.Sc. (Lond.), D.I.C., F.R.I.C.
Head of Chemistry Department, Woolwich Polytechnic:
Sometime Brit Scientific Research Fellow of the
Imperial College, London

With Diagrams and Illustrations

SECOND EDITION

LONGMANS, GREEN AND CO.
LONDON • NEW YORK • TORONTO
The kind reception accorded to the First Edition has encouraged the author in the belief that his main aims have been largely achieved. These include the provision of a text-book which will be of value: (i) to the student throughout the whole of his career and (ii) to practising analytical chemists and to all those workers who have occasion to utilise methods of quantitative inorganic analysis.

During the eleven years that have elapsed since the previous edition was published, inorganic analytical chemistry has developed in numerous directions, more particularly in the introduction of instrumental methods of analysis. It is now generally accepted that a training in at least some of the instrumental methods is highly desirable; it is hoped that sufficient new matter has been incorporated to meet this objective. It will be appreciated that some instruments are beyond the financial resources of the average College laboratory, and an attempt has been made to overcome this difficulty in a few cases by supplying full details for the construction of home-made instruments. Nevertheless, it is of the greatest importance that the balance between what might be termed the classical method and the modern instrumental method of training the student in inorganic analysis be maintained; this can be achieved only if due emphasis be placed upon classical methods in the course of instruction.

The task of revision has occupied several years, and new experimental work carried out in the author's laboratory has been included. In order to incorporate the very extensive changes and additions, the book has been entirely reset. It may be regarded as virtually a new work in which the desirable features of the First Edition have been retained: the broad aim has been to present, as far as is possible within the compass of a volume of moderate size, an up-to-date picture of quantitative inorganic analysis. The task of selecting, checking, and suitably arranging the extensive literature has not been easy; the author ventures to hope that he has at least succeeded in giving a reasonable account of the subjects which are of importance to the student during his period of training in analytical chemistry. The Selected Bibliography at the end of each chapter will assist the reader in locating the sources where further information may be found. The insertion of references to the literature throughout the text would have increased the length (and the price) of the book considerably; this feature, although of great value to advanced students and to practising analysts, has, after very careful consideration, not been included in the present edition. On the whole, it was decided that the volume was sufficiently large as a text-book, and that the inclusion of Selected Bibliographies might be acceptable as a reasonable compromise.

The text has been carefully revised, and due consideration has been given to comments, criticisms, and suggestions made by teachers and others throughout the world. The major changes in the Second Edition may now be enumerated:
Preface to Second Edition

Chapter I (THEORETICAL BASIS OF QUANTITATIVE INORGANIC ANALYSIS).

(i) Some of the Sections (e.g., determination of pH, experimental details concerning potentiometric titrations, polarographic methods, etc.) have been deleted, and are now included in an expanded form as individual Chapters.

(ii) A brief account of Flame Photometry and of Emission Spectrography is given.

(iii) Table XVIII (Forms in which Elements and Radicals are commonly Precipitated and Weighed in Gravimetric Analysis) has been revised, and may be regarded as a summary of modern gravimetric analysis.

(iv) Section I, 62, on Organic Precipitants has been completely revised.

(v) A new Section, I, 71, on the theory of the Electrolytic Separation of Metals with Controlled Cathode Potential has been added, as has also a brief account of Internal Electrolysis (I, 72).

Chapter II (EXPERIMENTAL TECHNIQUE OF QUANTITATIVE INORGANIC ANALYSIS).

(i) Section II, 9 (Other Types of Balances) has been expanded considerably.

(ii) Section II, 10D, includes an account of the mixed-resin procedure for preparing pure water.

(iii) The tables of tolerances for volumetric apparatus have been revised to conform with the pamphlet Tests on Volumetric Glassware issued by the Metrology Division of the National Physical Laboratory in January 1946.

(iv) Section II, 33 (Crucibles fitted with permanent porous plates) has been revised and enlarged.

(v) A new Section, II, 39 (Reductions with metals), which includes an account of the preparation and uses of the cadmium and silver reductors and of amalgamated zinc spirals, has been introduced.

Chapter III (VOLUMETRIC ANALYSIS).

(i) The use of pure anhydrous potassium ferrocyanide in the standardisation of potassium permanganate solutions (Sections III, 46, and III, 48, Procedure D).

(ii) The determination of manganese in steel by the persulphate-arsenite method (Section III, 61B).

(iii) The Sections dealing with Oxidations with Ceric Sulphate have been considerably modified. New procedures are given for the preparation of ceric sulphate solutions (Section III, 74), the determination of copper (III, 79), and the determination of molybdenum (III, 80).

(iv) Sections III, 97, Reductions with Vanadous Salts (based upon the work of C. M. Ellis in the author’s laboratory), and III, 98, Reductions with Chromous Salts, have been completely rewritten.

(v) An account is given of the preparation and uses of sodium starch glycollate indicator (III, 100), anhydrous sodium thiosulphate as a primary standard (III, 101 and III, 1040), the use of irreversible indicators in potassium iodate titrations (Sections III, 122, and III, 125), and the determination of iron with standard potassium iodate solution (III, 133).
Preface to Second Edition

Under Miscellaneous Volumetric Determinations are included:

(a) orthophosphate (III, 146);
(b) hardness of water with disodium dihydrogen ethylenediamine tetra-acetate (III, 148);
(c) ferric iron by titration with standard mercurous perchlorate solution (III, 152);
(d) zirconium (III, 153);
(e) silica (III, 154);
(f) calcium by the urea hydrolysis method (III, 155); and
(g) fluorine by titration with standard thorium nitrate solution (III, 156).

Chapter IV (Gravimetric Analysis).

The new determinations of individual elements and radicals are too numerous to be listed individually, but the following may be mentioned by way of illustration:

(a) sulphate as barium sulphate using agar-agar as coagulant (IV, 6);
(b) bismuth as bismuth orthophosphate (IV, 17E);
(c) aluminium as the basic benzoate and subsequent ignition to the oxide (IV, 28C);
(d) ferric iron as the oxinate (IV, 310);
(e) nickel as the dicyandiamidime complex (IV, 32D);
(f) cobalt as the α-nitroso-β-naphthol complex and weighing as cobalt sulphate or as metallic cobalt (IV, 33A); and
(g) thorium as thorium iodate (IV, 38C).

Sections IV, 77–86 (Electrolytic Determinations) have been considerably revised. Sections IV, 87–89 deal with Depositions with Controlled Potential at the Cathode, and full details are given, inter alia, for the construction of an apparatus for automatic control of the cathode potential. Extensive changes have been made in Section IV, 96 (Analysis of Steel).

Chapter V (Colorimetric Analysis—Spectrophotometry—Turbidimetry and Nephelometry—Fluorimetry).

This Chapter has been enlarged by the incorporation of accounts of more recent apparatus; several new determinations have been added.

Chapter VI (Potentiometric Titration Methods), Chapter VII (Conductometric Titration Methods), Chapter VIII (Polarography), and Chapter IX (Amperometric Titrations) are new. Attention is directed to the details for the construction of a polarograph in Chapter VIII.

Chapter IX (Gas Analysis) remains substantially unchanged. It was felt that a comprehensive text-book should contain an account of micro-analysis. A new Chapter XI (Micro-gravimetric and Micro-volumetric Analysis) has accordingly been included, and it is hoped that this will provide a useful introduction to this important subject.

It is impossible to make adequate acknowledgment to all who have contributed either directly or indirectly to the present volume. Commercial firms and organisations have always been willing to help in providing diagrams, descriptive literature, and special information, and
the names of these firms are given in the appropriate sections of the text. The author wishes to place on record the debt he owes to these firms and organisations, and takes this opportunity of thanking them for their assistance. In connexion with the experimental work, he is indebted to a number of undergraduates and staff (both laboratory and teaching) of the Chemistry Department of this Polytechnic.

Especial thanks are due to:

(i) H. E. Akerman and D. G. H. Ballard for their work with dicyandiamidine sulphate as a reagent for nickel.

(ii) C. M. Ellis, B.Sc., for checking and developing many of the determinations involving instrumental methods of analysis (potentiometric titrations, polarography, and amperometric titrations) and also for his experiments on vanadous sulphate solutions.

(iii) J. Leicester, M.Sc., F.R.I.C., for checking many of the new volumetric and some gravimetric procedures.

(iv) J. Palmer and C. Wadsworth for the construction of the polarograph and the apparatus for the automatic control of the potential at the cathode.

(v) J. Palmer and J. Watling for assistance in the preparation of many of the new diagrams.

(vi) C. M. Ellis, J. Leicester, and Dr. G. H. Jeffery for reading all the galley proofs and making a number of helpful suggestions.

(vii) Dr. G. H. Jeffery, F.R.I.C., for his assistance in a supervisory capacity in numerous ways; his advice upon many matters of detail has led to the elimination of much ambiguity.

I must acknowledge my indebtedness to Dr. A. Claassen of Eindhoven, Holland, who has given me the benefit of his wide experience and has also made a number of suggestions for new procedures which have been used.

The author would appreciate constructive suggestions for the improvement of the book and also to have his attention drawn to any errors which may have escaped his notice. 

Arthur I. Vogel


January, 1951.
In writing this book, the author had as his primary object the provision of a complete up-to-date text-book of quantitative inorganic analysis, both theory and practice, at a moderate price to meet the requirements of University and College students of all grades. It is believed that the material contained therein is sufficiently comprehensive to cover the syllabuses of all examinations in which quantitative inorganic analysis plays a part. The elementary student has been provided for, and those sections devoted to his needs have been treated in considerable detail. The volume should therefore be of value to the student throughout the whole of his career. The book will be suitable inter alia for students preparing for the various Intermediate B.Sc. and Higher School Certificate Examinations, the Ordinary and Higher National Certificates in Chemistry, the Honours and Special B.Sc. of the Universities, the Associateship of the Institute of Chemistry, and other examinations of equivalent standard. It is hoped, also, that the wide range of subjects discussed within its covers will result in the volume having a special appeal to practising analytical chemists and to all those workers in industry and research who have occasion to utilise methods of inorganic quantitative analysis.

The kind reception accorded to the author's Text Book of Qualitative Chemical Analysis by teachers and reviewers seems to indicate that the general arrangement of that book has met with approval. The companion volume on Quantitative Inorganic Analysis follows essentially similar lines. Chapter I is devoted to the theoretical basis of quantitative inorganic analysis, Chapter II to the experimental technique of quantitative analysis, Chapter III to volumetric analysis, Chapter IV to gravimetric analysis (including electro-analysis), Chapter V to colorimetric analysis, and Chapter VI to gas analysis; a comprehensive Appendix has been added, which contains much useful matter for the practising analytical chemist. The experimental side is based essentially upon the writer's experience with large classes of students of various grades. Most of the determinations have been tested out in the laboratory in collaboration with the author's colleagues and senior students, and in some cases this has resulted in slight modifications of the details given by the original authors. Particular emphasis has been laid upon recent developments in experimental technique. Frequently the source of certain apparatus or chemicals has been given in the text; this is not intended to convey the impression that these materials cannot be obtained from other sources, but merely to indicate that the author's own experience is confined to the particular products mentioned.

The ground covered by the book can best to judged by perusal of the Table of Contents. An attempt has been made to strike a balance between the classical and modern procedures, and to present the subject of analytical chemistry as it is to-day. The theoretical aspect
Preface to First Edition

has been stressed throughout, and numerous cross-references are given to Chapter I (the theoretical basis of quantitative inorganic analysis).

No references to the original literature are given in the text. This is because the introduction of such references would have considerably increased the size and therefore the price of the book. However, a discussion on the literature of analytical chemistry is given in the Appendix (Section A, 3). With the aid of the various volumes mentioned therein—which should be available in all libraries of analytical chemistry—and the Collective Indexes of Chemical Abstracts or of British Chemical Abstracts, little difficulty will, in general, be experienced in finding the original sources of most of the determinations described in the book.

In the preparation of this volume, the author has utilised pertinent material wherever it was to be found. While it is impossible to acknowledge every source individually (see, for example, Section A, 3), mention must, however, be made of Hillebrand and Lundell's Applied Inorganic Analysis (1929) and of Mitchell and Ward's Modern Methods in Quantitative Chemical Analysis (1932). In conclusion, the writer wishes to express his thanks: to Dr. G. H. Jeffery, A.I.C., for reading the galley proofs and making numerous helpful suggestions; to Mr. A. S. Nickelson, B.Sc., for reading some of the galley proofs; to his laboratory steward, Mr. F. Mathie, for preparing a number of the diagrams, including most of those in Chapter VI, and for his assistance in other ways; to Messrs. A. Gallenkamp and Co., Ltd., of London, E.C.2, and to Messrs. Fisher Scientific Co., of Pittsburgh, Pa., for providing a number of diagrams and blocks;* and to Mr. F. W. Clifford, F.I.A., Librarian to the Chemical Society, and his able assistants for their help in the task of searching the extensive literature.

Any suggestions for improving the book will be gratefully received by the author.

June, 1939.

* Acknowledgment to other firms and individuals is made in the body of the text.
CONTENTS

CHAPTER I

THE THEORETICAL BASIS OF QUANTITATIVE INORGANIC ANALYSIS

I, 1. Electrolytic dissociation ........................................... page 1
I, 2. The law of mass action ........................................... 3
I, 3. Application of the law of mass action to solutions of electrolytes 4
I, 4. Strengths of acids and bases ..................................... 5
I, 5. Activity and activity coefficient .................................. 6
I, 6. Ionisation of polybasic acids ...................................... 8
I, 7. Common ion effect ................................................ 9
I, 8. Solubility product .................................................. 11
I, 9. Completeness of precipitation. Quantitative effects of a common ion 14
I, 10. Limitations of the solubility product principle ................. 15
I, 11. Fractional precipitation .......................................... 17
I, 12. Complex ions ..................................................... 18
I, 13. Effect of acids upon the solubility of a precipitate .......... 20
I, 14. Effect of temperature upon the solubility of a precipitate .... 21
I, 15. Effect of the solvent upon the solubility of a precipitate .... 22
I, 16. The ionic product of water ...................................... 22
I, 17. The hydrogen-ion exponent, pH .................................. 23
I, 18. The hydrolysis of salts ........................................... 25
I, 19. Hydrolysis constant and degree of hydrolysis ............... 27
I, 20. Buffer solutions .................................................. 30

VOLUMETRIC ANALYSIS

I, 21. Volumetric analysis ............................................... 35
I, 22. Classification of reactions in volumetric analysis .......... 36
I, 23. Equivalent weights, Normal solutions .............................. 36
I, 24. Advantages of the use of the equivalent system for the preparation of standard solutions ......................................... 43
I, 25. Preparation of standard solutions ................................ 45
I, 26. Primary standard substances ...................................... 46

THEORY OF ACIDIMETRY AND ALKALIMETRY

I, 27. Neutralisation indicators ............................................ 47
I, 28. Preparation of indicator solutions ............................... 53
I, 29. Mixed indicators .................................................... 55
I, 30. Universal or multiple range indicators ......................... 56
I, 31. Neutralisation curves ............................................. 57
I, 32. Neutralisation of a strong acid and a strong base .......... 57
I, 33. Neutralisation of a weak acid with a strong base ............ 60
I, 34. Neutralisation of a weak base with a strong acid .............. 62
I, 35. Neutralisation of a weak acid with a weak base ............... 63
I, 36. Neutralisation of a polybasic acid with a strong base ........ 64
I, 37. Titration of solutions of hydrolysed salts. Displacement titration ................................................................. 66
I, 38. Choice of indicators in neutralisation reactions ............ 68
### THEORY OF PRECIPITATION AND COMPLEX-FORMATION PROCESSES

| I, 39. Precipitation reactions | Page 69 |
| I, 40. Complex-formation reactions | 70 |
| I, 41. Determination of end points in precipitation and in complex-formation reactions | 72 |

### THEORY OF OXIDATION–REDUCTION REACTIONS

| I, 42. THEORY OF OXIDATION–REDUCTION REACTIONS | Page 77 |
| I, 43. Electrode potentials | 78 |
| I, 44. Concentration cells | 80 |
| I, 45. Calculation of the e.m.f. of a voltaic cell | 81 |
| I, 46. Oxidation–reduction cells | 81 |
| I, 47. Calculation of the oxidation potential | 83 |
| I, 48. Equilibrium constants of oxidation–reduction reactions | 83 |
| I, 49. Change of the electrode potential during the titration of an oxidant and a reductant. Oxidation–reduction curve | 87 |
| I, 50. Indicators for the detection of the end point in oxidation–reduction titrations | 90 |
| I, 51. Potentiometric titration | 93 |

### OTHER PHYSICO-CHEMICAL METHODS OF ANALYSIS

| I, 52. Other physico-chemical methods of analysis | Page 94 |
| I, 53. Selected bibliography on the theory of volumetric analysis and some physico-chemical methods of analysis | 99 |

### THEORY OF GRAVIMETRIC ANALYSIS

| I, 54. Gravimetric analysis | Page 100 |
| I, 55. Precipitation methods | 100 |
| I, 56. The colloidal state | 104 |
| I, 57. Supersaturation and precipitate formation | 108 |
| I, 58. The purity of the precipitate. Co-precipitation | 109 |
| I, 59. Conditions of precipitation | 110 |
| I, 60. Washing of the precipitate | 111 |
| I, 61. Fractional precipitation | 112 |
| I, 62. Organic precipitants | 117 |
| I, 63. Volatilisation or evolution methods | 127 |

### ELECTRO-ANALYTICAL METHODS

| I, 64. Theory of electro-analysis | Page 128 |
| I, 65. Decomposition potential | 129 |
| I, 66. Electrode reactions | 131 |
| I, 67. Overvoltage | 132 |
| I, 68. Completeness of deposition | 132 |
| I, 69. Electrolytic separation of metals | 134 |
| I, 70. Character of the deposit | 135 |
| I, 71. Electrolytic separation of metals with controlled cathode potential | 136 |
| I, 72. Internal electrolysis | 138 |
| I, 73. Separation by miscellaneous physical methods | 139 |
| I, 74. Errors in quantitative analysis | 142 |
| I, 75. Classification of errors | 143 |
| I, 76. Minimisation of errors | 146 |
| I, 77. Significant figures and computations | 147 |
| I, 78. Selected bibliography on the theory of gravimetric analysis, organic reagents, electro-analysis and related subjects | 149 |
# CHAPTER II

**EXPERIMENTAL TECHNIQUE OF QUANTITATIVE ANALYSIS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II, 1.</td>
<td>Balance, weights, and weighing</td>
<td>151</td>
</tr>
<tr>
<td>II, 2.</td>
<td>Description of a typical analytical balance</td>
<td>151</td>
</tr>
<tr>
<td>II, 3.</td>
<td>The requirements of a good balance</td>
<td>152</td>
</tr>
<tr>
<td>II, 4.</td>
<td>Weights, reference masses</td>
<td>153</td>
</tr>
<tr>
<td>II, 5.</td>
<td>Care and use of the balance</td>
<td>154</td>
</tr>
<tr>
<td>II, 6.</td>
<td>Methods of weighing</td>
<td>155</td>
</tr>
<tr>
<td>II, 7.</td>
<td>Errors in weighing</td>
<td>161</td>
</tr>
<tr>
<td>II, 8.</td>
<td>Calibration of weights</td>
<td>164</td>
</tr>
<tr>
<td>II, 9.</td>
<td>Other types of balances</td>
<td>169</td>
</tr>
</tbody>
</table>

**GENERAL APPARATUS, REAGENTS AND OPERATIONS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II, 10.</td>
<td>General apparatus</td>
<td>176</td>
</tr>
<tr>
<td>II, 11.</td>
<td>Reagents</td>
<td>182</td>
</tr>
<tr>
<td>II, 12.</td>
<td>Purification of substances</td>
<td>184</td>
</tr>
<tr>
<td>II, 13.</td>
<td>Heating apparatus</td>
<td>185</td>
</tr>
<tr>
<td>II, 14.</td>
<td>Sampling of solids</td>
<td>187</td>
</tr>
<tr>
<td>II, 15.</td>
<td>Crushing and grinding</td>
<td>189</td>
</tr>
<tr>
<td>II, 16.</td>
<td>Solution of the sample</td>
<td>189</td>
</tr>
</tbody>
</table>

**TECHNIQUE OF VOLUMETRIC ANALYSIS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II, 17.</td>
<td>Unit of volume</td>
<td>191</td>
</tr>
<tr>
<td>II, 18.</td>
<td>Standard temperature</td>
<td>192</td>
</tr>
<tr>
<td>II, 19.</td>
<td>Volumetric apparatus</td>
<td>192</td>
</tr>
<tr>
<td>II, 20.</td>
<td>Measuring flasks</td>
<td>193</td>
</tr>
<tr>
<td>II, 21.</td>
<td>Pipettes</td>
<td>195</td>
</tr>
<tr>
<td>II, 22.</td>
<td>Burettes</td>
<td>197</td>
</tr>
<tr>
<td>II, 23.</td>
<td>Weight burettes</td>
<td>203</td>
</tr>
<tr>
<td>II, 24.</td>
<td>Graduated cylinders</td>
<td>203</td>
</tr>
<tr>
<td>II, 26.</td>
<td>Storage and preservation of solutions in volumetric analysis</td>
<td>204</td>
</tr>
</tbody>
</table>

**TECHNIQUE OF GRAVIMETRIC ANALYSIS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II, 26.</td>
<td>Precipitation</td>
<td>206</td>
</tr>
<tr>
<td>II, 27.</td>
<td>Filtration</td>
<td>207</td>
</tr>
<tr>
<td>II, 28.</td>
<td>Filter-papers</td>
<td>207</td>
</tr>
<tr>
<td>II, 29.</td>
<td>Macerated filter-paper</td>
<td>210</td>
</tr>
<tr>
<td>II, 30.</td>
<td>Filter-mats. Gooch crucibles</td>
<td>210</td>
</tr>
<tr>
<td>II, 31.</td>
<td>Preparation of a Gooch crucible</td>
<td>211</td>
</tr>
<tr>
<td>II, 32.</td>
<td>Munroe crucibles</td>
<td>213</td>
</tr>
<tr>
<td>II, 33.</td>
<td>Crucibles fitted with permanent porous plates</td>
<td>213</td>
</tr>
<tr>
<td>II, 34.</td>
<td>Washing of precipitates</td>
<td>215</td>
</tr>
<tr>
<td>II, 35.</td>
<td>Technique of filtration</td>
<td>216</td>
</tr>
<tr>
<td>II, 36.</td>
<td>Drying and ignition of precipitates</td>
<td>217</td>
</tr>
<tr>
<td>II, 37.</td>
<td>The care and use of platinum vessels</td>
<td>220</td>
</tr>
<tr>
<td>II, 38.</td>
<td>Perforated screens for crucibles</td>
<td>222</td>
</tr>
</tbody>
</table>

**MISCELLANEOUS OPERATIONS**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II, 39.</td>
<td>Reduction with metals</td>
<td>222</td>
</tr>
<tr>
<td>II, 40.</td>
<td>Selected bibliography on technique of quantitative analysis</td>
<td>226</td>
</tr>
</tbody>
</table>
CHAPTER III

VOLUMETRIC ANALYSIS

ACIDIMETRY AND ALKALIMETRY

III, 1. Preparation of a standard acid ........................................... 227
III, 2. Preparation of constant-boiling-point hydrochloric acid .......... 228
III, 3. Direct preparation of 0.1N-hydrochloric acid from the
    constant-boiling-point acid ........................................... 229
III, 4. Preparation of 0.1N-hydrochloric acid and standardisation ...... 229
III, 5. Preparation of standard alkali ........................................ 233
III, 6. Standardisation of the approximately 0.1N-sodium hydroxide ... 235
III, 7. Other standard substances for acidimetry and alkalimetry ....... 236
III, 8. Standard barium hydroxide (baryta) solution ....................... 239
III, 9. D.* of the Na₂CO₃ content of washing soda ......................... 239
III, 10. D. of the strength of glacial acetic acid ......................... 240
III, 11. D. of sulphuric acid in the concentrated acid .................... 241
III, 12. D. of sulphuric acid in the fuming acid (oleum) ................. 241
III, 13. D. of carbon dioxide in the atmosphere ........................... 242
III, 14. D. of a mixture of carbonate and hydroxide. Analysis of com-
    mercial caustic soda .................................................. 242
III, 15. D. of a mixture of carbonate and bicarbonate ................... 244
III, 16. D. of phosphoric acid in commercial orthophosphoric acid .... 245
III, 17. D. of boric acid and borax ....................................... 245
III, 18. D. of ammonia in an ammonium salt ................................ 246
III, 19. D. of nitrates (sodium nitrate in Chili saltpetre) .............. 248
III, 20. D. of nitrogen by Kjeldahl’s method ............................... 248

PRECIPITATION AND COMPLEX-FORMATION REACTIONS

III, 21. General discussion .................................................. 250
III, 22. Preparation of 0.1N-silver nitrate ................................ 250
III, 23. Standardisation of the silver nitrate solution .................... 251
III, 24. D. of chlorides .................................................... 252
III, 25. D. of bromides .................................................... 252
III, 26. D. of chlorides and bromides with standard mercurous per-
    chlorate solution ..................................................... 253
III, 27. D. of iodides ...................................................... 254
III, 28. D. of thiocyanates ................................................ 255
III, 29. D. of mixtures of halides with adsorption indicators .......... 255
III, 30. D. of mixtures of halides by an indirect method ................. 256
III, 31. Preparation and use of 0.1N-ammonium or potassium thioc-
    cyanate. Titrations according to Volhard’s method ................ 256
III, 32. D. of silver in a silver alloy .................................... 257
III, 33. D. of chlorides (Volhard’s method) ............................... 258
III, 34. D. of bromides (Volhard’s method) ................................ 259
III, 35. D. of iodides (Volhard’s method) ................................ 259
III, 36. D. of hyposulphites ............................................... 260
III, 37. D. of cobalt ....................................................... 260
III, 38. D. of nickel ....................................................... 261
III, 39. D. of fluoride as lead chlorofluoride ................................ 261
III, 40. D. of arsenic as silver arsenate .................................. 262
III, 41. D. of cyanides ..................................................... 263
III, 42. D. of nickel by potassium cyanide ................................ 264
III, 43. D. of thiocyanates ................................................ 265
III, 44. D. of barium and of sulphates .................................... 267

*D. = Determination.
## Contents

**OXIDATION–REDUCTION TITRATIONS. OXIDIMETRY AND REDUCTIMETRY**

### III. 45. General discussion

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXIDATIONS WITH POTASSIUM PERMANGANATE</td>
<td>268</td>
</tr>
<tr>
<td>General discussion</td>
<td>268</td>
</tr>
<tr>
<td>Preparation of 0.1N-potassium permanganate</td>
<td>271</td>
</tr>
<tr>
<td>Standardisation of permanganate solutions</td>
<td>272</td>
</tr>
<tr>
<td>Permanence of potassium permanganate solutions</td>
<td>275</td>
</tr>
<tr>
<td>Determination of ferrous iron</td>
<td>276</td>
</tr>
<tr>
<td>Reduction of ferric to ferrous iron</td>
<td>276</td>
</tr>
<tr>
<td>D. of iron in ferric ammonium sulphate</td>
<td>281</td>
</tr>
<tr>
<td>D. of the total iron in an iron ore</td>
<td>282</td>
</tr>
<tr>
<td>D. of calcium in calcium carbonate</td>
<td>282</td>
</tr>
<tr>
<td>Analysis of hydrogen peroxide</td>
<td>283</td>
</tr>
<tr>
<td>Analysis of sodium peroxide</td>
<td>284</td>
</tr>
<tr>
<td>D. of manganese dioxide in pyrolusite</td>
<td>284</td>
</tr>
<tr>
<td>D. of nitrites</td>
<td>285</td>
</tr>
<tr>
<td>D. of persulphates</td>
<td>286</td>
</tr>
<tr>
<td>D. of manganese in steel</td>
<td>287</td>
</tr>
<tr>
<td>D. of formates and of formic acid</td>
<td>289</td>
</tr>
<tr>
<td>D. of selenium</td>
<td>290</td>
</tr>
</tbody>
</table>

### III. 63. General discussion

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXIDATIONS WITH POTASSIUM DICHROMATE</td>
<td>292</td>
</tr>
<tr>
<td>Preparation of 0.1N-potassium dichromate</td>
<td>294</td>
</tr>
<tr>
<td>Standardisation of potassium dichromate solution against iron</td>
<td>294</td>
</tr>
<tr>
<td>D. of ferrous iron (iron in ferric ammonium sulphate)</td>
<td>295</td>
</tr>
<tr>
<td>D. of the total iron in an iron ore</td>
<td>296</td>
</tr>
<tr>
<td>D. of ferrous and ferric iron in an iron ore</td>
<td>296</td>
</tr>
<tr>
<td>D. of chromium in a chromic salt</td>
<td>297</td>
</tr>
<tr>
<td>D. of chromium in chromite</td>
<td>297</td>
</tr>
<tr>
<td>D. of manganese in steel or in manganese ore (Pattinson’s method)</td>
<td>299</td>
</tr>
</tbody>
</table>

### III. 73. General discussion

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXIDATIONS WITH CERIC SULPHATE</td>
<td>300</td>
</tr>
<tr>
<td>Preparation of 0.1N-ceric sulphate</td>
<td>302</td>
</tr>
<tr>
<td>Standardisation of ceric sulphate solutions</td>
<td>303</td>
</tr>
<tr>
<td>D. of oxalates</td>
<td>306</td>
</tr>
<tr>
<td>D. of iron in an iron ore</td>
<td>307</td>
</tr>
<tr>
<td>D. of nitrites</td>
<td>308</td>
</tr>
<tr>
<td>D. of copper</td>
<td>308</td>
</tr>
<tr>
<td>D. of molybdenum</td>
<td>309</td>
</tr>
<tr>
<td>D. of tellurium</td>
<td>310</td>
</tr>
<tr>
<td>D. of cerium</td>
<td>310</td>
</tr>
</tbody>
</table>

### III. 88. General discussion

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXIDATIONS WITH MANGANIC SULPHATE</td>
<td>312</td>
</tr>
<tr>
<td>Preparation and standardisation of manganic sulphate solutions</td>
<td>312</td>
</tr>
<tr>
<td>Applications of manganic sulphate solutions</td>
<td>313</td>
</tr>
</tbody>
</table>
Contents

REDUCTIONS WITH TITANOUS SALTS

III. 86. General discussion ........................................... 314
III. 87. Preparation of titanous solutions .......................... 314
III. 88. Standardisation of the titanous sulphate (or titanous chloride) solution ........... 315
III. 89. D. of iron in an ore ........................................ 316

REDUCTIONS WITH AMALGAMATED ZINC AND WITH LIQUID AMALGAMS

III. 90. General discussion ........................................... 317
III. 91. D. of uranium ................................................ 318
III. 92. D. of titanium ................................................ 318
III. 93. D. of molybdenum .......................................... 318
III. 94. D. of vanadium ............................................. 319
III. 95. D. of titanium (zinc amalgam method) .................... 319
III. 96. D. of tungsten .............................................. 321

III. 97. Reductions with vanadous (vanadium II) salts .......... 322
III. 98. Reductions with chromous salts ......................... 325

OXIDATION AND REDUCTION PROCESSES INVOLVING IODINE—IODIMETRY AND IODOMETRY

III. 99. General discussion ........................................... 328
III. 100. Detection of the end point ................................. 330
III. 101. Preparation of 0.1N-sodium thiosulphate ................. 333
III. 102. Standardisation of sodium thiosulphate solutions .... 334
III. 103. Preparation of 0.1N-iodine solution .................... 339
III. 104. Standardisation of iodine solutions ..................... 341
III. 105. D. of copper in crystallised copper sulphate ........... 343
III. 106. D. of copper in an ore .................................... 344
III. 107. D. of manganese dioxide in pyrolusite .................. 345
III. 108. D. of chlorates and of bromates ........................ 346
III. 109. Volumetric determination of lead ......................... 347
III. 110. Analysis of hydrogen peroxide ................................ 348
III. 111. D. of the available chlorine in bleaching powder .... 349
III. 112. D. of hypochlorites ........................................ 350
III. 113. D. of antimony ............................................ 350
III. 114. D. of antimony in antimonial oxide and in antimonates .... 351
III. 115. D. of arsenic in arsenic oxide and in arsenates .......... 351
III. 116. D. of tin .................................................. 352
III. 117. D. of antimony and tin in type metal .................... 353
III. 118. D. of sulphurous acid and of sulphites .................. 354
III. 119. D. of hydrogen sulphide and sulphides ................... 355
III. 120. D. of ferricyanides ....................................... 356
III. 121. D. of ferric iron (iodometric method) ................. 356

OXIDATIONS WITH POTASSIUM IODATE

III. 122. General discussion ........................................... 358
III. 123. Preparation of 0.1N (0.025M)-potassium iodate ........ 360
III. 124. D. of iodides ............................................. 361
III. 125. D. of arsenic or of antimony ............................. 362
III. 126. D. of copper .............................................. 362
III. 127. D. of mercury ............................................ 363
Contents

III, 128. D. of tin 363
III, 129. D. of peroxides (lead, barium, and manganese dioxides) 364
III, 130. D. of hydrogen peroxide 365
III, 131. D. of hydrazine 365
III, 132. D. of thallium 366
III, 133. D. of iron 366
III, 134. D. of vanadium 367

OXIDATIONS WITH POTASSIUM BROMATE
III, 135. General discussion 368
III, 136. Preparation of 0.1N-potassium bromate 369
III, 137. D. of antimony or of arsenic 369
III, 138. D. of metals by means of 8-hydroxyquinoline ("oxine") 371
III, 139. D. of hydroxylamine 375

OXIDATIONS WITH CHLORAMINE-T
III, 140. General discussion. Preparation and standardisation of 0.1N-solution 376
III, 141. D. of antimony 376
III, 142. D. of nitrites 377
III, 143. D. of tin 377
III, 144. D. of ferrocyanides 378

MISCELLANEOUS VOLUMETRIC DETERMINATIONS
III, 145. D. of zinc with standard potassium ferrocyanide solution 379
III, 146. D. of phosphorus 380
III, 147. D. of temporary and permanent hardness of water 382
III, 148. D. of the hardness of water ("didiette" or "Trilon B" method) 386
III, 149. D. of sodium 387
III, 150. D. of potassium 388
III, 151. D. of cadmium 388
III, 152. D. of ferrous iron with standard mercurous perchlorate solution 388
III, 153. D. of zirconium as the normal selenite, Zr(SeO₃)₂ 389
III, 154. D. of silica 390
III, 155. D. of calcium (urea hydrolysis method) 392
III, 156. D. of fluorine 393
III, 157. Selected bibliography on volumetric analysis 396

CHAPTER IV

GRAVIMETRIC ANALYSIS

IV, 1. General discussion 397
IV, 2. Note-book, entries, and calculations 397
IV, 3. Calculations of gravimetric analysis. Chemical factors 397

SIMPLE GRAVIMETRIC DETERMINATIONS
IV, 4. D. of water of hydration in crystallised barium chloride 398
IV, 5. D. of chloride as silver chloride 399
IV, 6. D. of sulphate as barium sulphate 401
IV, 7. D. of sulphur in iron pyrites 404
IV, 8. D. of iron as ferrie oxide 407
Contents

IV, 9. D. of aluminium as aluminium oxide 410
IV, 10. D. of calcium as oxalate 411
IV, 11. D. of magnesium as the ammonium phosphate hexahydrate and as the pyrophosphate 414
IV, 12. D. of nickel as the dimethylglyoxime complex 417

SYSTEMATIC GRAVIMETRIC ANALYSIS

IV, 13. General discussion 419
IV, 14. Lead 420
IV, 15. Silver 422
IV, 16. Mercury 423
IV, 17. Bismuth 425
IV, 18. Cadmium 427
IV, 19. Copper 430
IV, 20. Arsenic 433
IV, 21. Antimony 435
IV, 22. Tin 437
IV, 23. Molybdenum 439
IV, 24. Selenium and tellurium 441
IV, 25. Platinum 443
IV, 26. Palladium 444
IV, 27. Gold 445
IV, 28. Aluminium 447
IV, 29. Beryllium 450
IV, 30. Chromium 452
IV, 31. Iron 455
IV, 32. Nickel 457
IV, 33. Cobalt 461
IV, 34. Zinc 463
IV, 35. Manganese 465
IV, 36. Vanadium 468
IV, 37. Uranium 469
IV, 38. Thorium 470
IV, 39. Cerium 471
IV, 40. Titanium 473
IV, 41. Zirconium 473
IV, 42. Thallium 475
IV, 43. Calcium 477
IV, 44. Strontium 478
IV, 45. Barium 479
IV, 46. Magnesium 479
IV, 47. Sodium 481
IV, 48. Potassium 482
IV, 49. Lithium 484
IV, 50. Ammonium 490
IV, 51. Tungsten 491
IV, 52. Chloride 492
IV, 53. Bromide 493
IV, 54. Iodide 493
IV, 55. Thiocyanate 493
IV, 56. Cyanide 494
IV, 57. Fluoride 494
IV, 58. Chlorate 496
IV, 59. Perchlorate 496
IV, 60. Iodate 497
IV. 61. Sulphate .......................... 497
IV. 62. Sulphide ................................ 498
IV. 63. Sulphite ................................ 498
IV. 64. Thiosulphate .......................... 498
IV. 65. Phosphate .......................... 499
IV. 66. Phosphite ................................ 501
IV. 67. Hypophosphite .......................... 501
IV. 68. Oxalate ................................ 501
IV. 69. Borate ................................ 502
IV. 70. Silicate ................................ 502
IV. 71. Fluosilicate ................................ 505
IV. 72. Ferrocyancide .......................... 505
IV. 73. Ferricyancide .......................... 505
IV. 74. Nitrite ................................ 505
IV. 75. Nitrate ................................ 505
IV. 76. Carbonate ................................ 505

ELECTROLYTIC DETERMINATIONS

IV. 77. Apparatus ................................ 509
IV. 78. Copper ................................ 518
IV. 79. Lead ................................ 520
IV. 80. Cadmium ................................ 522
IV. 81. Nickel ................................ 523
IV. 82. Cobalt ................................ 524
IV. 83. Silver ................................ 524
IV. 84. Zinc ................................ 524
IV. 85. Bismuth ................................ 525
IV. 86. Electrolytic separation and determination of copper and nickel 526

DEPOSITIONS WITH CONTROLLED POTENTIAL AT THE CATHODE

IV. 87. General considerations .......................... 527
IV. 88. Controlled potential electro-analysis. Apparatus for automatic control of cathode potential ....... 530
IV. 89. Determination of metals in alloys using controlled potential of the cathode ................................ 545

IV. 90. SIMPLE GRAVIMETRIC SEPARATIONS 548

ANALYSES OF COMPLEX MATERIALS

IV. 91. Analysis of brass .......................... 555
IV. 92. Analysis of bronze .......................... 560
IV. 93. Analysis of nickel silver .......................... 562
IV. 94. Analysis of solder ................................ 563
IV. 95. Analysis of a silver coinage alloy .......................... 565
IV. 96. Analysis of steel ................................ 566
IV. 97. Analysis of an aluminium alloy .......................... 581
IV. 98. Analysis of a limestone or dolomite .......................... 582
IV. 99. Analysis of a felspar ................................ 588
IV. 100. Analysis of portland cement .......................... 592
IV. 101. Selected bibliography on gravimetric analysis .......................... 596
CHAPTER V
COLORIMETRIC ANALYSIS—SPECTROPHOTOMETRY—TURBIDIMETRY AND NEPHELOMETRY—FLUORIMETRY

V, 1. General discussion .......................................................... 598
V, 2. Theory of spectrophotometry and colorimetry ......................... 599
V, 3. Classification of methods of "colour" measurement or comparison. 603
V, 4. Standard series method ...................................................... 605
V, 5. Duplication method ............................................................ 607
V, 6. Balancing method ............................................................... 608
V, 7. Photo-electric filter photometer method ................................ 611
V, 8. Turbidimetry, nephelometry and fluorimetry ............................ 634
V, 9. Determination of pH by colorimetric methods .......................... 633
V, 10. Some general remarks upon colorimetric determinations ......... 641
V, 11. Determination of ammonia ................................................ 643
V, 12. Determination of nitrites .................................................. 644
V, 13. Determination of iron ....................................................... 645
V, 14. Manganese ....................................................................... 648
V, 15. Titanium ........................................................................... 649
V, 16. Vanadium ......................................................................... 650
V, 17. Chromium ......................................................................... 651
V, 18. Aluminium ......................................................................... 652
V, 19. Molybdenum ...................................................................... 653
V, 20. Nickel ............................................................................... 654
V, 21. Cobalt ............................................................................... 655
V, 22. Arsenic .............................................................................. 656
V, 23. Antimony .......................................................................... 657
V, 24. Tin .................................................................................... 660
V, 25. Lead .................................................................................. 661
V, 26. Copper .............................................................................. 662
V, 27. Bismuth ............................................................................. 663
V, 28. Magnesium ........................................................................ 664
V, 29. Silicate .............................................................................. 665
V, 30. Sulphate ............................................................................ 666
V, 31. Determination of other elements and radicals ...................... 671
V, 32. Selected bibliography ......................................................... 672

CHAPTER VI
POTENTIOMETRIC TITRATION METHODS

VI, 1. General considerations .......................................................... 673
VI, 2. Determination of pH ............................................................. 675
VI, 3. Potentiometric titrations. Classical method .............................. 688
VI, 4. Potentiometric titrations. Simplified electrode systems and methods ................................................................. 692
VI, 5. Titrations with the Karl Fischer reagent .................................. 693
VI, 6. Some applications of the Karl Fischer reagent ....................... 708
VI, 7. Some experimental details for potentiometric titrations ........... 709
VI, 8. Standardisation of sodium thiosulphate or of iodine solution with potassium permanganate or with potassium dichromate 711
## Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI, 9</td>
<td>D. of the available chlorine in bleaching powder</td>
<td>711</td>
</tr>
<tr>
<td>VI, 10</td>
<td>D. of copper</td>
<td>712</td>
</tr>
<tr>
<td>VI, 11</td>
<td>D. of chromium</td>
<td>712</td>
</tr>
<tr>
<td>VI, 12</td>
<td>D. of manganese</td>
<td>713</td>
</tr>
<tr>
<td>VI, 13</td>
<td>D. of cobalt</td>
<td>715</td>
</tr>
<tr>
<td>VI, 14</td>
<td>Selected bibliography</td>
<td>717</td>
</tr>
<tr>
<td>VII, 1</td>
<td>General considerations</td>
<td>718</td>
</tr>
<tr>
<td>VII, 2</td>
<td>Apparatus and measurements</td>
<td>720</td>
</tr>
<tr>
<td>VII, 3</td>
<td>Applications of conductometric titrations</td>
<td>725</td>
</tr>
<tr>
<td>VII, 4</td>
<td>Some experimental details for conductometric titrations</td>
<td>730</td>
</tr>
<tr>
<td>VII, 5</td>
<td>Selected bibliography</td>
<td>733</td>
</tr>
<tr>
<td>VIII, 1</td>
<td>General introduction</td>
<td>734</td>
</tr>
<tr>
<td>VIII, 2</td>
<td>Theoretical principles</td>
<td>737</td>
</tr>
<tr>
<td>VIII, 3</td>
<td>Quantitative technique</td>
<td>743</td>
</tr>
<tr>
<td>VIII, 4</td>
<td>Evaluation of quantitative results</td>
<td>745</td>
</tr>
<tr>
<td>VIII, 5</td>
<td>Simple homemade polarograph</td>
<td>746</td>
</tr>
<tr>
<td>VIII, 6</td>
<td>Ancillary equipment</td>
<td>750</td>
</tr>
<tr>
<td>VIII, 7</td>
<td>Commercial manual non-recording polarographs</td>
<td>755</td>
</tr>
<tr>
<td>VIII, 8</td>
<td>Commercial recording polarographs</td>
<td>758</td>
</tr>
<tr>
<td>VIII, 9</td>
<td>D. of the half-wave potential of the cadmium ion in N-potassium chloride solution</td>
<td>762</td>
</tr>
<tr>
<td>VIII, 10</td>
<td>D. of the half-wave potentials of the zinc and manganese ions in N-potassium chloride solution</td>
<td>764</td>
</tr>
<tr>
<td>VIII, 11</td>
<td>D. of cadmium in solution</td>
<td>765</td>
</tr>
<tr>
<td>VIII, 12</td>
<td>Investigation of the influence of dissolved oxygen</td>
<td>766</td>
</tr>
<tr>
<td>VIII, 13</td>
<td>D. of magnesium with 8-hydroxyquinoline</td>
<td>766</td>
</tr>
<tr>
<td>VIII, 14</td>
<td>Selected bibliography</td>
<td>768</td>
</tr>
<tr>
<td>IX, 1</td>
<td>Theoretical considerations</td>
<td>769</td>
</tr>
<tr>
<td>IX, 2</td>
<td>Technique of amperometric titrations with the dropping mercury electrode</td>
<td>772</td>
</tr>
<tr>
<td>IX, 3</td>
<td>D. of lead with standard potassium dichromate solution</td>
<td>773</td>
</tr>
<tr>
<td>IX, 4</td>
<td>D. of sulphate with standard lead nitrate solution</td>
<td>774</td>
</tr>
<tr>
<td>IX, 5</td>
<td>D. of nickel with dimethylglyoxime</td>
<td>775</td>
</tr>
<tr>
<td>IX, 6</td>
<td>Selected bibliography</td>
<td>777</td>
</tr>
</tbody>
</table>
Contents

CHAPTER X

GAS ANALYSIS

X, 1. General discussion 778
X, 2. Sampling 779
X, 3. Purification of mercury 780
X, 4. Correction of volume of gas for temperature and pressure 781
X, 5. Calibration of gas measuring vessels 783
X, 6. Apparatus employed in gas analysis 784
X, 7. Absorbents for various gases 800
X, 8. Determination by explosion and combustion methods 804
X, 9. Exercises in gas analysis 806

GAS-VOLUMETRIC METHODS OF ANALYSIS FOR SOLIDS AND LIQUIDS

X, 10. The Lange nitrometer 808
X, 11. D. of nitrates 808
X, 12. D. of hydrogen peroxide 810
X, 13. Evaluation of pyrolusite 811
X, 14. D. of the available chlorine in bleaching powder 812
X, 15. Evaluation of zine dust 812
X, 16. D. of ammonium salts 812
X, 17. Selected bibliography 813

CHAPTER XI

MICRO-GRAVIMETRIC AND MICRO-VOLUMETRIC ANALYSIS

XI, 1. General discussion 814
XI, 2. Micro-balances 814
XI, 3. Miscellaneous apparatus for micro-analysis 816
XI, 4. Apparatus for quantitative filtration 823
XI, 5. Apparatus for micro-volumetric analysis 829
XI, 6. Some simple micro-gravimetric determinations 835
XI, 7. Some simple micro-volumetric determinations 837
XI, 8. Selected bibliography on micro-gravimetric and micro-volumetric analysis 840

APPENDIX

A, 1. International atomic weights, 1949 841
A, 2. Chemical factors 842
A, 3. The literature of analytical chemistry 845
A, 4. Densities of acids at 20° C. 851
A, 5. Densities of alkaline solutions at 20° C. 853
A, 6. Data on the strength of aqueous solutions of the common acids and of ammonium hydroxide 853
A, 7. Samples and solutions for elementary analysis 854
A, 8. Analyzed samples 855
A, 9. Solubilities of some inorganic compounds in water at various temperatures 866
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, 10. Buffer solutions</td>
<td>868</td>
</tr>
<tr>
<td>A, 11. Comparison of metric and other units</td>
<td>873</td>
</tr>
<tr>
<td>A, 12. Decimals of an inch, I.S.W.G., and millimetres</td>
<td>875</td>
</tr>
<tr>
<td>A, 13. The Greek alphabet</td>
<td>875</td>
</tr>
<tr>
<td>A, 14. Suggested scheme of study for the general certificate of education (advanced level), ordinary national certificate examinations in chemistry, and examinations of similar character</td>
<td>876</td>
</tr>
<tr>
<td>A, 15. Suggested scheme of study for B.Sc. Special Chemistry, Honours B.Sc. Chemistry, Associateship of the Royal Institute of Chemistry, and examinations of similar scope</td>
<td>878</td>
</tr>
<tr>
<td>A, 16. Saturated solutions of some reagents at 20°C</td>
<td>883</td>
</tr>
<tr>
<td>A, 17. Four-figure logarithms</td>
<td>884</td>
</tr>
<tr>
<td>A, 18. Five-figure logarithms</td>
<td>886</td>
</tr>
<tr>
<td>Index</td>
<td>905</td>
</tr>
</tbody>
</table>
CHAPTER I

THEORETICAL BASIS OF QUANTITATIVE INORGANIC ANALYSIS

I. 1. Electrolytic dissociation.—Many of the reactions of qualitative and quantitative analysis take place in aqueous solution. It is therefore necessary to have a general knowledge of the conditions which exist in such solutions. It is assumed that the reader is familiar with the broad concepts of the simple theory of electrolytic dissociation.

Ionisation of acids and bases in solution. An acid may be defined as a substance which, when dissolved in water, undergoes dissociation with the formation of hydrogen ions as the only positive ion:

\[
\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^- \\
\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-
\]

Actually the free hydrogen ions \( \text{H}^+ \) (or protons) do not exist in the free state in aqueous solution; each hydrogen ion combines with one molecule of water to form the hydronium ion \( \text{H}_3\text{O}^+ \). The hydronium ion is a hydrated proton. The above equations are therefore more accurately written:

\[
\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^- \\
\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_3^-
\]

The ionisation may be attributed to the great tendency of the free hydrogen ions \( \text{H}^+ \) or protons to combine with water molecules to form hydronium ions. Hydrochloric and nitric acids are almost completely dissociated in aqueous solution in accordance with the above equations; this is readily detected by freezing-point measurements and by other methods.

Polybasic acids ionise in stages. In sulphuric acid, the first hydrogen atom is almost completely ionised:

\[
\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^- \\
\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^-
\]

The second hydrogen atom is only partially ionised, except in very dilute solution:

\[
\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \\
\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}
\]

Phosphoric acid also ionises in stages:

\[
\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}
\]

or

\[
\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^- \\
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-} \\
\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{PO}_4^{3-}
\]

The successive stages of ionisation are known as the primary, secondary, and tertiary ionisations respectively. As already mentioned, these
Quantitative Inorganic Analysis

do not take place to the same degree. The primary ionisation is always greater than the secondary, and the secondary very much greater than the tertiary.

Acids of the type of acetic acid $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ give an almost normal freezing-point depression in aqueous solution; the extent of dissociation is accordingly small. It is usual, therefore, to distinguish between acids which are completely or almost completely ionised in solution and those which are only slightly ionised. The former are termed strong acids (examples: hydrochloric, hydrobromic, hydriodic, iodic, nitric, and perchloric acids, primary ionisation of sulphuric acid), and the latter are called weak acids (examples: nitrous acid, acetic acid, carbonic acid, boric acid, phosphorous acid, phosphoric acid, hydrocyanic acid, and hydrogen sulphide). There is, however, no sharp division between the two classes. Methods for the measurement of the relative strengths of acids are described in Section I, 4.

A base may be defined as a substance which, when dissolved in water, undergoes dissociation with the formation of hydroxyl ions $\text{OH}^{-}$ as the only negative ions. Thus sodium hydroxide, potassium hydroxide, and the hydroxides of the alkaline-earth metals are almost completely dissociated in aqueous solution:

$$\text{NaOH} \rightleftharpoons \text{Na}^{+} + \text{OH}^{-}$$

$$\text{Ba(OH)}_{2} \rightleftharpoons \text{Ba}^{++} + 2\text{OH}^{-}$$

These are strong bases. Ammonium hydroxide solution, however, is a weak base. Only a small concentration of hydroxyl ions is produced in aqueous solution:

$$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^{+} + \text{OH}^{-}$$

or

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^{+} + \text{OH}^{-}$$

Modern views regarding acids and bases. The simple concepts given in the preceding paragraphs suffice for most of the requirements of quantitative inorganic analysis. However, a brief account of more general concepts as applied to aqueous solutions would appear to be justified.* The most general definition, due to G. N. Lewis, is that an acid is an electron-pair acceptor, and a base is an electron-pair donor. A more practical definition, put forward by Lowry and by Brønsted, is that an acid is a donor of protons, and a base is an acceptor of protons. This may be expressed:

$$\text{Acid} \rightleftharpoons \text{Proton} + \text{Conjugate Base}$$

i.e., an acid always forms a conjugate system with a base. Acids may be neutral molecules, positive ions, or negative ions:

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{COOH}$</td>
<td>$\text{H}^{+} + \text{CH}_3\text{COO}^{-}$</td>
</tr>
<tr>
<td>$\text{HCl}$</td>
<td>$\text{H}^{+} + \text{Cl}^{-}$</td>
</tr>
<tr>
<td>$\text{NH}_4^{+}$</td>
<td>$\text{H}^{+} + \text{NH}_3$</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_4^{-}$</td>
<td>$\text{H}^{+} + \text{HPO}_4^{2-}$</td>
</tr>
</tbody>
</table>

The Theoretical Basis of Quantitative Analysis

Acid.

\[ \text{Al}(\text{H}_2\text{O})_\text{6}^{+++} \rightleftharpoons \text{H}^+ + \text{Al}(\text{H}_2\text{O})_\text{6}\text{OH}^{++} \]

\[ \text{H}_\text{2}\text{O}^+ \rightleftharpoons \text{H}^+ + \text{H}_\text{2}\text{O} \]

\[ \text{H}_\text{2}\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

Attention is drawn to the duality in acid-base systems in which each acid has a conjugated base related to it. The interaction of an acid \( A_1 \) of one system with a base \( B_2 \) of another system, i.e., the acid-base reaction, may be written:

\[ \text{Acid}_1 (A_1) \rightleftharpoons \text{Base}_1 (B_1) + \text{Proton} \]

\[ \text{Acid}_2 (A_2) \rightleftharpoons \text{Base}_2 (B_2) + \text{Proton} \]

or

\[ A_1 + B_2 \rightleftharpoons A_2 + B_1 \]

Thus

\[ \text{HCl} + \text{H}_\text{2}\text{O} \rightleftharpoons \text{H}_\text{3}\text{O}^+ + \text{Cl}^- \]

\[ \text{NH}_4^+ + \text{CH}_3\text{COO}^- \rightleftharpoons \text{CH}_3\text{COOH} + \text{NH}_3 \]

Salts. The structure of numerous salts in the solid state has been investigated by means of X-rays and by other methods, and it has been shown that they are composed of charged atoms or groups of atoms held together in a crystal lattice. When these salts are dissolved in a solvent of high dielectric constant such as water, or are heated to the melting point, the crystal forces are weakened and the substances dissociate into the pre-existing charged particles or ions, so that the resultant liquids are good conductors of electricity. The complete dissociation of salts in aqueous solution is the modern view, and is now almost universally accepted. There are, however, some exceptions, and these have, in some cases, been supported by X-ray measurements. Feebly ionised salts (weak electrolytes) are exemplified by the cyanides, thiocyanates, and halides of mercury and cadmium, and by lead acetate.

The theoretical implications of the theory of complete ionisation, due to Debye, Hückel, and Onsager, have been fully worked out by these authors. In particular, they have been able to account for the increasing equivalent conductance with decreasing concentration over the concentration range 0-0.002N. For full details the reader must be referred to text-books of physical chemistry; a short account will be found in the author's Text Book of Qualitative Chemical Analysis (Third Edition, 1945).

It is important to realise that whilst complete ionisation occurs with strong electrolytes, this does not mean that the effective concentrations of the ions are the same at all concentrations, for if this were the case, the osmotic properties of aqueous solutions could not be accounted for. The variation of osmotic properties is ascribed to changes of the activity of the ions; these are dependent upon the electrical forces between the ions. Expressions for the variations of the activity or of related quantities, applicable to dilute solutions, have also been deduced by the Debye-Hückel-Onsager theory. Further consideration of the concept of activity will be found in Section I, 5.

I. 2. THE LAW OF MASS ACTION

Guldberg and Waage in 1867 clearly stated the law of mass action (sometimes termed the law of chemical equilibrium) in the form: the velocity of a chemical reaction is proportional to the product of the
active masses of the reacting substances. For the present we shall interpret "active mass" by concentration and express it in gram-molecules (or mols.) per litre. By applying the law to homogeneous systems, i.e., to systems in which all the reacting molecules are present in one phase, for example in solution, we can arrive at a mathematical expression for the condition of equilibrium in a reversible reaction.

Let us consider first the simple reversible reaction at constant temperature:

$$A + B \rightleftharpoons C + D$$

The velocity with which A and B react is proportional to their concentrations, or

$$v_1 = k_1 \times [A] \times [B]$$

where $k_1$ is a constant known as the velocity coefficient, and the square brackets in heavy type denote the molecular concentrations of the substances enclosed within the brackets. Similarly, the velocity with which the reverse reaction occurs is given by:

$$v_2 = k_2 \times [C] \times [D]$$

At equilibrium, the velocities of the reverse and the forward reactions will be equal (the equilibrium is a dynamic and not a static one) and therefore $v_1 = v_2$,

$$k_1 \times [A] \times [B] = k_2 \times [C] \times [D]$$

or

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = K$$

$K$ is the equilibrium constant of the reaction at the given temperature.

The expression may be generalised. For a reversible reaction represented by:

$$p_1A_1 + p_2A_2 + p_3A_3 + \ldots \rightleftharpoons q_1B_1 + q_2B_2 + q_3B_3 + \ldots$$

where $p_1, p_2, p_3$ and $q_1, q_2, q_3$ are the number of molecules of reacting substances, the condition for equilibrium is given by the expression:

$$\frac{[B_1]^{q_1} \times [B_2]^{q_2} \times [B_3]^{q_3} \ldots}{[A_1]^{p_1} \times [A_2]^{p_2} \times [A_3]^{p_3} \ldots} = K$$

This result may be expressed in words: when equilibrium is reached in a reversible reaction, at constant temperature, the product of the molecular concentrations of the resultants (the substances on the right-hand side of the equation) divided by the product of the molecular concentrations of the reactants (the substances on the left-hand side of the equation), each concentration being raised to a power equal to the number of molecules of that substance taking part in the reaction, is constant.

It must be pointed out that there is no relation between the velocity at which a reaction attains equilibrium and the equilibrium constant. The velocity of a reaction increases rapidly with rise of temperature, and is also affected by certain substances. Those substances which increase the rate of reaction are termed positive catalysts, whilst those which decrease it are called negative catalysts.

\section*{Application of the law of mass action to solutions of electrolytes.}

Weak (or slightly dissociated) electrolytes, such as acetic acid and
ammonium hydroxide, undergo reversible dissociation when dissolved in water. The equilibrium between the undissociated molecules and the ions for such electrolytes can be investigated by the law of mass action. The law cannot be applied to strong electrolytes, such as salts, since dissociation is complete, or virtually complete.

The equilibrium which exists in a dilute solution of acetic acid at constant temperature is:

\[ H\cdot C_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^- \]

Applying the law of mass action, we have:

\[ [C_2H_3O_2^-] \times [H^+] / [H\cdot C_2H_3O_2] = K \]

\( K \) is the ionisation constant or dissociation constant at constant temperature. The term affinity constant is sometimes employed for acids and bases. If one gram-equivalent of the electrolyte is dissolved in \( V \) litres of solution (\( V = 1/c \), where \( c \) is the concentration in gram-equivalents per litre), and if \( \alpha \) is the degree of ionisation at equilibrium, then the amount of unionised electrolyte will be \((1 - \alpha)\) gram-equivalents, and the amount of each of the ions will be \( \alpha \) gram-equivalents. The concentration (gram-equivalents per litre) of unionised acetic acid will therefore be \((1 - \alpha)/V\), and the concentration of each of the ions \( \alpha/V \).

Substituting in the equilibrium equation, we obtain the expression:

\[ \alpha^2 / (1 - \alpha)V = K \text{ or } \alpha c / (1 - \alpha) = K. \]

This is known as Ostwald's dilution law. The agreement of the "law" with experiment is illustrated by the following results for acetic acid (Table I).

**Table I.** — Equivalent Conductance and Dissociation Constant of Acetic Acid at 25° C.

<table>
<thead>
<tr>
<th>Conc. ( \times 10^4 )</th>
<th>( \Lambda_\alpha )</th>
<th>( \alpha )</th>
<th>( K \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.873</td>
<td>102.5</td>
<td>0.264</td>
<td>1.78</td>
</tr>
<tr>
<td>5.180</td>
<td>85.06</td>
<td>0.170</td>
<td>1.76</td>
</tr>
<tr>
<td>9.400</td>
<td>50.56</td>
<td>0.130</td>
<td>1.83</td>
</tr>
<tr>
<td>24.78</td>
<td>31.94</td>
<td>0.080</td>
<td>1.82</td>
</tr>
<tr>
<td>38.86</td>
<td>25.78</td>
<td>0.066</td>
<td>1.83</td>
</tr>
<tr>
<td>56.74</td>
<td>21.48</td>
<td>0.055</td>
<td>1.84</td>
</tr>
<tr>
<td>68.71</td>
<td>19.58</td>
<td>0.050</td>
<td>1.84</td>
</tr>
<tr>
<td>92.16</td>
<td>16.09</td>
<td>0.044</td>
<td>1.84</td>
</tr>
<tr>
<td>112.2</td>
<td>15.41</td>
<td>0.040</td>
<td>1.84</td>
</tr>
<tr>
<td>338.8</td>
<td>13.82</td>
<td>0.035</td>
<td>1.84</td>
</tr>
</tbody>
</table>

The mean classical or Ostwald dissociation constant of acetic acid at 25° C, is \( 1.82 \times 10^{-4} \). Similar results—the individual variations may sometimes be slightly greater—are obtained for other weak electrolytes.

I. 4. Strengths of acids and bases. It has already been stated (Section I, 1) that the properties of acids are the properties of the hydrogen ion \( H^+ \) (or, more correctly, the hydroxonium ion \( H_3O^+ \)). For any given total concentration of acid, the concentration of hydrogen

* Strictly speaking the equilibrium should be written:

\[ H\cdot C_2H_3O_4 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_4^- \]

no free protons (\( H^+ \)) exist in aqueous solution. The older form will, however, be retained for the sake of simpliity.
ions will depend upon the degree of dissociation $\alpha$; the strength of an acid will thus depend upon the value of $\alpha$ at a given concentration. The dissociation constant gives a relationship between $\alpha$ and the concentration, and it accordingly also represents a measure of the strength of the acid or a measure of its tendency to undergo dissociation.

The properties of bases, according to the most elementary view, depend upon the hydroxyl ion, and the ionisation constant will likewise be a measure of the strength of the base.

For very weak or slightly ionised electrolytes, the expression $\alpha^2/(1 - \alpha)V = K$ reduces to $\alpha^2 = KV$ or $\alpha = \sqrt{KV}$, since $\alpha$ may be neglected in comparison with unity. Hence for any two weak acids or bases at a given dilution $V$ (in litres), we have $\alpha_1 = \sqrt{K_1V}$ and $\alpha_2 = \sqrt{K_2V}$; or $\alpha_1/\alpha_2 = \sqrt{K_1/K_2}$. Expressed in words, for any two weak or slightly dissociated electrolytes at equal dilutions, the degrees of dissociation are proportional to the square roots of their ionisation constants. Some values for the dissociation constants at 25° C. for weak acids and bases are collected in Table II.

I. 5. Activity and activity coefficient.—In our deduction of the law of mass action it was assumed that the effective concentrations or active masses of the components could be expressed by the stoichiometric concentrations. According to modern thermodynamics, this is not strictly true. The rigid equilibrium equation for, say, a binary electrolyte:

$$AB \rightleftharpoons A^+ + B^-$$

is

$$a_{A^+} \times a_{B^-}/a_{AB} = K_a$$

where $a_{A^+}$, $a_{B^-}$, and $a_{AB}$ represent the activities of $A^+$, $B^-$, and $AB$ respectively, and $K_a$ is the true or thermodynamic dissociation constant. The concept of activity, a thermodynamic quantity, is due to G. N. Lewis. The quantity is related to the concentration by a factor, termed the activity coefficient:

$$\text{activity} = \text{concentration} \times \text{activity coefficient}$$

Thus at any molar concentration

$$a_{A^+} = f_{A^+} \cdot [A^+], \quad a_{B^-} = f_{B^-} \cdot [B^-], \quad \text{and} \quad a_{AB} = f_{AB} \cdot [AB]$$

where $f$ refers to the activity coefficients, and the square brackets to the molar concentrations. Substituting in the above equation, we obtain:

$$\frac{f_{A^+} \cdot [A^+] \times f_{B^-} \cdot [B^-]}{f_{AB} \cdot [AB]} = \frac{[A^+] \cdot [B^-]}{[AB]} \times \frac{f_{A^+} \times f_{B^-}}{f_{AB}} = K_a$$

This is the rigorously correct expression for the law of mass action as applied to weak electrolytes.

The activity coefficient varies with the concentration. For ions it varies with the valency, and is the same for all dilute solutions having the same ionic strength, the latter being a measure of the electrical field existing in the solution. The term ionic strength, designated by the symbol $\mu$, was introduced by Lewis and Randall in 1921, and is defined as equal to one half of the sum of the products of the concentration of each ion multiplied by the square of its valency, or $\mu = 0.5 \Sigma q_i z_i^2$, where $q_i$ is the ionic concentration in gram-molecules per litre of solution.
**Table II.—Dissociation Constants at 25° C.**

<table>
<thead>
<tr>
<th>Acid.</th>
<th>Formula.</th>
<th>$K_a$</th>
<th>$pK_a = -\log K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>H$_2$C$_2$H$_4$O$_2$</td>
<td>$1.82 \times 10^{-5}$</td>
<td>4.75</td>
</tr>
<tr>
<td>Benzoic</td>
<td>H$_2$C$_6$H$_5$O$_2$</td>
<td>$6.37 \times 10^{-5}$</td>
<td>4.20</td>
</tr>
<tr>
<td>o-Chlorobenzoic</td>
<td>H$_2$C$_6$H$_4$ClO$_2$</td>
<td>$1.20 \times 10^{-3}$</td>
<td>2.92</td>
</tr>
<tr>
<td>Formic</td>
<td>H$\cdot$CHO$_2$</td>
<td>$1.77 \times 10^{-4}$</td>
<td>3.75</td>
</tr>
<tr>
<td>Furoic</td>
<td>H$_2$C$_2$H$_2$O$_3$</td>
<td>$6.78 \times 10^{-5}$</td>
<td>4.17</td>
</tr>
<tr>
<td>Hydrocyanic</td>
<td>H-CN</td>
<td>$7.2 \times 10^{-10}$</td>
<td>9.14</td>
</tr>
<tr>
<td>Nitrous</td>
<td>H-N$_2$O</td>
<td>$4.6 \times 10^{-4}$</td>
<td>3.33</td>
</tr>
<tr>
<td>o-Nitrobenzoic</td>
<td>H$_2$C$_6$H$_4$ON$_2$</td>
<td>$6.00 \times 10^{-4}$</td>
<td>3.22</td>
</tr>
<tr>
<td>Pheny lacetic</td>
<td>H$_2$C$_6$H$_5$O$_4$</td>
<td>$4.68 \times 10^{-5}$</td>
<td>4.31</td>
</tr>
<tr>
<td>Adipic</td>
<td>H$_4$C$_6$H$_6$O$_4$</td>
<td>$K_1:3.72 \times 10^{-3}$</td>
<td>4.63</td>
</tr>
<tr>
<td>Carbonic</td>
<td>H$_2$O$_2$</td>
<td>$K_1:4.31 \times 10^{-7}$</td>
<td>6.37</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>H$_2$S</td>
<td>$K_1:0.1 \times 10^{-5}$</td>
<td>7.04</td>
</tr>
<tr>
<td>Malonic</td>
<td>H$_2$C$_4$H$_6$O$_4$</td>
<td>$K_1:1.40 \times 10^{-3}$</td>
<td>2.85</td>
</tr>
<tr>
<td>Oxalic</td>
<td>H$_2$C$_4$O$_4$</td>
<td>$K_1:2.20 \times 10^{-6}$</td>
<td>5.66</td>
</tr>
<tr>
<td>Phthalic</td>
<td>H$_2$C$_6$H$_4$O$_4$</td>
<td>$K_1:1.2 \times 10^{-14}$</td>
<td>14.92</td>
</tr>
<tr>
<td>Succinic</td>
<td>H$_2$C$_6$H$_6$O$_4$</td>
<td>$K_1:0.63 \times 10^{-5}$</td>
<td>4.13</td>
</tr>
<tr>
<td>Sulphuric</td>
<td>H$_2$SO$_4$</td>
<td>$K_1:1.5 \times 10^{-3}$</td>
<td>1.94</td>
</tr>
<tr>
<td>Sulphurous</td>
<td>H$_2$SO$_2$</td>
<td>$K_1:1.7 \times 10^{-2}$</td>
<td>1.77</td>
</tr>
<tr>
<td>d-Tartaric</td>
<td>H$_2$C$_6$H$_8$O$_7$</td>
<td>$K_1:0.20 \times 10^{-4}$</td>
<td>3.04</td>
</tr>
<tr>
<td>Boric</td>
<td>H$_3$BO$_3$</td>
<td>$K_1:5.8 \times 10^{-4}$</td>
<td>3.97</td>
</tr>
<tr>
<td>Citric</td>
<td>H$_2$C$_6$H$_5$O$_7$</td>
<td>$K_1:2.9 \times 10^{-5}$</td>
<td>4.67</td>
</tr>
<tr>
<td>Phosphoric</td>
<td>H$_3$PO$_4$</td>
<td>$K_1:1.3 \times 10^{-5}$</td>
<td>3.38</td>
</tr>
</tbody>
</table>

**Base.**

<table>
<thead>
<tr>
<th>Base.</th>
<th>$K_a$</th>
<th>$pK_a = -\log K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium hydroxide</td>
<td>NH$_3$OH</td>
<td>$1.79 \times 10^{-5}$</td>
</tr>
<tr>
<td>Aniline</td>
<td>C$_6$H$_5$NH$_2$</td>
<td>$4.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>C$_2$H$_5$NH$_2$</td>
<td>$4.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Limethylamine</td>
<td>(CH$_3$)$_2$NH</td>
<td>$5.20 \times 10^{-4}$</td>
</tr>
<tr>
<td>Methylamine</td>
<td>CH$_3$NH$_2$</td>
<td>$4.38 \times 10^{-4}$</td>
</tr>
<tr>
<td>Piperidine</td>
<td>C$_4$H$_8$N$_2$</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>Quinoline</td>
<td>C$_9$H$_8$N</td>
<td>$6.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>(CH$_3$)$_3$N</td>
<td>$5.45 \times 10^{-4}$</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>Ca(OH)$_2$</td>
<td>$K_2:3.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>Barium hydroxide</td>
<td>Ba(OH)$_2$</td>
<td>$K_2:2.3 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

* All compounds marked with an asterisk are of the ammonium type, e.g., aniline is really anilinium hydroxide:

\[(C_6H_5NH_3)OH \Leftrightarrow (C_6H_5NH_2)^+ + OH^-\]

† Figures marked with a † are the true or thermodynamic dissociation constants. (See Section I, 5.)
and $z_i$ is the valency of the ion concerned. An example will make this clear. The ionic strength of $0.1 \text{M-HNO}_3$ solution containing $0.2 \text{M-Ba(NO}_3)_2$ is given by:

$$0.5 \times 0.1 \text{ (for H}^+\text{)} + 0.1 \text{ (for NO}_3^-\text{)} + 0.2 \times 2 \text{ (for Ba}^{2+}\text{)} + 0.2 \times 2 \text{ (for NO}_3^-\text{)} = 0.5 \times 1.4 = 0.7$$

The activity coefficient depends upon the total ionic strength of the solution in a manner which is discussed in Section I, 10. Generally speaking, it is comparatively difficult to determine activity coefficients experimentally, particularly in concentrated solutions and in mixtures of ions of several valency types. The activity coefficients of unionised molecules do not differ considerably from unity. For weak electrolytes in which the ionic concentration and therefore the ionic strength is small, the error introduced by neglecting the difference between the actual values of the activity coefficients of the ions, $f_{A^+}$ and $f_{B^-}$, and unity is small ($<5$ per cent). Hence for weak electrolytes, the true or thermodynamic expression reduces to $[A^+] \times [B^-]/[AB] = K$; the constants obtained by the use of simple concentrations will be accurate to 2-6 per cent. Such values are sufficiently precise for purposes of calculation in quantitative analysis. It must, however, be pointed out that precision values for the dissociation constants of weak electrolytes can be obtained by the use of special methods; the discussion of these is outside the scope of this volume.

Strong electrolytes will be assumed to be completely dissociated, and no correction for activity coefficients will be made for dilute solutions.

I. 6. Ionisation of polybasic acids.—When a polybasic acid is dissolved in water, the various hydrogen atoms undergo ionisation to different extents. For a dibasic acid $H_2A$, the primary and secondary ionisations can be represented by the equations:

$$H_2A \rightleftharpoons H^+ + HA^- \quad (1)$$
$$HA^- \rightleftharpoons H^+ + A^{2-} \quad (2)$$

If the dibasic acid is a weak electrolyte, the law of mass action may be applied, and the following expressions obtained:

$$[H^+] \times [HA^-]/[H_2A] = K_1 \quad (1')$$
$$[H^+] \times [A^{2-}]/[HA^-] = K_2 \quad (2')$$

$K_1$ and $K_2$ are known as the primary and secondary dissociation constants respectively. Each stage of the dissociation process has its own ionisation constant, and the magnitudes of these constants give a measure of the extent to which each ionisation has proceeded at any given concentration. The greater the value of $K_1$ relative to $K_2$, the smaller will be the secondary dissociation, and the greater must be the dilution before the latter becomes appreciable. It is therefore possible that a dibasic (or polybasic) acid may behave, so far as dissociation is concerned, as a monobasic acid. This is indeed characteristic of many polybasic acids (see Table II).

A tribasic acid $H_3A$ (e.g., orthophosphoric acid) will similarly yield three dissociation constants, $K_1$, $K_2$, and $K_3$, which may be computed in an analogous manner:

$$H_3A \rightleftharpoons H^+ + H_2A^- \quad (3)$$
$$H_2A^- \rightleftharpoons H^+ + HA^{2-} \quad (4)$$
$$HA^{2-} \rightleftharpoons H^+ + A^{3-} \quad (5)$$
We can now apply some of the theoretical considerations to actual examples encountered in analysis.

**Example 1.** To calculate the concentrations of HS⁻ and S⁻⁻ in a saturated solution of hydrogen sulphide.

A saturated aqueous solution of hydrogen sulphide at 25° C., at atmospheric pressure, is approximately 0-1 M. The primary and secondary dissociation constants are \(9.1 \times 10^{-8}\) and \(1.2 \times 10^{-15}\) respectively.

Thus
\[
[H^+] \times [HS^-]/[H_2S] = 9.1 \times 10^{-8} \quad \text{(i)}
\]

and
\[
[H^+] \times [S^{-}]\,[HS^-] = 1.2 \times 10^{-15} \quad \text{(ii)}
\]

The very much smaller value of \(K_a\) indicates that the secondary dissociation, and consequently \([S^{-}]\), is exceedingly small. It follows, therefore, that only the primary ionisation is of importance, and \([H^+]\) and \([HS^-]\) are practically equal in value. Substituting in equation (i):
\[
[H^+] = [HS^-] = 0.1, \text{ we obtain } [S^-] = \frac{9.1 \times 10^{-8} \times 0.1}{9.5 \times 10^{-5}}
\]

Both the equilibrium equations must be satisfied simultaneously; by substitution of these values for \([H^+]\) and \([HS^-]\) in equation (ii), we obtain
\[
9.5 \times 10^{-5} \times [S^-] = 1.2 \times 10^{-15} \times 9.5 \times 10^{-5}, \text{ or } [S^-] = 1.2 \times 10^{-15}
\]

which is the value for \(K_a\).

If we multiply equations (i) and (ii) together and transpose:
\[
[S^-] = 1.1 \times 10^{-23}/[H^+]^2
\]

Thus the concentration of the sulphide ion is inversely proportional to the square of the hydrogen ion concentration, i.e., if we, say, double \([H^+]\) by the addition of a strong acid, the \([S^-]\) will be reduced to \(\frac{1}{4}\) or \(\frac{1}{2}\) of its original value.

**1.7. Common ion effect.**—The concentration of a particular ion in an ionic reaction can be increased by the addition of a compound which produces that ion upon dissociation. The particular ion is thus derived from the compound already in solution and from the added reagent, hence the name common ion. We shall confine our attention to the case in which the original compound is a weak electrolyte in order that the law of mass action may be applicable. The result is usually that there is a higher concentration of this ion in solution than that derived from the original compound alone, and new equilibrium conditions will be produced. Examples of the calculation of the common ion effect are given below. In general, it may be stated that if the total concentration of the common ion is only slightly greater than that which the original compound alone would furnish, the effect is small; if, however, the concentration of the common ion is very much increased (e.g., by the addition of a completely dissociated salt), the effect is very great, and may be of considerable practical importance. Indeed, the common ion effect provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte.

**Example 2.** To calculate the sulphide-ion concentration in a 0.25 M hydrochloric acid solution saturated with hydrogen sulphide.

This concentration has been chosen since it is that at which the sulphides

* There is some evidence that the concentration is appreciably less than 0-1 M, but the rounded figure will be employed in the illustrative calculation.
Quantitative Inorganic Analysis

of the metals of Group II are precipitated. The total concentration of hydrogen sulphide may be assumed to be approximately the same as in aqueous solution, i.e., 0·1 M; the $[H^+]$ will be equal to that of the completely dissociated HCl, i.e., 0·25 M, but the $[S^-]$ will be reduced below $1·2 \times 10^{-16}$.

Substituting in equations (i) and (ii) (Section I, 8), we find:

$$[HS^-] = \frac{0·1 \times 10^{-8} \times [H_2S]}{0·25} = 9·1 \times 10^{-8} \times 0·1 = 3·6 \times 10^{-8}$$

$$[S^-] = \frac{1·2 \times 10^{-16} \times [HS^-]}{0·25} = 1·2 \times 10^{-16} \times 3·6 \times 10^{-8} = 1·7 \times 10^{-22}$$

Thus by changing the acidity from $9·5 \times 10^{-5} M$ (that present in saturated H$_2$S water) to 0·25 M, the sulphide ion concentration is reduced from $1·2 \times 10^{-16}$ to $1·7 \times 10^{-22}$.

**Example 3.** What effect has the addition of 0·1 g.-mol. (8·20 g.) of anhydrous sodium acetate to 1 litre of 0·1 M acetic acid upon the degree of dissociation of the acid?

The dissociation constant of acetic acid at 25° C. is $1·82 \times 10^{-5}$. The degree of ionisation $\alpha$ in 0·1 M solution ($\alpha = 0·1$) may be computed by solving the quadratic equation:

$$[H^+] \times [C_2H_3O_2^-] = \frac{\alpha^2}{(1 - \alpha)} = 1·82 \times 10^{-5}$$

For our purpose it is sufficiently accurate to neglect $\alpha$ in $(1 - \alpha)$ since $\alpha$ is small:

$$\therefore \alpha = \sqrt{K/c} = \sqrt{1·82 \times 10^{-4}} = 0·0135$$

Hence in 0·1 M acetic acid,

$$[H^+] = 0·00135, [C_2H_3O_2^-] = 0·00135, \text{ and } [H\cdot C_2H_3O_2] = 0·00386$$

The concentrations of sodium and acetate ions produced by the addition of the completely dissociated sodium acetate are:

$$[Na^+] = 0·1, \text{ and } [C_2H_3O_2^-] = 0·1 \text{ gram-molecule respectively.}$$

The acetate ions from the salt will tend to decrease the ionisation of the acetic acid since $K$ is constant, and consequently the acetate-ion concentration derived from it. Hence we may write $[C_2H_3O_2^-] = 0·1$ for the solution, and if $\alpha'$ is the new degree of ionisation, $[H^+] = \alpha'c = 0·1\alpha'$, and $[H\cdot C_2H_3O_2] = (1 - \alpha')c = 0·1$, since $\alpha'$ is negligibly small.

Substituting in the mass-action equation:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[H\cdot C_2H_3O_2]} = \frac{0·1\alpha' \times 0·1}{0·1} = 1·82 \times 10^{-5}$$

or

$$\alpha' = 1·8 \times 10^{-4}$$

$$[H^+] = \alpha'c = 1·8 \times 10^{-5}$$

The addition of a tenth of an equivalent weight of sodium acetate to a 0·1 M solution of acetic acid has decreased the degree of ionisation from 0·35 to 0·018 per cent, and the hydrogen-ion concentration from 0·00135 to 0·000018.

**Example 4.** What effect has the addition of 0·5 g.-mol. (20·75 g.) of ammonium chloride to 1 litre of 0·1 M ammonium hydroxide solution upon the degree of dissociation of the base?

(Dissociation constant of NH$_4$OH = $1·8 \times 10^{-5}$)
In 0.1M ammonia solution, $\alpha = \sqrt{1.8 \times 10^{-5}/0.1} = 0.0135$. Hence $[OH^-] = 0.00135$, $[NH_4^+] = 0.00135$, and $[NH_4OH] = 0.0086$. Let $\alpha'$ be the degree of ionisation in the presence of the added ammonium chloride. Then $[OH^-] = \alpha'c = 0.1\alpha'$, and $[NH_4OH] = (1 - \alpha')c = 0.1$, since $\alpha'$ may be taken as negligibly small. The addition of the completely ionised ammonium chloride will, of necessity, decrease the $[NH_4^+]$ derived from the base and increase $[NH_4OH]$, since $K$ is constant under all conditions. Now $[NH_4^+] = 0.5$, as a first approximation.

Substituting in the equation:

$$\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = \frac{0.5 \times 0.1\alpha'}{0.1} = 1.8 \times 10^{-5}$$

or

$$\alpha' = 3.6 \times 10^{-6} \text{ and } [OH^-] = 3.6 \times 10^{-6}$$

The addition of half an equivalent weight of ammonium chloride to a 0.1M solution of ammonium hydroxide has decreased the degree of ionisation from 0.35 to 0.0036 per cent, and the hydroxyl-ion concentration from 0.00135 to 0.0000036.

I. 8. Solubility product.—For sparingly soluble salts (i.e., those of which the solubility is less than 0.01 g.-mol. per litre) it is an experimental fact that the product of the total molecular concentrations of the ions is a constant at constant temperature. This product $S$ is termed the solubility product. For a binary electrolyte:

$$AB \rightleftharpoons A^+ + B^-$$

$$S_{AB} = [A^+] \times [B^-]$$

In general, for an electrolyte $A_pB_q$, which ionises into $pA^+$ and $qB^-$ ions:

$$A_pB_q \rightleftharpoons pA^+ + qB^-$$

$$S_{A_pB_q} = [A^+]^p \times [B^-]^q$$

A plausible deduction of the solubility product relation is the following. When excess of a sparingly soluble electrolyte, say silver chloride, is shaken up with water, some of it passes into solution to form a saturated solution of the salt and the reaction appears to cease. The following equilibrium is actually present (the silver chloride is completely ionised in solution):

$$AgCl \text{ (solid)} \rightleftharpoons Ag^+ + Cl^-$$

The velocity of the forward reaction depends only upon the temperature and at any given temperature:

$$v_1 = k_1$$

where $k_1$ is a constant. The velocity of the reverse reaction is proportional to the concentrations of each of the reacting substances; hence at any given temperature:

$$v_2 = k_2 \times [Ag^+] \times [Cl^-]$$

where $k_2$ is another constant. At equilibrium the two velocities are equal, i.e.,

$$k_1 = k_2 \times [Ag^+] \times [Cl^-]$$

or

$$[Ag^+] \times [Cl^-] = k_1 / k_2 = S_{AgCl}$$
Quantitative Inorganic Analysis

A more rigid deduction of the solubility product principle can be obtained along the following lines. For simplicity, we shall again consider a binary electrolyte:

$$\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$$

The solid is completely dissociated in dilute solution: no undissociated molecules will therefore be present. It can be shown by thermodynamics that in a saturated solution of any salt containing varying amounts of a more soluble salt with a common ion, the products of the activities of the two ions in the various saturated solutions are the same, i.e.,

$$a_{A^+} \times a_{B^-} = \text{constant (activity product)}$$

In the very dilute solutions with which we are at present concerned, the activities may be taken as practically equal to the concentrations,* so that $[A^+] \times [B^-] = \text{constant}$.

Some experimental results, due to Jahn (1904), illustrating the approximate constancy of the solubility product of silver chloride in the presence of varying concentrations of chloride ion (from potassium chloride) are collected in Table III.

<table>
<thead>
<tr>
<th>[KCl]</th>
<th>[Cl\textsuperscript{−}] × 10\textsuperscript{2}</th>
<th>[Ag\textsuperscript{+}] × 10\textsuperscript{8}</th>
<th>$S_{\text{AgCl}} = [\text{Ag}^+] [\text{Cl}^-] \times 10\textsuperscript{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·00670</td>
<td>6·4</td>
<td>1·75</td>
<td>1·12</td>
</tr>
<tr>
<td>0·00833</td>
<td>7·9</td>
<td>1·39</td>
<td>1·10</td>
</tr>
<tr>
<td>0·01114</td>
<td>10·5</td>
<td>1·07</td>
<td>1·12</td>
</tr>
<tr>
<td>0·01669</td>
<td>15·5</td>
<td>0·74</td>
<td>1·14</td>
</tr>
<tr>
<td>0·03349</td>
<td>30·3</td>
<td>0·39</td>
<td>1·14</td>
</tr>
</tbody>
</table>

It is important to note that the solubility product relation applies with sufficient accuracy for purposes of quantitative analysis only to saturated solutions of slightly soluble electrolytes and with small additions of other salts. In the presence of large concentrations of salts, the ionic concentration, and therefore the ionic strength of the solution, will increase. This will, in general, lower the activity coefficients of both ions, and consequently the ionic concentrations (and therefore the solubility) must increase in order to maintain the solubility product constant (see Section I, 10 for a more detailed discussion).

The great importance of the conception of solubility product lies in its bearing upon precipitation from solution, which is, of course, one of the principal operations of quantitative analysis. The solubility product is the ultimate value which is attained by the ionic concentration product when equilibrium has been established between the solid phase of a difficulty soluble salt and the solution. If the experimental conditions are such that the ionic concentration product is different from the solubility product, then the system will attempt to

* Activity = activity coefficient × concentration, i.e., $a = f_0$. The activity product may therefore be written:

$$f_0 [A^+] \times f_0 [B^-] = \text{constant}$$

In very dilute solution $f$ is proportional to $(1 - k\sqrt{c})$, and if $c$ is small, this quantity is approximately unity.
adjust itself in such a manner that the ionic and solubility products are equal in value. Thus, if, for a given electrolyte, the product of the concentrations of the ions in solution is arbitrarily made to exceed the solubility product, as, for example, by the addition of a salt with a common ion, the adjustment of the system to equilibrium results in the precipitation of the solid salt, provided supersaturation conditions are excluded. If the ionic concentration product is less than the solubility product or can arbitrarily be made so, as, for example, by complex salt formation or by the formation of weak electrolytes, then a further quantity of solute can pass into solution until the solubility product is attained, or, if this is not possible, until all the solute has dissolved.

Table IV contains the solubility products ($S$) at the laboratory temperature ($ca. 20^\circ C.$) of some common sparingly soluble substances. Values for \( pS = -\log_{10} S \) are given in the last column. The student is referred to text-books of physical chemistry for a description of the methods for determining solubility products. It must, however, be pointed out that the various methods do not always yield consistent results, and what appear to be the best representative figures are given in the table.

A few examples may help the reader to fully understand the subject. The concentrations are expressed in gram-molecules per litre for the calculation of solubility products.
Quantitative Inorganic Analysis

Example 5. The solubility of silver chloride is 0·0015 g. per litre. Calculate the solubility product.
The molecular weight of silver chloride is 143.5. The solubility is therefore 0·0015/143·5 = 1·05 \times 10^{-5} mols. per litre. In a saturated solution the dissociation, \(\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-\), is complete; 1 mol. of AgCl will give 1 mol. each of \(\text{Ag}^+\) and \(\text{Cl}^-\). Hence \([\text{Ag}^+] = 1·05 \times 10^{-5}\) and \([\text{Cl}^-] = 1·05 \times 10^{-8}\).

\[ S_{\text{AgCl}} = [\text{Ag}^+] \times [\text{Cl}^-] = (1·05 \times 10^{-5}) \times (1·05 \times 10^{-8}) = 1·1 \times 10^{-10} \]

Example 6. Calculate the solubility product of silver chromate, given that its solubility is 2·5 \times 10^{-2} g. per litre.

\(\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}\)
The molecular weight of \(\text{Ag}_2\text{CrO}_4\) is 332, hence the solubility = 2·5 \times 10^{-2}/332 = 7·5 \times 10^{-6} mols. per litre.

Now 1 mol. of \(\text{Ag}_2\text{CrO}_4\) gives 2 mols. of \(\text{Ag}^+\) and 1 mol. of \(\text{CrO}_4^{2-}\); therefore

\[ S_{\text{Ag}_2\text{CrO}_4} = [\text{Ag}^+]^2 \times [\text{CrO}_4^{2-}] \]

\[ = (2 \times 7·5 \times 10^{-6})^2 \times (7·5 \times 10^{-5}) \]

\[ = 1·1 \times 10^{-12} \]

Example 7. The solubility product of magnesium hydroxide is 3·4 \times 10^{-11}. Calculate its solubility in grams per litre.

\(\text{Mg(OH)}_2\) (solid) \(\rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-\)

\[ [\text{Mg}^{2+}] \times [\text{OH}^-]^2 = 3·4 \times 10^{-11} \]
The molecular weight of magnesium hydroxide is 58. Each molecule of magnesium hydroxide, when dissolved, yields 1 mol. of magnesium ions and 2 mols. of hydroxyl ions. If the solubility is \(x\) g.-mols. per litre, \([\text{Mg}^{2+}] = x\) and \([\text{OH}^-] = 2x\). Substituting these values in the solubility product expression:

\[ x \times (2x)^2 = 3·4 \times 10^{-11} \]
or

\[ x = 2·0 \times 10^{-4} \text{ g.-mols. per litre} \]

\[ = 2·0 \times 10^{-4} \times 58 = 1·2 \times 10^{-2} \text{ g. per litre} \]

I. 9. Completeness of precipitation. Quantitative effects of a common ion.—An important application of the solubility product principle is to the calculation of the solubility of sparingly soluble salts in solution of salts with a common ion. Thus the solubility of a salt \(\text{MA}\) in the presence of a relatively large amount of the common \(\text{M}^+\) ions,* supplied by a second salt \(\text{MB}\), follows from the definition of solubility products:

\[ [\text{M}^+] \times [\text{A}^-] = S_{\text{MA}} \]
or

\[ [\text{A}^-] = S_{\text{MA}}/[\text{M}^+] \] \[ \ldots \ldots \ldots \ldots \ldots (1) \]

The solubility of the salt is represented by the \([\text{A}^-]\) which it furnishes in solution. It is clear that the addition of a common ion will decrease the solubility of the salt.

Example 8. Calculate the solubility of silver chloride in 0·001M- and 0·01M-sodium chloride solutions respectively \(S_{\text{AgCl}} = 1·1 \times 10^{-10}\).

In a saturated solution of silver chloride \([\text{Cl}^-] = \sqrt{S_{\text{AgCl}}} = \sqrt{1·1 \times 10^{-10}} = 1·05 \times 10^{-5}\).

* This enables us to neglect the concentration of \(\text{M}^+\) ions supplied by the sparingly soluble salt itself, and thus to simplify the calculation.
10⁻⁶ g.-mol. per litre; this may be neglected in comparison with the excess of Cl⁻ ions added.

For [Cl⁻] = 1 × 10⁻⁶, [Ag⁺] = 1.1 × 10⁻¹⁵/1 × 10⁻³

= 1.1 × 10⁻⁷ g.-mol. per litre

For [Cl⁻] = 1 × 10⁻⁶, [Ag⁺] = 1.1 × 10⁻¹⁵/1 × 10⁻²

= 1.1 × 10⁻⁸ g.-mol. per litre

Thus the solubility is decreased 100 times in 0.001M-sodium chloride and 1000 times in 0.01M-sodium chloride. Similar results are obtained for 0.001M- and 0.01M-silver nitrate solution.

Example 9. Calculate the solubilities of silver chromate in 0.001M- and 0.01M-silver nitrate solutions, and in 0.001M- and 0.01M-potassium chromate solutions (Ag₂CrO₄ : S.P. = 1.7 × 10⁻¹², solubility = 7.5 × 10⁻⁵ mols. per litre).

\[ [\text{Ag}⁺]² × [\text{CrO}_₄⁻⁻] = 1.7 \times 10⁻¹² \]

\[ [\text{CrO}_₄⁻⁻] = 1.7 \times 10⁻¹²/[\text{Ag}⁺]² \]

For 0.001M-silver nitrate solution: [Ag⁺] = 1 × 10⁻⁶

\[ [\text{CrO}_₄⁻⁻] = 1.7 \times 10⁻¹²/1 \times 10⁻⁶ = 1.7 \times 10⁻⁸ \text{ mols. per litre} \]

For 0.01M-silver nitrate solution:

\[ [\text{CrO}_₄⁻⁻] = 1.7 \times 10⁻¹²/1 \times 10⁻⁴ = 1.7 \times 10⁻⁸ \text{ mols. per litre} \]

The solubility product equation gives:

\[ [\text{Ag}⁺] = \sqrt{1.7 \times 10⁻¹²/[\text{CrO}_₄⁻⁻]} \]

For [CrO₄⁻⁻] = 0.001, [Ag⁺] = \sqrt{1.7 \times 10⁻¹²/1 \times 10⁻³}

= 4.1 × 10⁻⁵ mols. per litre

For [CrO₄⁻⁻] = 0.01, [Ag⁺] = \sqrt{1.7 \times 10⁻¹²/1 \times 10⁻²}

= 1.3 × 10⁻⁵ mols. per litre

This decrease in solubility by the common-ion effect is of fundamental importance in gravimetric analysis. By the addition of a suitable excess of a precipitating agent, the solubility of a precipitate is usually decreased to so small a value that the loss by washing is negligible. Let us consider a specific case—the determination of silver as silver chloride. Here the chloride solution is added to the solution of the silver salt. If an exactly equivalent amount is added, the resultant saturated solution of silver chloride will contain 0.0015 g. per litre (Example 5). If 0.2 g. of silver chloride is produced and the volume of the solution and washings is 500 ml., the loss, owing to solubility, will be 0.00075 g. or 0.33 per cent of the weight of the salt; the analysis would then be 0.33 per cent too low. By using an excess of the precipitant, say, to a concentration of 0.01M, the solubility of the silver chloride is reduced to 1.5 × 10⁻⁶ g. per litre (Example 8), and the loss will be 1.5 × 10⁻⁶ × 0.5 × 100/0.2 = 0.0033 per cent. Silver chloride is therefore very suitable for the quantitative determination of silver with high accuracy.

I, 10. Limitations of the solubility product principle.—For a binary electrolyte MA, thermodynamical considerations lead to the result that the product of the activities of the two ions is constant at constant temperature, i.e.,

\[ a_\text{M}⁺ × a_\text{A}⁻ = \text{constant (activity product} = K_b) \]

(1)
Now activity = concentration × activity coefficient, or \( a = cf \). Substituting in (1), we obtain:

\[
[M^+] f_{M^+} \times [A^-] f_{A^-} = f S_{MA} = K_S \quad \ldots \ldots \quad (2)
\]

in which \( f_{M^+} \) and \( f_{A^-} \) denote the activity coefficients of \( M^+ \) and \( A^- \) respectively. For a saturated solution of a sparingly soluble salt in water, the ionic concentration is so small that \( f_{M^+} \) and \( f_{A^-} \) are not far removed from unity, and the expression (1) reduces to the classical solubility product equation.

Numerous experiments have been carried out to determine the accuracy with which the solubility product principle applies. Some results of Bray and Winninghoff (1911) upon the solubility of thallous chloride in the presence of various salts are shown in Fig. 1, 10, 1. The dotted line represents the effect of a simple uni-univalent salt with a common ion, calculated by assuming complete dissociation of the salt. The salts with a common ion decrease the solubility to nearly the same extent, and are in approximate agreement with the values computed on the basis of the simple solubility product principle. Fig. 1, 10, 2
shows graphically some selected results for silver sulphate. The addition, in moderate concentrations, of a common univalent ion, like Ag\(^+\), is in approximate agreement with the simple theory, but no such agreement is obtained by the addition of a common divalent ion, like SO\(_4\)\(^-\). A striking fact that emerges from these studies is that the solubility increases in most cases upon the addition of electrolytes with no common ion; we may term this influence the salt effect. Furthermore, it was found that the salt effect depends upon the valency of the ions of the precipitate and upon the nature of the added electrolyte; usually it increases markedly with increasing valency of the ions of the precipitate. The addition of a salt with no common ion will increase the ionic strength of the solution and hence decrease the activity coefficients of both ions of the sparingly soluble salt; the solubility of the latter must increase in order that the activity product, \([M^+]\cdot[A^-]\cdot f_{M^+}\cdot f_{A^-}\), may be kept constant. It can be shown on the basis of the Debye–Hückel–Onsager theory that for aqueous solutions at 25\(^\circ\) C.:

\[
\log f_i = - \frac{0.505 z_i^2 \cdot \mu^{0.5}}{1 + 3.3 \times 10^7 a \cdot \mu^{0.5}}
\]

where \(f_i\) is the activity coefficient of the ion, \(z_i\) is the valency of the ion concerned, \(\mu\) is the ionic strength of the solution (Section I, 5), and \(a\) is the average "effective diameter" of all the ions in the solution. For very dilute solutions (\(\mu^{0.5} < 0.1\)) the second term of the denominator is negligible and the equation reduces to:

\[
\log f_i = - 0.505 z_i^2 \cdot \mu^{0.5}
\]

For more concentrated solutions (\(\mu^{0.5} > 0.3\)) an additional term \(B\mu\) is added to the equation; \(B\) is an empirical constant. For a more detailed treatment of the influence of salts upon solubility and solubility product, particularly of the work of Brönsted and of La Mer, the reader is referred to textbooks of electrochemistry.*

It will be clear from the above short discussion that two factors may come into play when a solution of a salt containing a common ion is added to a saturated solution of a slightly soluble salt. At moderate concentrations of the added salt, the solubility will generally decrease, but with higher concentrations of the soluble salt, when the ionic strength of the solution increases considerably and the activity coefficients of the ions decrease, the solubility may actually increase. This is one of the reasons, provided complex-ion formation is absent, why a very large excess of the precipitating agent is avoided in quantitative analysis.

I. 11. Fractional precipitation.—We have thus far considered the solubility product principle in connexion with the precipitation of one sparingly soluble salt. We shall now extend our studies to the case where two slightly soluble salts may be formed. For simplicity, we shall study the situation which arises when a precipitating agent is added to a solution containing two anions, both of which form slightly soluble salts with the same cation, e.g., when silver nitrate solution is added to a solution containing both chloride and iodide ions. The questions which arise are: which salt will be precipitated first, and

* See, for example, S. Glasstone, *The Electrochemistry of Solutions*, Third Edition, 1945, p. 127 (Methuen and Co.).
how completely will the first salt be precipitated before the second ion begins to react with the reagent?

The solubility products of silver chloride and silver iodide are respectively $1.2 \times 10^{-10}$ and $1.7 \times 10^{-16}$; i.e.,

\[
[\text{Ag}^+] \times [\text{Cl}^-] = 1.2 \times 10^{-10} \quad \text{(1)}
\]
\[
[\text{Ag}^+] \times [\text{I}^-] = 1.7 \times 10^{-16} \quad \text{(2)}
\]

It is evident that silver iodide, being less soluble, will be precipitated first since its solubility product will be first exceeded. Silver chloride will be precipitated when the $[\text{Ag}^+]$ ion concentration is greater than

\begin{align*}
S_{\text{AgCl}} &= 1.2 \times 10^{-10} \\
[S_{\text{AgCl}}] &= \frac{1.2 \times 10^{-10}}{[\text{I}^-]}
\end{align*}

and then both salts will be precipitated simultaneously. When silver chloride commences to precipitate, silver ions will be in equilibrium with both salts, and equations (1) and (2) will be simultaneously satisfied, or

\begin{align*}
[\text{Ag}^+] &= \frac{S_{\text{AgI}}}{[\text{Cl}^-]} \quad \text{(3)}
\end{align*}

and

\begin{align*}
&[\text{I}^-] = \frac{S_{\text{AgI}}}{S_{\text{AgCl}}} \quad 1.7 \times 10^{-16} = \frac{1}{7.1 \times 10^5} \quad \text{(4)}
\end{align*}

Hence when the concentration of the iodide ion is about one millionth part of the chloride-ion concentration, silver chloride will be precipitated. If the initial concentration of both chloride and iodide ions is $0.1 N$, then silver chloride will be precipitated when

\[
[I^-] = 0.1 / 7.1 \times 10^5 = 1.4 \times 10^{-7} N = 1.8 \times 10^{-5} \text{ g. per litre}
\]

Thus an almost complete separation is theoretically possible. The separation is feasible in practice if the point at which the iodide precipitation is complete can be detected. This may be done: (a) by the use of an adsorption indicator (see Section I, 410), or (b) by a potentiometric method with a silver electrode (see Section VI, 2).

For a mixture of bromide and iodide:

\[
\frac{[\text{I}^-]}{[\text{Br}^-]} = \frac{S_{\text{AgI}}}{S_{\text{AgBr}}} = \frac{1.7 \times 10^{-16}}{3.5 \times 10^{-13}} = \frac{1}{2.0 \times 10^3}
\]

Precipitation of silver bromide will occur when the concentration of the bromide ion in the solution is $2.0 \times 10^8$ times that of the iodide concentration. The separation is therefore not quite so complete as in the case of chloride and iodide, but can nevertheless be effected with fair accuracy with the aid of adsorption indicators (Sections I, 410 and III, 29).

I, 12. Complex ions.—The increase in solubility of a precipitate upon the addition of excess of the precipitating agent is frequently due to the formation of a complex ion. A complex ion is formed by the union of a simple ion with either other ions of opposite charge or with neutral molecules. Let us examine a few examples in detail.

When potassium cyanide solution is added to a solution of silver
Theoretical Basis of Quantitative Analysis

nitrate, a white precipitate of silver cyanide is first formed because the solubility product of silver cyanide:

\[ [\text{Ag}^+] \times [\text{CN}^-] = S_{\text{AgCN}} \]  

is exceeded. The reaction is expressed:

\[ \text{K}^+ + \text{CN}^- + \text{Ag}^+ + \text{NO}_3^- = \text{AgCN} + \text{K}^+ + \text{NO}_3^- \]

or \[ \text{CN}^- + \text{Ag}^+ = \text{AgCN} \]

The precipitate dissolves upon the addition of excess of potassium cyanide, the complex ion \([\text{Ag(CN)}_2]^\text{−}\) being produced:

\[ \text{AgCN (solid)} + \text{CN}^- \text{ (excess)} \rightleftharpoons [\text{Ag(CN)}_2]^\text{−} \]

(or \( \text{AgCN} + \text{KCN} = \text{K}[\text{Ag(CN)}_2] \) — a soluble complex salt)

This complex ion dissociates to give silver ions, since the addition of sulphide ions yields a precipitate of silver sulphide (solubility product \(1.6 \times 10^{-49}\)), and also silver is precipitated from the complex cyanide solution upon electrolysis. The complex ion thus dissociates in accordance with the equation:

\[ [\text{Ag(CN)}_2]^\text{−} \rightleftharpoons \text{Ag}^+ + 2\text{CN}^- \]

By applying the law of mass action to (2), we obtain the dissociation constant or instability constant of the complex ion:

\[ \frac{[\text{Ag}^+] \times [\text{CN}^-]^2}{[(\text{Ag(CN)}_2)^\text{−}]} = K \]

The constant has a value of \(1.0 \times 10^{-21}\) at the ordinary temperature. By inspection of this expression, and bearing in mind that excess of cyanide ion is present, it should be evident that the silver-ion concentration must be very small, so small in fact that the solubility product of silver cyanide is not exceeded.

Consider now a somewhat different type of complex ion formation, viz., the production of a complex ion with constituents other than the common ion present in the solution. This is exemplified by the solubility of silver chloride in ammonia solution. The reactions are:

\[ \text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl} \]

\[ \text{AgCl (solid)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- + 2\text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3)_2]^+ + \text{Cl}^- \]

(or \( \text{AgCl} + 2\text{NH}_3 = [\text{Ag(NH}_3)_2]\text{Cl} \))

Here again, for reasons similar to those already given, silver ions are present in solution. The dissociation of the complex ion is represented by:

\[ [\text{Ag(NH}_3)_2]^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3 \]

and the instability constant is given by:

\[ \frac{[\text{Ag}^+] \times [\text{NH}_3]^2}{[(\text{Ag(NH}_3)_2]^+]} = K = 6.8 \times 10^{-3} \]

* It is usual to employ square brackets to include the whole of a complex ion. In order to avoid confusion with concentrations for which square brackets are also widely used, concentrations will be represented in heavy type and complex ions either in lighter type or between curly brackets.
Quantitative Inorganic Analysis

The magnitude of the instability constant clearly shows that only a very small silver-ion concentration is produced by the dissociation of the complex ion.

The stability of complex ions varies within very wide limits. It is quantitatively expressed by means of the dissociation or instability constant. The more stable the complex, the smaller is the instability constant, i.e., the smaller is the tendency of the complex ion to dissociate into its constituent ions. When the complex ion is very stable, e.g., the ferrocyanide ion $\text{[Fe(ON)6]}^{-}$, the ordinary ionic reactions of the components are not shown. A few selected values of these constants at the ordinary temperature, determined by methods involving potentiometric titration (Chapter VI), are collected in Table V; this is instructive and also useful for reference purposes.

**Table V.**--Instability Constants of Complex Ions

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Instability Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[Ag(NH$_3$)$_2$]}^{++}$</td>
<td>$6.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{[Cu(NH$_3$)$_2$]}^{++}$</td>
<td>$5.0 \times 10^{-28}$</td>
</tr>
<tr>
<td>$\text{[Cd(NH$_3$)$_4$]}^{++}$</td>
<td>$2.5 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\text{[Cd}(\text{CN})_4]^{-}$</td>
<td>$2.2 \times 10^{-24}$</td>
</tr>
<tr>
<td>$\text{[Hg}(\text{CN})_4]^{-}$</td>
<td>$1.0 \times 10^{-23}$</td>
</tr>
<tr>
<td>$\text{[Hg}(\text{SCN})_4]^{-}$</td>
<td>$1.0 \times 10^{-23}$</td>
</tr>
</tbody>
</table>

The application of complex-ion formation in chemical separations depends upon the fact that one component may be transformed into a complex ion which is no longer precipitable with the precipitating agent, whereas another component is precipitated. One example may be mentioned here. This is concerned with the separation of cadmium and copper. Excess of potassium cyanide solution is added to the solution containing the two salts when the complex ions $\text{[Cd(CN)$_4$]}^{-}$ and $\text{[Cu(CN)$_4$]}^{-}$ respectively are formed. Upon passing hydrogen sulphide into the solution containing excess of CN$^-$ ions, a precipitate of cadmium sulphide is produced. Despite the higher solubility product of CdS ($1.4 \times 10^{-28}$ as against $6.5 \times 10^{-45}$ for copper sulphide), the former is precipitated because the complex cadmium cyanide ion has a greater instability constant (see Table V).

I, 13. Effect of acids upon the solubility of a precipitate.—For sparingly soluble salts of a strong acid the effect of the addition of an acid will be similar to that of any other indifferent electrolyte (compare salt effect in Section I, 10). If the sparingly soluble salt MA is the salt of a weak acid HA, then acids will, in general, have a solvent effect upon it. Let us suppose that hydrochloric acid is added to an aqueous suspension of such a salt. The following equilibrium will be established:

$$\text{M}^+ + \text{A}^- + \text{H}^+ + \text{Cl}^- \rightleftharpoons \text{HA} + \text{M}^+ + \text{Cl}^-$$

If the dissociation constant of the acid HA is very small, the anion A$^-$...
will be removed from the solution to form the undissociated acid HA. Consequently more of the salt will pass into solution to replace the anions removed in this way, and this process will continue until equilibrium is established (i.e., until \([M^+] \times [A^-] \) has become equal to the solubility product of \(MA\)) or, if sufficient hydrochloric acid is present, until the sparingly soluble salt has dissolved completely. Similar reasoning may be applied to salts of polybasic acids, such as phosphoric acid \((K_1 = 7.5 \times 10^{-3}; \ K_2 = 6.2 \times 10^{-8}; \ K_3 = 5 \times 10^{-13})\), oxalic acid \((K_1 = 5.9 \times 10^{-2}; \ K_2 = 6.4 \times 10^{-5})\), and arsenic acid. Thus the solubility of, say, silver orthophosphate is due to the removal of the \(PO_4^{3-}\) ion as \(HPO_4^{2-}\) and/or \(H_2PO_4^-\):

\[
PO_4^{3-} + H^+ \rightleftharpoons HPO_4^{2-}
\]

\[
HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^{-}
\]

With weak acids, such as carbonic \((K_1 = 4.3 \times 10^{-7}; \ K_2 = 5.6 \times 10^{-11})\), sulphurous \((K_1 = 1.7 \times 10^{-2}; \ K_2 = 1.0 \times 10^{-7})\), and nitrous \((K_1 = 4.6 \times 10^{-4})\) acids, an additional factor contributing to the increased solubility is the actual disappearance of the acid from solution either spontaneously or on gentle warming. An explanation is thus provided for the well-known solubility of the sparingly soluble sulphites, carbonates, oxalates, phosphates, arsenites, arsenates, acetates, cyanides (with the exception of silver cyanide, which is actually a salt of the strong acid \(H[Ag(CN)_2]\)), fluorides, and salts of other organic acids in strong acids.

The sparingly soluble sulphates (e.g., those of barium, strontium, and lead) also exhibit increased solubility in acids as a consequence of the weakness of the second stage of ionisation of sulphuric acid \((K_2 = 1.2 \times 10^{-2})\); the first stage is completely ionised:

\[
Ba^{++} + SO_4^{2-} + H^+ + Cl^- \rightleftharpoons HSO_4^- + Ba^{++} + Cl^-
\]

Since \(K_2\) is comparatively large, the solvent effect is relatively small. However, in the quantitative separation of barium sulphate, precipitation is usually carried out in slightly acid solution in order to obtain a more easily filterable precipitate and to reduce co-precipitation (Section I, 58).

The precipitation of substances within a controlled range of \(pH\) is discussed in Section I, 61B.

I, 14. Effect of temperature upon the solubility of a precipitate.—The solubility of the precipitates encountered in quantitative analysis increases with rise of temperature. With some substances the influence of temperature is small, but with others it is quite appreciable. Thus the solubility of silver chloride at 10° and 100° C. is 1.72 and 21.1 mg. per litre respectively, whilst that of barium sulphate at these two temperatures is 2.2 and 3.9 mg. per litre respectively. In many instances, the common-ion effect reduces the solubility to so small a value that the temperature effect, which is otherwise appreciable, becomes very small. Wherever possible it is advantageous to filter while the solution is hot; the rate of filtration is increased, as is also the solubility of foreign substances, thus rendering their removal from the precipitate more complete. The double phosphates of ammonium with magnesium, manganese or zinc, as well as lead sulphate and silver chloride, are usually filtered at the laboratory temperature to avoid solubility losses.
I, 15. Effect of the solvent upon the solubility of a precipitate. — The solubility of most inorganic compounds is reduced by the addition of organic solvents, such as methyl, ethyl, and n-propyl alcohols, acetone, etc. For example, the addition of about 20 per cent by volume of ethyl alcohol renders the solubility of lead sulphate practically negligible, thus permitting quantitative separation. Similarly calcium sulphate separates quantitatively from 50 per cent ethyl alcohol. Other examples of the influence of solvent will be found in Chapter IV.

I, 16. The ionic product of water. — Kohlrausch and Heydweiller (1894) found that the most highly purified water that can be obtained possesses a small but definite conductivity. Water must therefore be slightly ionised in accordance with the equation:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying the law of mass action to this equation, we obtain, for any given temperature:

$$\frac{a_{H^+} \times a_{OH^-}}{[H_2O]} = \frac{[H^+] \times [OH^-]}{[H_2O]} = \frac{f_{H^+} \times f_{OH^-}}{f_{H_2O}} = a \text{ constant}$$

where $a_\text{x}$, $[\text{x}]$, and $f_\text{x}$ refer to the activity, concentration, and activity coefficient of the species $\text{x}$. Since water is only slightly ionised, the ionic concentrations will be small, and their activity coefficients may be regarded as unity; the activity of the unionised molecules may also be taken as unity. The expression thus becomes:

$$\frac{[H^+] \times [OH^-]}{[H_2O]} = a \text{ constant}$$

In pure water or in dilute aqueous solutions, the concentration of the undissociated water may be considered constant. Hence:

$$[H^+] \times [OH^-] = K_w$$

where $K_w$ is the ionic product of water. It must be pointed out that the assumption that the activity coefficients of the ions are unity and that that activity coefficient of water is constant applies strictly to pure water and to very dilute solutions (ionic strength $< 0.01$); in more concentrated solutions, i.e., in solutions of appreciable ionic strength, the electrical environment affects the activity coefficients of the ions (compare Section I, 10) and also the activity of the unionised water. The ionic product of water will then not be constant, but will depend upon the ionic environment. It is, however, difficult to determine the activity coefficients, except under specially selected conditions, so that in practice the ionic product $K_w$, although not strictly constant, is employed.

The ionic product varies with the temperature, but under ordinary experimental conditions (at about 25° C.) its value may be taken as $1 \times 10^{-14}$ with concentrations expressed in gram-ions per litre. This is sensibly constant in dilute aqueous solutions. If the product of $[H^+]$ and $[OH^-]$ in aqueous solution momentarily exceeds this value, the

* Strictly speaking the hydrogen ion $H^+$ exists in water as the hydroxonium ion $H_3O^+$. The electrolytic dissociation of water should therefore be written:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

For the sake of simplicity, the more familiar symbol $H^+$ will be retained.
excess ions will immediately combine to form water. Similarly, if the product of the two ionic concentrations is momentarily less than $10^{-14}$, more water molecules will dissociate until the equilibrium value is attained.

The hydrogen- and hydroxyl-ion concentrations are equal in pure water; therefore $[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}$ g.-ions per litre at about $25^\circ$ C. A solution in which the hydrogen- and hydroxyl-ion concentrations are equal is termed an exactly neutral solution. If $[H^+]$ is greater than $10^{-7}$, the solution is acid, and if less than $10^{-7}$, the solution is alkaline (or basic). It follows that at ordinary temperatures $[OH^-]$ is greater than $10^{-7}$ in alkaline solution and less than this value in acid solution.

In all cases the reaction of the solution can be quantitatively expressed by the magnitude of the hydrogen-ion (or hydroxonium-ion) concentration, or, less frequently, of the hydroxyl-ion concentration, since the following simple relations between $[H^+]$ and $[OH^-]$ exist:

$$[H^+] = \frac{K_w}{[OH^-]} \quad \text{and} \quad [OH^-] = \frac{K_w}{[H^+]},$$

The variation of $K_w$ with temperature is shown in Table VI.

<table>
<thead>
<tr>
<th>Temp. (° C.)</th>
<th>$K_w \times 10^{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>0.12</td>
</tr>
<tr>
<td>5°</td>
<td>0.19</td>
</tr>
<tr>
<td>10°</td>
<td>0.29</td>
</tr>
<tr>
<td>15°</td>
<td>0.45</td>
</tr>
<tr>
<td>20°</td>
<td>0.68</td>
</tr>
<tr>
<td>25°</td>
<td>1.01</td>
</tr>
<tr>
<td>30°</td>
<td>1.47</td>
</tr>
</tbody>
</table>

I.17. The hydrogen-ion exponent, $pH$.—For many purposes, especially when dealing with small concentrations, it is cumbersome to express concentrations of hydrogen and hydroxyl ions in terms of gram-equivalents per litre. A very convenient method was proposed by S. P. L. Sorensen (1909). He introduced the hydrogen-ion exponent $pH$ defined by the relationships:

$$pH = -\log_{10}[H^+] = \log_{10} \frac{1}{[H^+]}, \quad \text{or} \quad [H^+] = 10^{-pH},$$

The quantity $pH$ is thus the logarithm (to the base 10) of the reciprocal of the hydrogen-ion concentration, or is equal to the logarithm of the hydrogen-ion concentration with negative sign. This method has the advantage that all states of acidity and alkalinity between those of solutions molar (or normal) with respect to hydrogen and hydroxyl ions can be expressed by a series of positive numbers between 0 and 14. Thus a neutral solution with $[H^+] = 10^{-7}$ has a $pH$ of 7; a solution with molar (or normal) concentration of hydrogen ions has a $pH$ of 0 ($= 10^0$); and a solution molar with respect to hydroxyl ions has $[H^+] = \frac{K_w}{[OH^-]} = 10^{-14}/10^0 = 10^{-14}$, and possesses a $pH$ of 14. A neutral solution is therefore one in which $pH = 7$, an acid solution one in which $pH < 7$, and an alkaline solution one in which $pH > 7$. An alternative definition for a neutral solution, applicable to all temperatures, is
one in which the hydrogen-ion and hydroxyl-ion concentrations are equal. In an acid solution the hydrogen-ion concentration exceeds the hydroxyl-ion concentration, whilst in an alkaline or basic solution, the hydroxyl-ion concentration is greater.

**Example 10.** (i) Find the pH of a solution of which \([H^+] = 4.0 \times 10^{-5}\).

\[
\log 4.0 = 0.602, \text{ hence } \log 4.0 \times 10^{-5} = 0.602 - 5 = -4.398
\]

(the decimal part or mantissa of the logarithm is always positive).

\[
pH = -\log [H^+] = -(-4.398) = 4.398
\]

(ii) Find the hydrogen-ion concentration corresponding to \(pH = 5.643\).

\[
pH = -\log [H^+] = 5.643 \implies \log [H^+] = -5.643
\]

This must be written in the usual form containing a negative characteristic and a positive mantissa:

\[
\log [H^+] = -5.643 = 0.357
\]

Referring to a table of antilogarithms, the number corresponding to the logarithm 0.357 is 2.28; the number corresponding to the logarithm 0.357 is accordingly 2.28 \(\times 10^{-8}\).

\[
[H^+] \text{ is therefore } 2.28 \times 10^{-8}
\]

(iii) Calculate the \(pH\) of a 0.01\(M\) solution of acetic acid (the degree of dissociation is 12.5 per cent).

The hydrogen-ion concentration is \(0.125 \times 0.01 = 1.25 \times 10^{-3}\). Now

\[
\log 1.25 = 0.097
\]

\[
pH = -(3 + 0.097) = 2.903
\]

The hydroxyl-ion concentration may be expressed in a similar way:

\[
pOH = -\log_{10}[OH^-] = \log_{10} 1/[OH^-], \text{ or } [OH^-] = 10^{-pOH}
\]

If we write the equation:

\[
[H^+] \times [OH^-] = K_w = 10^{-14}
\]

in the form:

\[
\log [H^+] + \log [OH^-] = \log K_w = -14
\]

then

\[
pH + pOH = pK_w = 14
\]

This relationship should hold for all dilute solutions at about 25\(^{\circ}\) C.

Fig. I, 17, 1 will serve as a useful mnemonic for the relation between \([H^+], pH, [OH^-]\), and \(pOH\) in acid and alkaline solution.
The logarithmic or exponential method has also been found useful for expressing other small quantities which arise in quantitative analysis. These include: (i) dissociation constants (Section I, 4), (ii) other ionic concentrations, and (iii) solubility products (Section I, 8).

(i) For any acid with a dissociation constant of $K_a$:

$$pK_a = -\log K_a = \log 1/K_a$$

Similarly for any base with dissociation constant $K_b$:

$$pK_b = -\log K_b = \log 1/K_b$$

(ii) For any ion $I$ of concentration $[I]$:

$$pI = -\log [I] = \log 1/[I]$$

Thus for $[Na^+] = 8 \times 10^{-5}$, $pI = 4.1$.

(iii) For a salt with a solubility product $S$:

$$pS = -\log S = \log 1/S$$

I, 18. The hydrolysis of salts.—Salts may be divided into four main groups:

(i) those derived from the strong acids and strong bases, e.g., potassium chloride;
(ii) those derived from weak acids and strong bases, e.g., sodium acetate;
(iii) those derived from strong acids and weak bases, e.g., ammonium chloride; and
(iv) those derived from weak acids and weak bases, e.g., ammonium formate or aluminium acetate.

When any of these is dissolved in water, the solution, as is well known, is not always neutral in reaction. Interaction occurs with the ions of water, and the resulting solution may be neutral, acid, or alkaline according to the nature of the salt.

With an aqueous solution of a salt of group (i), neither the anions have any tendency to combine with the hydrogen ions nor the cations with the hydroxyl ions of water, since the related acids and bases are strong electrolytes. The equilibrium between the hydrogen and hydroxyl ions in water:

$$H_2O \rightleftharpoons H^+ + OH^- \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldot
The hydrogen ions required for this reaction can be obtained only from the further dissociation of the water; this dissociation produces simultaneously an equivalent quantity of hydroxyl ions. The hydrogen ions are utilised in the formation of HA, consequently the hydroxyl-ion concentration of the solution will increase and the solution will react alkaline. The net result is that the anions of the salt react with the hydrogen ions of the water, yielding the weak acid HA, and there is an increase in the concentration of hydroxyl ions over that present in water.

It is usual in writing equations involving equilibria between completely dissociated and slightly dissociated or sparingly soluble substances to employ the ions of the former and the molecules of the latter. The reaction is therefore written:

\[ A^- + H_2O \rightleftharpoons OH^- + HA \quad \ldots \quad (3) \]

This equation can also be obtained by combining (1) and (2), since both equilibria must co-exist.

This interaction between the ion (or ions) of a salt and the ions of water is called hydrolysis. Formerly the chemical reaction was written:

\[ MA + H_2O \rightarrow MOH + HA \]

or as

\[ \text{Salt} + \text{Water} \rightleftharpoons \text{Base} + \text{Acid} \]

The reaction of the solution was clearly dependent upon the relative strengths of MOH and HA. This led to the definition of hydrolysis as the decomposition of a salt into an acid and a base.

Let us now study the salt of a strong acid and a weak base (group (iii)). Here the initial high concentration of cations M+ will be reduced by combination with the hydroxyl ions of water to form the little dissociated base MOH until the equilibrium:

\[ M^+ + OH^- \rightleftharpoons MOH \quad \ldots \quad (4) \]

is attained. The hydrogen-ion concentration of the solution will thus be increased, and the solution will react acid. The hydrolysis is here represented by:

\[ M^+ + H_2O \rightleftharpoons MOH + H^+ \quad \ldots \quad (5) \]

For salts of group (iv), in which both the acid and the base are weak, two reactions will occur simultaneously:

\[ M^+ + H_2O \rightleftharpoons MOH + H^+ \quad \ldots \quad (6) \]

\[ A^- + H_2O \rightleftharpoons HA + OH^- \quad \ldots \quad (7) \]

The reaction of the solution will clearly depend upon the relative dissociation constants of the acid and the base. If they are equal in strength, the solution will be neutral; if \( K_a > K_b \), it will be acid, and if \( K_b > K_a \), it will be alkaline.

Having considered all the possible cases, we are now in a position to give a more general definition of hydrolysis. **Hydrolysis** is the interaction between the ion (or ions) of a salt and the ions of water with the production of (a) a weak acid or a weak base, or (b) of both a weak acid and a weak base.
I, 10. Hydrolysis constant and degree of hydrolysis.—Case 1. Salt of a weak acid and a strong base. The equilibrium in a solution of a salt MA may be represented by:

\[ M^+ + A^- + H_2O \rightleftharpoons M^+ + OH^- + HA \]

or by

\[ A^- + H_2O \rightleftharpoons OH^- + HA \] (1)

Applying the law of mass action, we obtain:

\[ \frac{a_{OH^-} \times a_{HA}}{a_{A^-}} = \frac{[OH^-] \times [HA]}{[A^-]} \times f_{OH^-} \times f_{HA} = K_h \] (2)

where \( a, f, \) and \([ ]\) refer to activities, activity coefficients, and concentrations respectively, and \( K_h \) is the hydrolysis constant. The solution is assumed to be dilute; the activity of the unionised water may be taken as constant. In dilute solutions, the ionic strength is small, and the approximation that the activity coefficient of the unionised acid is unity and that both ions have the same activity coefficient may be introduced. Equation (2) then reduces to:

\[ K_h = \frac{[OH^-] \times [HA]}{[A^-]} \] (3)

This is often written in the form:

\[ K_h = \frac{[\text{Base}] \times [\text{Acid}]}{[\text{Unhydrolysed salt}]} \] (4)

the free strong base and the unhydrolysed salt are completely dissociated and the acid is very little dissociated.

The degree of hydrolysis is the fraction of each gram-molecule hydrolysed at equilibrium. Let 1 g.-mol. of salt be dissolved in \( V \) litres of solution, and let \( x \) be the degree of hydrolysis. The concentrations in gram-molecules or gram-ions per litre are:

\[ A^- + H_2O \rightleftharpoons OH^- + HA \]

Substituting these values in (3):

\[ K_h = \frac{[OH^-] \times [HA]}{[A^-]} = \frac{x/V \times x/V}{(1-x)/V} = \frac{x^2}{(1-x)V} \] (5)

This expression enables us to calculate the degree of hydrolysis from the value of the hydrolysis constant at the dilution \( V \). It is evident that as \( V \) increases, the degree of hydrolysis \( x \) must increase.

The two equilibria:

\[ H_2O \rightleftharpoons H^+ + OH^- \]

and

\[ HA \rightleftharpoons H^+ + A^- \]

must co-exist with the hydrolytic equilibrium:

\[ A^- + H_2O \rightleftharpoons HA + OH^- \]

Hence the two relationships:

\[ [H^+] \times [OH^-] = K_w \]

and

\[ [H^+] \times [A^-]/[HA] = K_a \]
Quantitative Inorganic Analysis

must hold in the same solution as:

$$\frac{[\text{OH}^-] \times [\text{HA}]/[\text{A}^-]}{[\text{H}^+] \times [\text{OH}^-] \times [\text{HA}]} = \frac{[\text{OH}^-] \times [\text{HA}]}{[\text{A}^-]} = K_h$$

But

$$\frac{K_w}{K_a} = \frac{[\text{H}^+] \times [\text{OH}^-] \times [\text{HA}]}{[\text{HA}] \times [\text{A}^-]}$$

dependence

$$K_w/K_a = K_h \quad \cdots \cdots \quad (6)$$

or

$$pK_h = pK_w - pK_a \quad \cdots \cdots \quad (7)$$

The hydrolysis constant is thus related to the ionic product of the water and the ionisation constant of the acid. Since $K_a$ varies slightly and $K_w$ varies considerably with temperature, $K_h$ and consequently the degree of hydrolysis will be largely influenced by changes of temperature.

The hydrogen-ion concentration of a solution of a hydrolysed salt can be readily computed. The amounts of HA and OH\(^-\) ions formed as a result of hydrolysis are equal, therefore in a solution of the pure salt in water $[\text{HA}] = [\text{OH}^-]$. If the concentration of the salt is $c$ g.-mols. per litre, then:

$$\frac{[\text{HA}] \times [\text{OH}^-]}{[\text{A}^-]} = \left(\frac{\text{OH}^-}{c}\right)^2 = K_h = \frac{K_w}{K_a}$$

and

$$[\text{OH}^-] = \sqrt{c \cdot K_w/K_a} \quad \cdots \cdots \quad (8)$$

or

$$[\text{H}^+] = \sqrt{K_w \cdot K_a/c}, \text{ since } [\text{H}^+] = K_w/[\text{OH}^-] \quad \cdots \cdots \quad (9)$$

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log c \star \quad \cdots \cdots \quad (10)$$

Equation (10) can be employed for the calculation of the $pH$ of a solution of a salt of a weak acid and a strong base. Thus the $pH$ of a $0.05N$ solution of sodium benzoate is given by:

$$pH = 7.0 + 2 \cdot 10 + \frac{1}{2} (-1.30) = 8.45$$

(Benzoic acid: $K_a = 6.87 \times 10^{-5}$; $pK_a = 4.20$)

Such a calculation will provide useful information as to the indicator which should be employed in the titration of a weak acid and a strong base (see Section I, 33).

Example 11. Calculate: (i) the hydrolysis constant, (ii) the degree of hydrolysis, and (iii) the hydrogen-ion concentration of a $0.01M$ solution of sodium acetate at the laboratory temperature.

$$K_h = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.82 \times 10^{-5}} = 5.5 \times 10^{-10}$$

The degree of hydrolysis $x$ is given by:

$$x = \frac{K_h}{1 - x}$$

Substituting for $K_h$ and $V (= 1/c)$, we obtain:

$$5.5 \times 10^{-10} = \frac{a^2 \times 0.01}{(1 - x)}$$

Solving this quadratic equation for $a$, we obtain $pH = 0.000235$ or 0.0235 per cent

$$\text{C}_2\text{H}_2\text{O}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H} \cdot \text{C}_2\text{H}_2\text{O}_3 + \text{OH}^-$$

$x$ mols. \hspace{1cm} $x$ mols. \hspace{1cm} $x$ mols.

* To be consistent we should write $p_a = - \log a$. 


If the solution were completely hydrolysed, the concentration of acetic acid produced would be 0.01M. But the degree of hydrolysis is 0.0235 per cent, therefore the concentration of acetic acid is 2.35 x 10^-3M. This is also equal to the hydroxyl-ion concentration produced, i.e., pOH = 5.63.

\[ pH = 14.0 - 5.63 = 8.37 \]

The pH may also be computed from equation (10):

\[ pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log c \]

\[ = 7.0 + 2.37 + \frac{1}{2} (-2) = 8.37 \]

Case 2. Salt of a strong acid and a weak base. The hydrolytic equilibrium is represented by:

\[ \text{M}^+ + \text{H}_2\text{O} \rightleftharpoons \text{MOH} + \text{H}^+ \quad \ldots \quad (11) \]

By applying the law of mass action along the lines of Case 1, the following equations are obtained:

\[ K_h = \frac{[\text{H}^+] \times [\text{MOH}]}{[\text{M}^+]^2} = \frac{[\text{Acid}] \times [\text{Base}]}{[\text{Unhydrolysed Salt}]} = \frac{K_w}{K_b}. \quad (12) \]

\[ = \frac{2^2}{(1 - x)V} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (13) \]

\[ K_b \] is the dissociation constant of the base. Furthermore, since \([\text{MOH}]\) and \([\text{H}^+]\) are equal (equation (11)):

\[ K_h = \frac{[\text{H}^+] \times [\text{MOH}]}{[\text{M}^+]^2} = \frac{[\text{H}^+]^2}{c} = \frac{K_w}{K_b}. \]

or

\[ pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c \quad \ldots \quad \ldots \quad (14) \]

Equation (14) may be applied to the calculation of the pH of solutions of salts of strong acids and weak bases. Thus the pH of a 0.02N solution of ammonium chloride is:

\[ pH = 7.0 - 2.37 - \frac{1}{2} (-0.70) = 4.98 \]

(Ammonium hydroxide: \( K_b = 1.85 \times 10^{-5} \); \( pK_b = 4.74 \))

Case 3. Salt of a weak acid and a weak base. The hydrolytic equilibrium is expressed by the equation:

\[ \text{M}^+ + \text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{MOH} + \text{HA} \quad \ldots \quad (15) \]

Applying the law of mass action and taking the activity of unionised water as unity, we have:

\[ K_h = \frac{a_{\text{MOH}} \times a_{\text{HA}}}{a_{\text{M}^+} \times a_{\text{A}^-}} = \frac{[\text{MOH}] \times [\text{HA}]}{[\text{M}^+] \times [\text{A}^-]} = \frac{f_{\text{MOH}} \times f_{\text{HA}}}{f_{\text{M}^+} \times f_{\text{A}^-}}. \quad (16) \]

By the usual approximations, that is, by assuming that the activity coefficients of the unionised molecules and, less justifiably, of the ions are unity, the following approximate equation is obtained:

\[ K_h \]

\[ = \frac{[\text{MOH}] \times [\text{HA}]}{[\text{M}^+] \times [\text{A}^-]} \quad \ldots \quad \ldots \quad (17) \]

\[ = \frac{[\text{Base}] \times [\text{Acid}]}{[\text{Unhydrolysed Salt}]^2} \quad \ldots \quad \ldots \quad (18) \]
If \( x \) is the degree of hydrolysis of 1 g.-mol. of the salt dissolved in \( V \) litres of solution, then the individual concentrations are:

\[
[\text{MOH}] = [\text{HA}] = x/V; \quad [\text{M}^+] = [\text{A}^-] = (1 - x)/V
\]

Substituting these values in (17):

\[
K_h = \frac{x/V \cdot x/V}{(1 - x)/V \cdot (1 - x)/V} = \frac{x^2}{(1 - x)^2} \quad \ldots \quad (19)
\]

The degree of hydrolysis and consequently the \( \text{pH} \) is independent of the concentration of the solution.*

As in Case 1 the expressions:

\[
K_w = [\text{H}^+] \times [\text{OH}^-]
\]

\[
K_a = \frac{[\text{HA}] \times [\text{A}^-]}{[\text{H}^+]} \quad \text{and} \quad K_b = \frac{[\text{A}^-]}{[\text{MOH}]}
\]

hold simultaneously with equation (15) for the hydrolytic equilibrium. By substitution in the last-named equation, it can be readily shown that:

\[
K_h = K_w/K_a \times K_b \quad \ldots \quad \ldots \quad \ldots \quad (20)
\]

or

\[
\frac{pK_h}{pK_a} = pK_w - pK_a - pK_b \quad \ldots \quad \ldots \quad \ldots \quad (21)
\]

This expression enables us to compute the value of the degree of hydrolysis \( x \) from the dissociation constants of the acid and the base.

The hydrogen-ion concentration of the hydrolysed solution is calculated in the following manner:

\[
[H^+] = K_a \times \frac{[HA]}{[A^-]} = K_a \times \frac{x/V}{(1 - x)/V} = K_a \times \frac{x}{(1 - x)}
\]

But \( x/(1 - x) = \sqrt{K_h} \) (by equation (19)):

\[
[H^+] = K_a \cdot \sqrt{K_h} = \sqrt{K_w} \times K_a/K_h \quad \ldots \quad (22)
\]

or

\[
\text{pH} = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b \quad \ldots \quad (23)
\]

If the ionisation constants of the acid and the base are equal, that is, \( K_a = K_b \), \( \text{pH} = 7.0 \), and the solution is neutral, although hydrolysis may be considerable. If \( K_a > K_b \), \( \text{pH} < 7 \) and the solution is acid, but when \( K_b > K_a \), \( \text{pH} > 7 \) and the solution reacts alkaline.

The \( \text{pH} \) of a solution of ammonium acetate is given by:

\[
\text{pH} = 7.0 + 2.37 - 2.37 = 7.0
\]

i.e., the solution is approximately neutral. On the other hand, for a dilute solution of ammonium formate:

\[
\text{pH} = 7.0 + 1.88 - 2.37 = 6.51
\]

(Formic acid: \( K_a = 1.77 \times 10^{-4} \); \( pK_a = 3.75 \))

i.e., the solution reacts slightly acid.

I. 20. Buffer solutions.—A solution of 0.001\( N \)-hydrochloric acid should have a \( \text{pH} \) equal to 4, but the solution is extremely sensitive to traces of alkali from the glass of the containing vessel and to am-

* This applies only if the original assumptions as to activity coefficients are justified. In solutions of appreciable ionic strength, the activity coefficients of the ions will vary with the total ionic strength.
monia from the air. Likewise a 0.0001N solution of sodium hydroxide, which should have a pH of 10, is sensitive to traces of carbon dioxide from the atmosphere. Aqueous solutions of potassium chloride and of ammonium acetate have a pH of about 7. The addition of 1 ml. of normal hydrochloric acid to 1 litre of the solution results in a change of pH to 3 in the former case and in very little change in the latter. The resistance of a solution to changes in hydrogen-ion concentration upon the addition of small amounts of acid or alkali is termed buffer action; a solution which possesses such properties is known as a buffer solution. It is said to possess "reserve acidity" and "reserve alkalinity." Solutions of which the pH values (determined by reference to the hydrogen electrode) are known, which can be readily prepared, and which are unaffected by small additions of alkali or acid, are required for the colorimetric and potentiometric determinations of hydrogen-ion concentration (see Sections V, 9 and VI, 12 respectively) and for other purposes.

Buffer solutions usually consist of solutions containing a mixture of a weak acid or base and its salt. In order to understand buffer action, let us study first the equilibrium between a weak acid and its salt. The dissociation of a weak acid is given by:

\[ HA \rightleftharpoons H^+ + A^- \]

and its magnitude is controlled by the value of the dissociation constant \( K_a \):

\[ \frac{a_{H^+} \times a_{A^-}}{a_{HA}} = K_a, \text{ or } a_{H^+} = \frac{a_{HA}}{a_{A^-}} \times K_a \ldots \ldots (1) \]

where \( a_x \) refers to the activity of the species \( x \). The expression may be approximated by writing concentrations for activities (strictly speaking, it will be recalled (Section I, 5), activity = concentration \times activity coefficient):

\[ [H^+] = \left[ \frac{[HA]}{[A^-]} \right] \times K_a \ldots \ldots \ldots (2) \]

This equilibrium applies to a mixture of an acid HA and its salt, say MA. If the concentration of the acid be \( c_a \) and that of the salt be \( c_s \), then the concentration of the undissociated portion of the acid is \( c_a - [H^+] \). The solution is electrically neutral, hence \( [A^-] = c_s + [H^+] \) (the salt is completely dissociated). Substituting these values in the equilibrium equation (2), we have:

\[ [H^+] = \frac{c_a - [H^+]}{c_s + [H^+]} \times K_a \ldots \ldots \ldots (3) \]

This is a quadratic equation for \([H^+]\) and may be solved in the usual manner. It can, however, be simplified by introducing the following further approximations. In a mixture of a weak acid and its salt, the dissociation of the acid is repressed by the common ion effect, and \([H^+]\) may be taken as negligibly small by comparison with \( c_a \) and \( c_s \). Equation (3) then reduces to:

\[ [H^+] = \frac{c_a}{c_s} K_a, \text{ or } [H^+] = \left[ \frac{[\text{Acid}]}{[\text{Salt}]} \right] \times K_a \ldots \ldots \ldots (4) \]

or

\[ pH = pK_a + \log \left[ \frac{[\text{Salt}]}{[\text{Acid}]} \right] \ldots \ldots \ldots (5) \]
Similarly for a mixture of a weak base of dissociation constant $K_b$ and its salt with a strong acid:

$$[\text{OH}^-] = \frac{[\text{Base}]}{[\text{Salt}]} \times K_b \quad \ldots \ldots \quad (6)$$

or

$$p\text{OH} = pK_b + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \ldots \ldots \quad (7)$$

Let us confine our attention to the case in which the concentrations of the acid and its salt are equal, i.e., of a half-neutralised acid. Then $p\text{H} = pK_a$. Thus the $p\text{H}$ of a half-neutralised solution of a weak acid is equal to the negative logarithm of the dissociation constant of the acid. For acetic acid, $K_a = 1.82 \times 10^{-5}$, $pK_a = 4.74$; a half-neutralised solution of, say, 0.1N-acetic acid will have a $p\text{H}$ of 4.74. If we add a small concentration of $\text{H}^+$ ions to such a solution, the former will combine with the acetate ions to form undissociated acetic acid:

$$\text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^- \leftrightarrow \text{H}\cdot\text{C}_2\text{H}_2\text{O}_2$$

Similarly, if a small concentration of hydroxyl ions be added, the latter will combine with the hydrogen ions arising from the dissociation of the acetic acid and form unionised water; the equilibrium will be disturbed, and more acetic acid will dissociate to replace the hydrogen ions removed in this way. In either case, the concentration of the acetic acid and acetate ion (or salt) will not be appreciably changed. It follows from equation (5) that the $p\text{H}$ of the solution will not be materially affected.

The solution containing equal concentrations of acid and its salt, or a half-neutralised solution of the acid, has the maximum buffer capacity. Other mixtures also possess considerable buffer capacity, but the $p\text{H}$ will differ slightly from the half-neutralised acid. Thus in a quarter-neutralised solution of acid, $[\text{Acid}] = 3[\text{Salt}]$:

$$p\text{H} = pK_a + \log \frac{1}{3} = pK_a + 1.52$$

In general, we may state that the buffering capacity is maintained for mixtures within the range 1 acid : 10 salt and 10 acid : 1 salt. The approximate $p\text{H}$ range of a weak acid buffer is:

$$p\text{H} = pK_a \pm 1$$

The concentration of the acid is usually of the order 0.05-0.2M. Similar remarks apply to weak bases.

The preparation of a buffer solution of a definite $p\text{H}$ is a simple process if the acid (or base) of appropriate dissociation constant is found: small variations in $p\text{H}$ are obtained by variations in the ratio of the acid to the salt concentration. One example is given in Table VII.

Before leaving the subject of buffer solutions, it is necessary to draw attention to a possible erroneous deduction from equation (5), namely, that the hydrogen-ion concentration of a buffer solution is dependent
The Theoretical Basis of Quantitative Analysis

### Table VII. pH of Acetic Acid–Sodium Acetate Buffer Mixtures*

10 ml. mixtures of \( x \) ml. of 0·2M-acetic acid and \( y \) ml. of 0·2M-sodium acetate.

<table>
<thead>
<tr>
<th>Acetic Acid (x ml.)</th>
<th>Sodium Acetate (y ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>9·5</td>
<td>0·5</td>
<td>3·42</td>
</tr>
<tr>
<td>9·0</td>
<td>1·0</td>
<td>3·72</td>
</tr>
<tr>
<td>8·0</td>
<td>2·0</td>
<td>4·05</td>
</tr>
<tr>
<td>7·0</td>
<td>3·0</td>
<td>4·27</td>
</tr>
<tr>
<td>6·0</td>
<td>4·0</td>
<td>4·45</td>
</tr>
<tr>
<td>5·0</td>
<td>5·0</td>
<td>4·65</td>
</tr>
<tr>
<td>4·0</td>
<td>6·0</td>
<td>4·80</td>
</tr>
<tr>
<td>3·0</td>
<td>7·0</td>
<td>4·99</td>
</tr>
<tr>
<td>2·0</td>
<td>8·0</td>
<td>5·23</td>
</tr>
<tr>
<td>1·0</td>
<td>9·0</td>
<td>5·57</td>
</tr>
<tr>
<td>0·5</td>
<td>9·5</td>
<td>5·89</td>
</tr>
</tbody>
</table>

* See Appendix, Section A, 10.

only upon the ratio of the concentrations of acid and salt and upon \( K_a \), and not upon the actual concentrations; otherwise expressed, that the \( \text{pH} \) of such a buffer mixture should not change upon dilution with water. This is approximately although not strictly true. In deducing equation (2), concentrations have been substituted for activities, a step which is not entirely justifiable except in dilute solutions. Theoretically, the expression controlling buffer action is:

\[
a_{\text{H}^+} = \frac{a_{\text{HA}}}{a_{\text{H}^-}} \times K_a = \frac{c_a \cdot f_{\text{A}^-}}{c_r \cdot f_{\text{A}^-}} \times K_a \quad \ldots \quad (8)
\]

where \( a \) and \( f \) refer to activities and activity coefficients respectively of the species indicated in the subscript. The activity coefficient \( f_a \) of the undissociated acid is approximately unity in dilute aqueous solution. Expression (8) thus becomes:

\[
a_{\text{H}^+} = \frac{[\text{Acid}]}{[\text{Salt}]} \times f_{\text{A}^-} \times K_a \quad \ldots \quad (9)
\]

or

\[
\text{pH} = \text{pK}_a + \log [\text{Salt}]/[\text{Acid}] + \log f_{\text{A}^-} \quad \ldots \quad (10)
\]

According to the Debye–Hückel–Onsager theory, the activity coefficient of an ion \( f_i \) in aqueous solution at 25°C is given by:

\[
\log f_i = -0.505z_i^2\mu^{0.5} + B\mu
\]

where \( z_i \) is the valency of the ion, \( \mu \) is the ionic strength of the solution, and \( A \) and \( B \) are constants. This may be written in the form

\[
\log f_i = -0.505z_i^2\mu^{0.5} + C\mu
\]

where \( C \) is another constant approximately equal to 0·605z_i^2A + B and usually has a value varying between 0·2 and 1·5. Substituting for \( f_{\text{A}^-} \) in (8), we obtain:

\[
\text{pH} = \text{pK}_a + \log [\text{Salt}]/[\text{Acid}] - 0.505z_i^2\mu^{0.5} + C\mu \quad (11)
\]

The activity coefficient of the ion \( f_{\text{A}^-} \) generally increases with decrease of concentration, so that when a buffer solution is diluted, \( f_{\text{A}^-} \) increases and consequently \( a_{\text{H}^+} \) will increase (equation (9)). For most practical
purposes the change is small, but for exact work the change must be taken into account. The addition of salts to buffer mixtures results in a change of the ionic strength of the solution; this will affect the pH of the solution (equation (11)). Indeed, in all buffer solutions a correction should, strictly speaking, be applied for the ionic strength of the solution.

Buffer mixtures are not confined to mixtures of monobasic acids or monoacid bases and their salts. We may employ a mixture of salts of a polybasic acid, e.g., \( \text{NaH}_2\text{PO}_4 \) and \( \text{Na}_2\text{HPO}_4 \). The salt \( \text{NaH}_2\text{PO}_4 \) is completely dissociated:

\[
\text{NaH}_2\text{PO}_4 \rightleftharpoons \text{Na}^+ + \text{H}_2\text{PO}_4^-
\]

The ion \( \text{H}_2\text{PO}_4^- \) acts as a monobasic acid:

\[
\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}
\]

for which \( K(=K_a \text{ for phosphoric acid}) = 6.2 \times 10^{-8} \). The addition of the salt \( \text{Na}_2\text{HPO}_4 \) is analogous to the addition of, say, acetate ions to a solution of acetic acid, since the tertiary ionisation of phosphoric acid (\( \text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-} \)) is small (\( K_3 = 5 \times 10^{-13} \)). The mixture of \( \text{NaH}_2\text{PO}_4 \) and \( \text{Na}_2\text{HPO}_4 \) is therefore an effective buffer over the range \( \text{pH} 7.2 \pm 1 \) (\( = pK \pm 1 \)).

Buffer solutions find many applications in quantitative analysis. Many precipitations are made in certain ranges of pH values. Examples are given in Section I, 61 under Separations; many others will be found scattered throughout the text. Buffer solutions are also employed in the colorimetric determination of pH with the aid of indicators (Section V, 9).
In the foregoing pages we have studied some general theory, a knowledge of which is indispensable for the comprehension of the processes of quantitative analysis, both gravimetric and volumetric. We will now confine our attention to the principles of volumetric analysis and postpone the parallel study of gravimetric analysis to a later stage (Section I, 54).

I, 21. Volumetric analysis, or quantitative chemical analysis by measure, consists essentially in determining the volume of a solution of accurately known concentration which is required to react quantitatively with the solution of the substance being determined. The solution of accurately known strength is called the standard solution; it contains a definite number of gram-equivalents (see Section I, 23) per litre. The weight of the substance to be determined is then calculated from the volume of the standard solution and the known laws of chemical equivalence.

The standard solution is usually added from a graduated vessel called a burette. The process of adding the standard solution until the reaction is just complete is termed a titration, and the substance to be determined is titrated. The point at which this occurs is called the equivalence point or the theoretical (or stoichiometric) end point. The completion of the titration should, as a rule, be detectable by some change unmistakable to the eye produced by the standard solution itself (e.g., potassium permanganate) or, more usually, by the addition of an auxiliary reagent, known as an indicator. After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change (either a colour change or the formation of a turbidity) in the liquid being titrated. The point at which this occurs is called the end point of the titration. In the ideal titration the visible end point will coincide with the stoichiometric or theoretical end point. In practice, however, a very small difference usually occurs; this represents the titration error. We should always endeavour to select an indicator and also the experimental conditions such that the difference between the visible end point and the equivalence point is as small as possible.

For use in volumetric analysis a reaction must fulfil the following conditions:

1. There must be a simple reaction which can be expressed by a chemical equation; the substance to be determined should react completely with the reagent in stoichiometric or equivalent proportions.

2. The reaction should be practically instantaneous or proceed with very great speed. (Most ionic reactions satisfy this condition.) In some cases the addition of a catalyst increases the speed of a reaction.

3. There must be a marked change in some physical or chemical property of the solution at the equivalence point.

4. An indicator should be available which, by a change in physical properties (colour or formation of a precipitate), should sharply define the end point of the reaction. (If no visible indicator is available for the detection of the equivalence point, the latter can often be determined by following during the course of the titration: (a) the potential
between an indicator electrode and a reference electrode (potentiometric titration, see Chapter VI); (b) the change in electrical conductance of the solution (conductometric titration, see Chapter VII); and (c) the current which passes through the titration cell between an indicator electrode (e.g., the dropping mercury electrode) and a depolarised reference electrode (e.g., the saturated calomel electrode) at a suitable applied e.m.f. (amperometric titration, see Chapter IX.)

Volumetric methods are, as a rule, susceptible of high accuracy (1 part in 1000) and possess several advantages, wherever applicable, over gravimetric methods. They need simpler apparatus, and are, generally, quickly performed; tedious and difficult separations can often be avoided. The following are required for volumetric analysis: (i) calibrated measuring vessels, including burettes, pipettes, and measuring-flasks (see Sections II, 20–22); (ii) substances of known purity for the preparation of standard solutions; (iii) an indicator or other device (see Section I, 58) for detecting the completeness of the reaction.

I. 22. Classification of reactions in volumetric analysis.—The reactions employed in volumetric analysis fall into two main classes:

(a) Those in which no change in valency occurs; these are dependent upon the combination of ions.

(b) Oxidation-reduction reactions; these involve a change of valency or, otherwise expressed, a transfer of electrons.

For purposes of convenience, however, these two types of reactions are divided into three main classes:

1. Neutralisation reactions, or acidimetry and alkalimetry. These include the titration of free bases, or those formed from salts of weak acids by hydrolysis, with a standard acid (acidimetry), and the titration of free acids, or those formed by the hydrolysis of salts of weak bases, with a standard base (alkalimetry). These reactions involve the combination of hydrogen and hydroxyl ions to form water.

2. Precipitation and complex-formation reactions. These depend upon the combination of ions, other than hydrogen and hydroxyl ions, to form either a simple precipitate, as in the titration of silver with a solution of a chloride (Section III, 24), or a complex ion, as in the titration of a cyanide with silver nitrate solution (Section III, 41; 2CN⁻ + Ag⁺ ⇌ [Ag(ON)₂]⁻).

3. Oxidation-reduction reactions. Under this heading are included all reactions involving change in oxidation number (Section I, 23) or transfer of electrons (Section I, 23) among the reacting substances. The standard solutions are either oxidising or reducing agents. The principal oxidising agents are potassium permanganate, potassium dichromate, ceric sulphate, manganic sulphate, iodine, potassium iodate, potassium bromate, and chloramine-T. Frequently used reducing agents are ferrous and stannous compounds, sodium thiosulphate, arsenious oxide, and titanous chloride or sulphate.

I. 23. Equivalent weights. Normal solutions.—A standard solution is one which contains a known weight of the reagent in a definite volume of the solution. A molar solution is one which contains 1 g. molecular weight of the reagent per litre of solution. A normal solution of a reagent is one that contains 1 g. equivalent weight.

* Sometimes also called equivalent, gram equivalent or equivalent weight.
The Theoretical Basis of Quantitative Analysis

per litre of solution. It is designated by \( N \). Semi-normal, penti-normal, and centi-normal solutions are often required; these are shortly written \( N/2 \) or \( 0.5N \), \( N/5 \) or \( 0.2N \), \( N/10 \) or \( 0.1N \), and \( N/100 \) or \( 0.01N \) respectively.

The above definition of normal solution utilises the term “equivalent weight.” This quantity varies with the type of reaction, and, since it is difficult to give a clear definition of “equivalent weight” which will cover all reactions, it is proposed to discuss this subject in some detail below. It often happens that the same compound possesses different equivalent weights in different chemical reactions. The situation may therefore arise in which a solution may have normal concentration when employed for one purpose, and a different normal concentration when used in another chemical reaction.

Neutralisation reactions. The equivalent weight of an acid is that weight of it which contains one replaceable hydrogen, i.e., 1.008 (more accurately 1.0078) g. of hydrogen. The equivalent weight of a monobasic acid, such as hydrochloric, hydrobromic, hydriodic, nitric, perchloric, or acetic acid, is identical with its molecular weight. A normal solution of a monobasic acid will therefore contain 1 g. molecular weight (or 1 mol.) in a litre of solution. The equivalent weight of a dibasic acid (e.g., sulphuric or oxalic acid), or of a tribasic acid (e.g., phosphoric acid) is likewise \( \frac{1}{2} \) and \( \frac{1}{3} \) respectively of its molecular weight.

The equivalent weight of a base is that weight of it which contains one replaceable hydroxyl group, i.e., 17.008 g. of ionisable hydroxyl. 17.008 g. of hydroxyl are equivalent to 1.008 g. of hydrogen. The equivalent weights of sodium hydroxide, potassium hydroxide, and ammonium hydroxide are 1 mol., of calcium hydroxide, strontium hydroxide, and barium hydroxide \( \frac{1}{2} \) mol.

Salts of strong bases and weak acids possess alkaline reactions in aqueous solution because of hydrolysis (Section I, 18). Sodium carbonate, with methyl orange as indicator, reacts with 2 mols. of hydrochloric acid to form 2 mols. of sodium chloride; hence its equivalent weight is \( \frac{1}{2} \) mol. Borax, under similar conditions, also reacts with 2 mols. of hydrochloric acid, and its equivalent weight is, likewise, \( \frac{1}{2} \) mol.

Precipitation reactions. Here the equivalent weight is the weight of the substance which contains or reacts with 1 g.-atom of a univalent metal (which is equivalent to 1.008 g. of hydrogen), \( \frac{1}{2} \) g.-atom of a bivalent metal, etc. For a metal, the equivalent weight is the atomic weight divided by the valency. For a reagent which reacts with this metal, the equivalent weight is the weight of it which reacts with one equivalent of the metal. The reactive constituents of a salt are its ions. The equivalent weight of a salt in a precipitation reaction is the gram molecular weight of the salt divided by the total valency of the reacting ion. Thus the equivalent weight of silver nitrate in the titration of chloride is its molecular weight.

In a complex formation reaction the equivalent weight is most simply deduced by writing down the ionic equation of the reaction. For example, the equivalent weight of potassium cyanide in the titration with silver ions is 2 mols., since the reaction is:

\[ 2CN^- + Ag^+ \rightarrow [Ag(CN)_2]^+ \]

Oxidation–reduction reactions. The equivalent weight of an oxidising
or reducing agent is most simply defined as that weight of the reagent which reacts with or contains 1.008 g. of available hydrogen or 8.000 g. of available oxygen. By "available" is meant capable of being utilised in oxidation or reduction. The amount of available oxygen may be indicated by writing the hypothetical equation, e.g.,

\[ 2\text{KMnO}_4 = \text{K}_2\text{O} + 2\text{MnO}_2 + 5\text{O} \]

i.e., in acid solution 2KMnO₄ gives up 5 atoms of available oxygen, which is taken up by the reducing agent, hence its equivalent weight is \( \frac{2\text{KMnO}_4}{10} \). For potassium dichromate in acid solution, the hypothetical equation is:

\[ \text{K}_2\text{Cr}_2\text{O}_7 = \text{K}_2\text{O} + 2\text{Cr}_2\text{O}_3 + 3\text{O} \]

The equivalent weight is \( \frac{\text{K}_2\text{Cr}_2\text{O}_7}{6} \). This elementary treatment is limited in application, but is useful for beginners.

A more general view is obtained by a consideration of:

(a) the number of electrons involved in the partial ionic equation representing the reaction, and
(b) the change in the "oxidation number" of a significant element in the oxidant or reductant. Both methods will be considered in some detail.

In quantitative analysis we are chiefly concerned with reactions which take place in solution, i.e., ionic reactions. We shall therefore limit our discussion of oxidation-reduction to such reactions. The oxidation of ferrous chloride by chlorine in aqueous solution may be written:

\[ 2\text{FeCl}_2 + \text{Cl}_2 = 2\text{FeCl}_3 \]

or may be expressed ionically:

\[ 2\text{Fe}^{++} + \text{Cl}_2 = 2\text{Fe}^{+++} + 2\text{Cl}^- \]

The ferrous ion \( \text{Fe}^{++} \) is converted into the ferric ion \( \text{Fe}^{+++} \) (oxidation), and the neutral chlorine molecule into negatively charged chloride ions \( \text{Cl}^- \) (reduction). According to the electronic conception of the constitution of matter, the conversion of \( \text{Fe}^{++} \) into \( \text{Fe}^{+++} \) requires the loss of one electron, and the transformation of the neutral chlorine molecule into chloride ions necessitates the gain of two electrons. This leads to the view that, for reactions in solution, oxidation is a process involving a loss of electrons, as in

\[ \text{Fe}^{++} - \varepsilon = \text{Fe}^{+++} \]

and reduction is the process resulting in a gain of electrons, as in

\[ \text{Cl}_2 + 2\varepsilon = 2\text{Cl}^- \]

In the actual oxidation-reduction process electrons are transferred from the reducing agent to the oxidising agent. This leads to the following definitions:

**Oxidation** is the process which results in the loss of one or more electrons by atoms or ions. **Reduction** is the process which results in the gain of one or more electrons by atoms or ions. An **oxidising agent** is one that gains electrons and is reduced to a lower valency condition. A **reducing agent** is one that loses electrons and is oxidised to a higher valency condition.

The following are examples of oxidising agents which are of importance in quantitative analysis: potassium permanganate, potassium
dichromate, ceric sulphate, manganic sulphate, iodine, potassium bromate, potassium iodate, and chloramine-T. Examples of reducing agents are: ferrous sulphate, metallic iron, sodium thiosulphate, sodium arsenite or arsenious oxide, oxalic acid, titanous chloride or sulphate, vanadous sulphate, and chromous sulphate.

In all oxidation-reduction processes (or redox processes) there will be a reactant undergoing oxidation and one undergoing reduction, since the two reactions are complementary to one another and occur simultaneously—one cannot take place without the other. The reagent suffering oxidation is termed the reducing agent or reductant, and the reagent undergoing reduction is called the oxidising agent or oxidant. The study of the electron changes in the oxidant and reductant forms the basis of the ion-electron method for balancing ionic equations, a method developed in some detail by Jette and La Mer in 1927. The equation is accordingly first divided into two balanced, partial equations representing the oxidation and reduction respectively. It must be remembered that the reactions take place in aqueous solution so that in addition to the ions supplied by the oxidant and reductant, the molecule of water $H_2O$, hydrogen ions $H^+$, and hydroxyl ions $OH^-$ are also present, and may be utilised in balancing the partial ionic equation. The unit change in oxidation or reduction is a charge of one electron, which will be denoted by $\epsilon$. To appreciate the principles involved, let us consider first the reaction between ferric chloride and stannous chloride in aqueous solution. The partial ionic equation for the reduction is:

\[
Fe^{+++} \rightarrow Fe^{++} \quad \ldots \ldots \quad (1)
\]

and for the oxidation is:

\[
Sn^{++} \rightarrow Sn^{++++} \quad \ldots \ldots \quad (2)
\]

The equations must be balanced not only with regard to the number and kind of atoms, but also electrically, that is, the net electric charge on each side must be the same. Equation (1) can be balanced by adding one electron to the left-hand side:

\[
Fe^{+++} + \epsilon \rightleftharpoons Fe^{++} \quad \ldots \ldots \quad (1')
\]

and equation (2) by adding two electrons to the right-hand side:

\[
Sn^{++} \rightleftharpoons Sn^{++++} + 2\epsilon \quad \ldots \ldots \quad (2')
\]

These partial equations must then be multiplied by coefficients which result in the number of electrons utilised in one reaction being equal to those liberated in the other. Thus equation (1') must be multiplied by two, and we have:

\[
2Fe^{+++} + 2\epsilon \rightleftharpoons 2Fe^{++} \quad \ldots \ldots \quad (1'')
\]

\[
Sn^{++} \rightleftharpoons Sn^{++++} + 2\epsilon \quad \ldots \ldots \quad (2'')
\]

Adding (1'') and (2''), we obtain:

\[
2Fe^{+++} + Sn^{++} + 2\epsilon \rightleftharpoons 2Fe^{++} + Sn^{++++} + 2\epsilon
\]

and by cancelling the electrons common to both sides, the simple ionic equation is obtained:

\[
2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}
\]
Quantitative Inorganic Analysis

The following facts must be borne in mind. All strong electrolytes are completely dissociated; hence only the ions actually taking part or resulting from the reaction need appear in the equation. Substances which are only slightly ionised, such as water, or which are sparingly soluble and thus yield only a small concentration of ions, e.g., silver chloride and barium sulphate, are, in general, written in the molecular form because most of the substance is present in this state.

The complete rules for the application of the ion-electron method may be expressed as follows:

(a) ascertain the products of the reaction;
(b) set up a partial equation for the oxidising agent;
(c) set up a partial equation for the reducing agent in the same way;
(d) multiply each partial equation by a factor so that when the two are added the electrons just compensate each other;
(e) add the partial equations and cancel out substances which appear on both sides of the equation.

A few examples follow.

Reaction I: the reduction of potassium permanganate in the presence of dilute sulphuric acid.

The first partial equation (reduction) is:

\[ \text{MnO}_4^- \rightarrow \text{Mn}^{++} \]

To balance atomically, 8H\(^+\) is required:

\[ \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Mn}^{++} + 4\text{H}_2\text{O} \]

and to balance it electrically 5\(\varepsilon\) is needed on the left-hand side:

\[ \text{MnO}_4^- + 8\text{H}^+ + 5\varepsilon \rightarrow \text{Mn}^{++} + 4\text{H}_2\text{O} \]

The second partial equation (oxidation) is:

\[ \text{Fe}^{++} \rightarrow \text{Fe}^{+++} \]

To balance this electrically one electron must be added to the right-hand side or subtracted from the left-hand side:

\[ \text{Fe}^{++} \equiv \text{Fe}^{+++} + \varepsilon \]

Now the gain and loss of electrons must be equal. One permanganate ion utilises 5 electrons, and one ferrous ion liberates 1 electron; hence the two partial equations must take place in the ratio of 1 : 5.

\[ \frac{\text{MnO}_4^- + 8\text{H}^+ + 5\varepsilon \rightarrow \text{Mn}^{++} + 4\text{H}_2\text{O}}{5(\text{Fe}^{++} \equiv \text{Fe}^{+++} + \varepsilon)} \]

or

\[ \frac{\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{++} = \text{Mn}^{++} + 5\text{Fe}^{+++} + 4\text{H}_2\text{O}}{\text{Cr}_2\text{O}_7^{--} \rightarrow \text{Cr}^{+++}} \]

Reaction II: the interaction of potassium dichromate and potassium iodide in the presence of dilute sulphuric acid.

\[ \text{Cr}_2\text{O}_7^{--} + 14\text{H}^+ \rightarrow 2\text{Cr}^{+++} + 7\text{H}_2\text{O} \]

To balance electrically, add 6\(\varepsilon\) to the left-hand side:

\[ \text{Cr}_2\text{O}_7^{--} + 14\text{H}^+ + 6\varepsilon \Rightarrow 2\text{Cr}^{+++} + 7\text{H}_2\text{O} \]
The Theoretical Basis of Quantitative Analysis

The various stages in the deduction of the second partial equation are:

\[ I^- \rightarrow I_2 \]
\[ 2I^- \rightarrow I_2 \]
\[ 2I^- \rightleftharpoons I_2 + 2\varepsilon \]

One dichromate ion uses 6\varepsilon, and two iodide ions liberate 2\varepsilon; hence the two partial equations take place in the ratio of 1 : 3:

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\varepsilon \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
\[ 3(2I^- \rightleftharpoons I_2 + 2\varepsilon) \]

or

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{I}_2 \]

We can now apply our knowledge of partial ionic equations to the subject of equivalents. The standard oxidation-reduction process is

\[ H^+ + e^- \rightarrow \text{H}_2\text{O} \]

where \( e \) represents an electron per atom or one Faraday (96,500 coulombs) per gram-atom. If we know the change in the number of electrons per ion in any oxidation-reduction reaction, the equivalent may be calculated. The equivalent weight of an oxidant or reductant is the molecular weight divided by the number of electrons which one molecule of the substance gains or loses in the reaction.

We will write down the partial equations for four typical reactions:

\[
\begin{align*}
\text{MnO}_4^- + 8\text{H}^+ + 5\varepsilon & \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} & \text{Eq. wt.} = \text{MnO}_4^-/5 = \text{KMnO}_4/5. \\
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\varepsilon & \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} & \text{Eq. wt.} = \text{Cr}_2\text{O}_7^{2-}/6 = K_2\text{Cr}_2\text{O}_7/6. \\
\text{Fe}^{3+} - \varepsilon & \rightarrow \text{Fe}^{2+} & \text{Eq. wt.} = \text{Fe}^{3+}/1 = \text{FeSO}_4/1. \\
\text{C}_2\text{O}_4^{2-} - 2\varepsilon & \rightarrow 2\text{CO}_2 & \text{Eq. wt.} = \text{C}_2\text{O}_4^{2-}/2 = \text{H}_2\text{C}_2\text{O}_4/2. \\
\end{align*}
\]

For convenience of reference the partial ionic equations for a number of oxidising and reducing agents are collected in Table VIII.

The other procedure which is of value in the calculation of the equivalent weights of substances is the “oxidation number” method. The student should be thoroughly conversant with the significance of “oxidation number” and its use in balancing oxidation-reduction equations.* The equivalent weight of an oxidising agent is determined by the change in oxidation number which the reduced element experiences. It is that quantity of oxidant which involves a change of one unit in the oxidation number. Thus in the normal reduction of potassium permanganate in the presence of dilute sulphuric acid to a manganous salt:

\[ \text{K}_2\text{MnO}_4 \rightarrow \text{K}_2\text{MnSO}_4 \]

the change in the oxidation number of the manganese is from +7 to +2. The equivalent weight of potassium permanganate is therefore \( \frac{1}{5} \) mol. Similarly for the reduction of potassium dichromate in acid solution:

\[ \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{K}_2\text{Cr}_2(\text{SO}_4)_3 \]

the change in oxidation number of two atoms of chromium is from +6 to +3, or by 3 units of reduction. The equivalent weight of potassium dichromate is accordingly \( \frac{1}{3} \) mol. In order to find the equivalent weight of an oxidising agent, we divide the molecular weight

* A detailed account will be found in the author’s *Test Book of Qualitative Chemical Analysis*, Third Edition, 1945. (Longmans, Green and Co.)
Quantitative Inorganic Analysis

by the change in oxidation number per molecule which some key element in the substance undergoes.

<table>
<thead>
<tr>
<th>Substance.</th>
<th>Partial Ionic Equation.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>OXIDANTS</strong></td>
<td></td>
</tr>
<tr>
<td>Potassium permanganate (acid)</td>
<td>$\text{MnO}_4^- + 8\text{H}^+ + 5\epsilon \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Potassium permanganate (neutral)</td>
<td>$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\epsilon \rightleftharpoons \text{MnO}_4^2- + 4\text{OH}^-$</td>
</tr>
<tr>
<td>Potassium permanganate (strongly alkaline)</td>
<td>$\text{Co}^{3+} + \epsilon \rightarrow \text{Co}^{2+}$</td>
</tr>
<tr>
<td>Ceric sulphate</td>
<td></td>
</tr>
<tr>
<td>Potassium dichromate</td>
<td>$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\epsilon \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$\text{Cl}_2 + 2\epsilon \rightleftharpoons 2\text{Cl}^-$</td>
</tr>
<tr>
<td>Bromine</td>
<td>$\text{Br}_2 + 2\epsilon \rightleftharpoons 2\text{Br}^-$</td>
</tr>
<tr>
<td>Iodine</td>
<td>$\text{I}_2 + 2\epsilon \rightarrow 2\text{I}^-$</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td></td>
</tr>
<tr>
<td>Potassium bromate</td>
<td>$\text{BrO}_3^- + 6\text{H}^+ + 6\epsilon \rightleftharpoons \text{Br}^- + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Potassium iodate</td>
<td>$\text{IO}_3^- + 6\text{H}^+ + 6\epsilon \rightarrow \text{I}^- + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Sodium hypochlorite</td>
<td>$\text{ClO}^- + \text{H}_2\text{O} + 2\epsilon \rightarrow \text{Cl}^- + 2\text{H}^+$</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\epsilon \rightarrow \text{H}_2\text{O} + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Manganese dioxide</td>
<td>$\text{MnO}_3^- + 4\text{H}^+ + 2\epsilon \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Sodium bisulphate</td>
<td>$\text{BiO}_3^- + 6\text{H}^+ + 2\epsilon \rightarrow \text{Bi}^{3+} + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Nitric acid (conc.)</td>
<td>$\text{NO}_3^- + 2\text{H}^+ + \epsilon \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Nitric acid (dilute)</td>
<td>$\text{NO}_3^- + 4\text{H}^+ + 3\epsilon \rightarrow \text{NO} + 2\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

| **REDUCTANTS** |                          |
| Hydrogen | $\text{H}_2 \rightarrow 2\epsilon \rightleftharpoons 2\text{H}^+$ |
| Zinc | $\text{Zn} \rightarrow 2\epsilon \rightleftharpoons \text{Zn}^{2+}$ |
| Hydrogen sulphide | $\text{H}_2\text{S} = 2\epsilon \rightarrow 2\text{H}^+ + \text{S}$ |
| Hydrogen iodide | $2\text{HI} = 2\epsilon \rightleftharpoons \text{I}_2 + 2\text{H}^+$ |
| Oxalic acid | $\text{C}_2\text{O}_4^{2-} = 2\epsilon \rightarrow 2\text{CO}_2$ |
| Ferric sulphate | $\text{Fe}^{3+} + \epsilon \rightarrow \text{Fe}^{2+}$ |
| Sulphurous acid | $\text{H}_2\text{SO}_3 + \text{H}_2\text{O} = 2\epsilon \rightleftharpoons \text{SO}_3^{2-} + 4\text{H}^+$ |
| Sodium thiosulphate | $2\text{S}_2\text{O}_3^{2-} = 2\epsilon \rightleftharpoons 2\text{SO}_3^{2-}$ |
| Titanous sulphate | $\text{Ti}^{2+} + \epsilon \rightarrow \text{Ti}^{3+}$ |
| Stannous chloride | $\text{Sn}^{2+} + 2\text{Cl}^- = 2\epsilon \rightleftharpoons \text{SnCl}_4^{2-}$ |
| Stannous chloride (in presence of hydrochloric acid) | $\text{H}_2\text{O}_2 \rightarrow 2\epsilon \rightarrow 2\text{H}^+ + \text{O}_2$ |

The equivalent weight of a reducing agent is similarly determined by the change in oxidation number which the oxidised element suffers. Consider the conversion of ferrous into ferric sulphate:

$$2(\text{FeSO}_4) \rightarrow \text{Fe}_2(\text{SO}_4)_3$$

Here the change in oxidation number per atom of iron is from +2 to +3, or by 1 unit of oxidation, hence the equivalent weight of ferrous sulphate is 1 mol. Another important reaction is the oxidation of oxalic acid to carbon dioxide and water:

$$\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO}_2 \rightarrow 2\text{H}_2\text{O}$$

The change in oxidation number of two atoms of carbon is from +6 to +4, or by 2 units of oxidation. The equivalent weight of oxalic acid is therefore $\frac{1}{2}$ mol.
In general, it may be stated:

(i) The equivalent weight of an element taking part in an oxidation-reduction (redox) reaction is the atomic weight divided by the change in oxidation number.

(ii) When an atom in any complex molecule suffers a change in oxidation number (oxidation or reduction), the equivalent weight of the substance is the molecular weight divided by the change in oxidation number of the oxidised or reduced element. If more than one atom of the reactive element is present, the molecular weight is divided by the total change in oxidation number.

A useful summary of the common oxidising and reducing agents, together with the various transformations which they undergo is given in Table IX.

We are now in a position to understand more clearly why the equivalent weights of some substances vary with the reaction. We will consider two familiar examples by way of illustration. A normal solution of ferrous sulphate \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \) will have an equivalent weight of 1 mol. when employed as a reductant, and \( \frac{1}{2} \) mol. when employed as a precipitant. A solution of ferrous sulphate which is normal as a precipitant will be half normal as a reductant. Potassium tetroxalate \( \text{KHC}_2\text{O}_4\cdot\text{H}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O} \) contains three replaceable hydrogen atoms; its equivalent weight in neutralisation reactions is therefore \( \frac{1}{3} \) mol.:

\[
\text{KHC}_2\text{O}_4\cdot\text{H}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O} + 3\text{KOH} = 2\text{K}_2\text{C}_2\text{O}_4 + 5\text{H}_2\text{O}
\]

As a reducing agent, a gram molecular weight contains \( 2\text{C}_2\text{O}_4^- \), and the equivalent weight is accordingly \( \frac{1}{2} \) mol.:

\[
\text{C}_2\text{O}_4^- - 2e = 2\text{CO}_2
\]

A solution of the salt which is \( 3N \) as an acid is \( 4N \) as a reducing agent.

**Advantages of the use of the equivalent system for the preparation of standard solutions.**—The most important advantage of the equivalent system is that the calculations of volumetric analysis are rendered very simple, since at the end point the number of equivalents of the substance titrated is equal to the number of equivalents of the standard solution employed. We may write:

\[
\text{Normality} = \frac{\text{Number of gram-equivalents}}{\text{Number of litres}} = \frac{\text{Number of milligram-equivalents}}{\text{Number of millilitres (ml.)}}
\]

Hence: number of mg.-equivalents = number of ml. \( \times \) normality.

If the volumes of solutions of two different substances \( A \) and \( B \) which exactly react with one another are \( V_A \) ml. and \( V_B \) ml. respectively, then these volumes severally contain the same number of g.-equivalents or mg.-equivalents of \( A \) and \( B \). Thus:

\[
V_A \times \text{normality}_A = V_B \times \text{normality}_B \quad . \quad . \quad (1)
\]

In practice, \( V_A, V_B \), and normality \( A \) (the standard solution) are known, hence normality \( B \) (the unknown solution) can be readily calculated.
### COMMON OXIDISING AGENTS

<table>
<thead>
<tr>
<th>Substance</th>
<th>Radical or Element involved</th>
<th>O.N. of &quot;Effective&quot; Element</th>
<th>Reduction Product</th>
<th>New O.N.</th>
<th>Decrease in O.N.</th>
<th>Gain in Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>KMnO$_4$ (acid)</td>
<td>MnO$_4^-$</td>
<td>+7</td>
<td>Mn$^{2+}$</td>
<td>+2</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>KMnO$_4$ (neutral)</td>
<td>MnO$_4^-$</td>
<td>+7</td>
<td>Mn$^{2+}$ or Mn$^{3+}$</td>
<td>+4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>KMnO$_4$ (strongly alkaline)</td>
<td>MnO$_4^-$</td>
<td>+7</td>
<td>MnO$_{4^-}$</td>
<td>+6</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$</td>
<td>Cr$_2$O$_7^{2-}$</td>
<td>+6</td>
<td>Cr$^{3+}$</td>
<td>+3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>HNO$_3$ (dil.)</td>
<td>NO$_3^-$</td>
<td>+5</td>
<td>NO</td>
<td>+2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>HNO$_3$ (cons.)</td>
<td>NO$_3^-$</td>
<td>+5</td>
<td>NO$_2$</td>
<td>+4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>Cl</td>
<td>0</td>
<td>Cl$^-$</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>Br</td>
<td>0</td>
<td>Br$^-$</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I$_2$</td>
<td>I</td>
<td>0</td>
<td>I$^-$</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>HCl: 1HNO$_3$</td>
<td>Cl</td>
<td>0</td>
<td>Cl$^-$</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>O</td>
<td>0</td>
<td>O$^-$</td>
<td>-2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Na$_2$O$_2$</td>
<td>O</td>
<td>0</td>
<td>O$^-$</td>
<td>-2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>KClO$_3$</td>
<td>ClO$_3^-$</td>
<td>+5</td>
<td>Cl$^-$</td>
<td>-1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>KBrO$_3$</td>
<td>BrO$_3^-$</td>
<td>+5</td>
<td>Br$^-$.</td>
<td>-1</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>KIO$_3$</td>
<td>IO$_3^-$</td>
<td>+5</td>
<td>I$^-$</td>
<td>-1</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>NaOCIO</td>
<td>OCl$^-$</td>
<td>+1</td>
<td>OCl$^-$</td>
<td>-1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>Fe$^{3+}$</td>
<td>+3</td>
<td>Fe$^{2+}$</td>
<td>+2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ce(SO$_4$)$_3$</td>
<td>Ce$^{3+}$</td>
<td>+4</td>
<td>Ce$^{2+}$</td>
<td>+3</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### COMMON REDUCING AGENTS

<table>
<thead>
<tr>
<th>Substance</th>
<th>Radical or Element involved</th>
<th>O.N. of &quot;Effective&quot; Element</th>
<th>Oxidation Product</th>
<th>New O.N.</th>
<th>Increase in O.N.</th>
<th>Loss in Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$SO$_4$ or Na$_2$SO$_3$</td>
<td>SO$_4^{2-}$</td>
<td>+4</td>
<td>SO$_4^{3-}$</td>
<td>+6</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>H$_2$</td>
<td>S</td>
<td>-2</td>
<td>S$^2-$</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>HCl</td>
<td>H</td>
<td>-1</td>
<td>H$^+$</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>SnCl$_2$</td>
<td>Sn$^{+}$</td>
<td>+2</td>
<td>Sn$^{3+}$</td>
<td>+4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Metals, e.g., Zn</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>0</td>
<td>H$^+$</td>
<td>+1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>FeSO$_4$ (or any ferrous salt)</td>
<td>Fe$^{2+}$</td>
<td>+2</td>
<td>Fe$^{3+}$</td>
<td>+3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Na$_2$AsO$_3$</td>
<td>AsO$_3^{3-}$</td>
<td>+3</td>
<td>AsO$_4^{3-}$</td>
<td>+5</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>O$_2$</td>
<td>+3</td>
<td>CO$_2$</td>
<td>+4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ti$_2$(SO$_4$)$_3$</td>
<td>Ti$^{3+}$</td>
<td>+3</td>
<td>Ti$^{4+}$</td>
<td>+4</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Example 12.** How many ml. of 0.2N-hydrochloric acid are required to neutralise 25.0 ml. of 0.1N-sodium hydroxide?

Substituting in equation (1), we obtain:

$$x \times 0.2 = 25.0 \times 0.1,$$

whence $x = 12.5$ ml.

**Example 13.** How many ml. of $N$-hydrochloric acid are required to precipitate completely 1 g. of silver nitrate?

The equivalent weight of AgNO$_3$ in a precipitation reaction is 1 mol. or 169.89 g.

Hence 1 g. of AgNO$_3$ = $1 \times 1000/169.89 = 5.886$ mg.-equivalents.
The Theoretical Basis of Quantitative Analysis

Now number of mg.-equivalents of HCl = number of mg.-equivalents of AgNO₃:

\[ x \times 1 = 5.886, \text{ whence } x = 5.90 \text{ ml.} \]

Example 14. 25 ml. of a ferrous sulphate solution react completely with 30 ml. of 0.125N-potassium permanganate. Calculate the strength of the ferrous sulphate solution in grams of FeSO₄ per litre.

A normal solution of FeSO₄ as a reductant contains 1 mol. per litre or 151.90 g. per litre (Table IX). Let the normality of the ferrous sulphate solution be \( n_A \). Then:

\[ 25 \times n_A = 30 \times 0.125 \]

or

\[ n_A = 30 \times 0.125/25 \]

Hence the solution will contain 0.15 \( \times \) 151.90 = 22.785 g. FeSO₄ per litre.

Example 15. What volume of 0.127N reagent is required for the preparation of 1000 ml. of 0.1N solution?

\[ V_A \times \text{normality}_A = V_B \times \text{normality}_B \]

\[ V_A \times 0.127 = 1000 \times 0.1 \]

or

\[ V_A = 1000 \times 0.1/0.127 = 787.4 \text{ ml.} \]

Hence it is necessary to dilute 787.4 ml. of 0.127N solution to 1 litre. Strictly speaking it is not correct to add 212.6 ml. of water, because there is usually a volume change on mixing. This change is so small, however, that diluted solutions are often prepared by the addition of the calculated amount of water to a measured volume of standard reagent.

I, 25. Preparation of standard solutions.—If a reagent is available in the pure state, a solution of definite normality is prepared simply by weighing out an equivalent weight, or a definite fraction or multiple thereof, dissolving it in the solvent, usually water, and making up the solution to a known volume. It is not really essential to weigh out the equivalent weight (or a multiple or sub-multiple thereof). In practice it is often more convenient to prepare the solution a little more concentrated than is ultimately required, and then to dilute it with distilled water until the desired normality is obtained. If \( N_1 \) is the required normality, \( V_1 \) the volume after dilution, \( N_2 \) the normality originally obtained, and \( V_2 \) the original volume taken, \( N_1 V_1 = N_2 V_2 \), or \( V_1 = N_2 V_2 / N_1 \). The volume of water to be added to the volume \( V_2 \) is \( (V_1 - V_2) \) ml. (compare Example 15 in Section I, 24). The following is a list of some of the substances which can be obtained in a state of high purity and are therefore suitable for the preparation of standard solutions: sodium carbonate, potassium hydrogen phthalate, benzoic acid, borax, furoic acid, adipic acid, sulphamic acid, potassium bi-iodate, sodium oxalate, silver nitrate, sodium chloride, potassium chloride, iodine, potassium bromate, potassium iodate, potassium dichromate, and arsenious oxide.

When the reagent is not available in the pure form as in the cases of most alkali hydroxides, some inorganic acids and various deliquescent substances, solutions of the approximate normality required are first prepared. These are then standardised by titration against a solution of a pure substance of known normality. It is generally best to standardise a solution by a reaction of the same type as that for which the
solution is to be employed, and as nearly as possible under identical experimental conditions. The titration error and other errors are thus considerably reduced or are made to cancel out. This indirect method is employed for the preparation of solutions of, *inter alia*, most acids (for hydrochloric acid, the constant-boiling-point mixture of definite composition can be weighed out directly, if desired), sodium, potassium and barium hydroxides, potassium permanganate, ammonium and potassium thiocyanates, and sodium thiosulphate.

I. 26. **Primary standard substances.**—A primary standard substance should satisfy the following requirements:

1. It must be easy to obtain, to purify, to dry (preferably at 110–120°C.), and to preserve in a pure state. (This requirement is not usually met by hydrated substances, since it is difficult to remove surface moisture completely without affecting partial decomposition.)

2. The substance should be unaltered in air during weighing; this condition implies that it should not be hygroscopic, nor oxidised by air, nor affected by carbon dioxide. The standard should maintain its composition unchanged during storage.

3. The substance should be capable of being tested for impurities by qualitative and other tests of known sensitivity. (The total amount of impurities should not, in general, exceed 0·01–0·02 per cent.)

4. It should have a high equivalent weight so that the weighing errors may be negligible. (The precision in weighing is ordinarily 0·01–0·02 mg.; for an accuracy of 1 part in 1000, it is necessary to employ samples weighing at least ca. 0·2 g.)

5. The substance should be readily soluble under the conditions in which it is employed.

6. The reaction with the standard solution should be stoichiometric and practically instantaneous. The titration error should be negligible, or easy to determine accurately by experiment.

In practice, an ideal primary standard is difficult to obtain, and a compromise between the above ideal requirements is usually necessary. The substances commonly employed as primary standards are:

- **Acidimetry and alkalimetry**—sodium carbonate Na₂CO₃, borax Na₂B₄O₇, potassium hydrogen phthalate KH·C₆H₄O₄, constant-boiling-point hydrochloric acid, potassium bi-iodate KH(IO₃)₂, thallous carbonate Tl₂CO₃ (poisonous), succinic acid H₂C₄H₄O₄, benzoic acid H·C₆H₅O₂, furfuroic acid H·C₅H₄O₂, and adipic acid H₂·C₆H₄O₄.

- **Precipitation reactions**—silver, silver nitrate, sodium chloride, potassium chloride, and potassium bromide (prepared from potassium bromate).

- **Oxidation-reduction reactions**—potassium dichromate K₂Cr₂O₇, potassium bromate KBrO₃, potassium iodate KIO₃, potassium bi-iodate KH(IO₃)₂, iodine I₂, sodium oxalate Na₂C₂O₄, arsenious oxide As₂O₃, and electrolytic, or otherwise pure, iron.

Hydrated salts, as a rule, do not make good standards because of the difficulty of efficient drying. However, those salts which do not effloresce, such as borax Na₂B₄O₇·10H₂O, oxalic acid H₂C₂O₄·2H₂O, and copper sulphate CuSO₄·5H₂O, are found by experiment to be satisfactory secondary standards.
THEOREY OF ACIDIMETRY AND ALKALIMETRY

I, 27. Neutralisation indicators.—The object of titrating, say, an alkaline solution with a standard solution of an acid is the determination of the amount of acid which is exactly equivalent chemically to the amount of base present. The point at which this is reached is the equivalence point, stoichiometrical point, or theoretical end point, and corresponds to an aqueous solution of the acid and the base. If both the acid and base are strong electrolytes, the resultant solution will be neutral and have a pH of 7 (Section I, 17). But if either the acid or the base is a weak electrolyte, the salt will be hydrolysed to a certain degree, and the solution at the equivalence point will be either slightly alkaline or slightly acid. The exact pH of the solution at the equivalence point can readily be calculated from the ionisation constant of the weak acid or the weak base and the concentration of the solution (see Section I, 19). For any actual titration the correct end point will be characterised by a definite value of the hydrogen-ion concentration of the solution, the value depending upon the nature of the acid and the base and the concentration of the solution.

A large number of substances are available, called neutralisation or acid-base indicators, which possess different colours according to the hydrogen-ion concentration of the solution. The chief characteristic of these indicators is that the change from a predominantly "acid" colour to a predominantly "alkaline" colour is not sudden and abrupt, but takes place within a small interval of pH (usually about two pH units) termed the colour-change interval of the indicator. The position of the colour-change interval in the pH scale varies widely with different indicators. For most acid-base titrations, we can therefore select an indicator which exhibits a distinct colour at a pH close to that obtaining at the equivalence point.

The first useful theory of indicator action was suggested by W. Ostwald. All indicators in general use are very weak organic acids or bases. Ostwald (1891) considered that the undissociated indicator acid (HIn) or base (InOH) had a different colour from that of its ion. The equilibria in aqueous solution may be written:

\[
\begin{align*}
\text{HIn} & \Leftrightarrow \text{H}^+ + \text{In}^- \quad \text{(1)} \\
\text{InOH} & \Leftrightarrow \text{OH}^- + \text{In}^+ \quad \text{(1')}
\end{align*}
\]

If the indicator is an anhydro-base (In), e.g., a free amine or substituted amine, the equilibrium is:

\[
\text{In} + \text{H}_2\text{O} \Leftrightarrow \text{OH}^- + \text{HIn}^+ \quad \text{(1'')}
\]

Let us consider an acid indicator. In acid solution, i.e., in the presence of excess of H\(^+\) ions, the ionisation will be depressed (common-ion effect) and the concentration of In\(^-\) will be very small; the colour will therefore be that of the unionised form. If the medium is alkaline, the decrease of [H\(^+\)] will result in the further ionisation of the indicator, [In\(^-\)] increases and the colour of the ionised form becomes apparent. By applying the law of mass action, we obtain:

\[
\frac{\text{a}_{\text{HIn}} \times \text{a}_{\text{In}^-}}{\text{a}_{\text{HIn}}} = \frac{[\text{H}^+] \times [\text{In}^-]}{[\text{HIn}]} \times \frac{f_{\text{H}^+} \cdot f_{\text{In}^-}}{f_{\text{HIn}}} = K_{\text{ina}} \quad \text{(2)}
\]
and
\[ [H^+] = \frac{[HIn]}{[In^-]} \times K_{Ina} \times \frac{f_{HIn}}{f_{H^+} \cdot f_{In^-}} \]
\[ = \frac{[\text{Unionised form}]}{[\text{Ionised form}]} \times K_{Ina} \times \frac{f_{HIn}}{f_{H^+} \cdot f_{In^-}} \quad \text{...(3)} \]

where \( K_{Ina} \) is the ionisation constant of the indicator. If the activity coefficients are assumed to be unity—a not entirely justifiable assumption, as will be evident from the ensuing discussion—equation (3) reduces to the simplified “concentration form”:
\[ [H^+] = \frac{[HIn]}{[In^-]} \times K_{Ina} = \frac{[\text{Unionised form}]}{[\text{Ionised form}]} \times K_{Ina} \quad \text{...(3')} \]

The actual colour of the indicator, which depends upon the ratio of the concentrations of the ionised and unionised forms, is thus directly related to the hydrogen-ion concentration. Equation (3’) (the simplified or “classical” form) may be written logarithmically:
\[ pH = \log \frac{[In^-]}{[HIn]} + pK_{Ina} \quad \text{...(4)} \]

For a base indicator an exactly analogous expression to (3) may be deduced, which in its simplified form is:
\[ [OH^-] = \frac{[InOH]}{[In^+]} \times K_{Inb} \quad \text{...(5)} \]

where \( K_{Inb} \) is the corresponding base-dissociation constant. This may be written:
\[ [H^+] = \frac{K_{Ina}}{K_{Inb}} \cdot \frac{[In^+]}{[InOH]} \quad \text{...(6)} \]

since
\[ K_{Ina} = [H^+] \times [OH^-] \quad \text{(approximately)} \]

The work of Hantzsch and others has shown that Ostwald’s simple theory of the colour change of indicators requires revision. The newer theory, however, leads to equations similar to the above. We can no longer regard the colour change as being due to ionisation alone, for it has been shown that an indicator consists of two or more different
tautomeric forms possessing different constitutional formulae and different colours; one of the forms is a non-electrolyte (a pseudo-acid or pseudo-base), the other form being an acid or a base. The ions of the true acid or true base possess the same colour as the undissociated form of the same structure. We can illustrate this by reference to phenolphthalein, the changes for which are characteristic of all phthalein indicators (Fig. I, 27, 1).
In the solid state or in acid solution, it exists chiefly as the colourless lactone I. This is in equilibrium in solution with a trace of the tautomer quinonoid form II, which is an acid since it possesses the carboxyl group —COOH and dissociates to yield the H⁺ ion and the indicator ion III.

Consider now an acid or, more correctly, a pseudo-acid indicator in the light of the new theory. Let HIn' represent the pseudo-acid and HIn the acid. Two equilibria must be considered in aqueous solution:

\[ \text{HIn'} \rightleftharpoons \text{HIn} \]  
\[ \text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^- \]  

Applying the law of mass action to both, we have:

for (7), \[ K_T = \frac{a_{\text{HIn}}}{a_{\text{HIn}'}} \]  
and for (8), \[ K_I = \frac{a_{\text{H}^+} \times a_{\text{In}^-}}{a_{\text{HIn}}} \]

The ion In⁻ has the same colour as the weak acid HIn. In acid solution, i.e., in the presence of excess of H⁺ ions, the indicator will exist largely as HIn and HIn'. Now these two forms have different colours, and HIn has the same colour as In⁻. The indicator will only be useful if the equilibrium constant for the tautomeric equilibrium (7) is very small; then practically the whole of the undissociated indicator will be in the form HIn'. Combining (9) and (10), we obtain:

\[ K_{\text{in}} = K_T \times K_I = \frac{a_{\text{HIn}}}{a_{\text{HIn}'}} \times \frac{a_{\text{H}^+} \times a_{\text{In}^-}}{a_{\text{HIn}}} = \frac{a_{\text{H}^+} \times a_{\text{In}^-}}{a_{\text{HIn}'}} \]  

where \( K_{\text{in}} \) is the apparent dissociation constant of the indicator. We have assumed that the activity (and therefore the concentration) of HIn' is very much greater than that of HIn, hence \( a_{\text{HIn}'} \) is virtually the activity of all the indicator not in the salt or ionic form, and the expression (11) is identical with (2) deduced from the Ostwald theory.

Equation (11) may be written in the following forms:

\[ K_{\text{in}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}']} \times \frac{f_{\text{H}^+} f_{\text{In}^-}}{f_{\text{HIn}'}} \]  

or \[ pH = \log \frac{[\text{In}^-]}{[\text{HIn}']} + pK_{\text{in}} + \log f_{\text{In}^-}/f_{\text{HIn}'} \]

The change from the benzenoid to the quinonoid form is believed to be responsible for the production of colour:

\[ \text{HIn}^- \rightarrow \text{HIn'} \]

or more probably a state of resonance or mesomorism obtains wherein the coloured ion possesses a structure intermediate between the various possible benzenoid and quinonoid forms.
If the activity coefficient of the indicator anion may be expressed by the usual equation (Section I, 20), it follows that:

\[ \text{pH} = \text{pK}_{\text{ina}} + \log \left[ \text{In}^- \right]/\left[ \text{HIn}' \right] - 0.505z_i^2\mu^{0.5} + C_\mu \]  

(13')

In dilute solution ($\mu \gg 0.01$) the term $C_\mu$ may be neglected, and the equation reduces to:

\[ \text{pH} = \text{pK}_{\text{ina}} + \log \left[ \text{In}^- \right]/\left[ \text{HIn}' \right] - 0.505z_i^2\mu^{0.5} \]  

(13'')

The colour of an indicator is determined by the ratio of the concentrations of $\text{HIn}'$ and $\text{In}^-$ (the pseudo-acid and the ionised form), but the actual $\text{pH}$ will depend upon the ionic strength of the solution (equation 13''). Hence when making a colour comparison for the determination of the $\text{pH}$ of a solution not only must the indicator concentration be the same in the two solutions, but the ionic strengths must be equal or approximately equal. Equations (13') and (13'') incidentally provide an explanation of the so-called "salt effect" which is observed with indicators.

For many practical purposes it is sufficient to write equation (13') in the form:

\[ \text{pH} = \text{pK}_{\text{ina}} + \log \left[ \text{In}^- \right]/\left[ \text{HIn}' \right] \]  

(13'''')

provided the influence of ionic strength be borne in mind. As already mentioned, the colour of an indicator is determined by the ratio of the concentrations of the "acid" and "alkaline" forms. Both forms are present at any hydrogen-ion concentration. It must be realised, however, that the human eye has a limited ability to detect either of the two colours when one of them predominates. Experience shows that the solution will appear to have the "acid" colour, i.e., of $\text{HIn}'$, when the ratio of $[\text{HIn}']$ to $[\text{In}^-]$ is above approximately 10, and the "alkaline" colour, i.e., of $\text{In}^-$, above a similar ratio of $[\text{In}^-]$ to $[\text{HIn}']$ of approximately 10. Thus only the "acid" colour will be visible when $[\text{HIn}']/[\text{In}^-] > 10$, the corresponding limit of $\text{pH}$ given by equation (13''') is:

\[ \text{pH} = \text{pK}_{\text{ina}} - 1 \]

only the "alkaline" colour will be visible when $[\text{In}^-]/[\text{HIn}'] > 10$, and the corresponding limit of $\text{pH}$ is:

\[ \text{pH} = \text{pK}_{\text{ina}} + 1 \]

The colour-change interval is accordingly $\text{pH} = \text{pK}_{\text{ina}} \pm 1$, i.e., over approximately two $\text{pH}$ units. Within this range the indicator will appear to change from one colour to the other. The change will be gradual, since it depends upon the ratio of the concentrations of the two coloured forms (pseudo-acid and ionised). When the $\text{pH}$ of the solution is equal to the apparent dissociation constant of the indicator $\text{pK}_{\text{ina}}$, the ratio $[\text{HIn}']$ to $[\text{In}^-]$ becomes equal to 1, and the indicator will have a colour due to an equal mixture of the "acid" and "alkaline" forms. This is sometimes known as the middle tint of the indicator. This applies strictly only if the two colours are of equal intensity. If one form is more intensely coloured than the other or if the eye is more sensitive to one colour than the other, then the middle tint will be slightly displaced along the $\text{pH}$ range of the indicator.
For an indicator base we have, according to the modified theory, the two equilibria:

$$\text{In'OH} \rightleftharpoons \text{InOH} \quad \ldots \quad \ldots \quad \ldots \quad (14)$$
$$\text{InOH} \rightleftharpoons \text{In}^+ + \text{OH}^- \quad \ldots \quad \ldots \quad \ldots \quad (15)$$

The following equation may be deduced along similar lines to that described for an indicator acid:

$$f_{\text{OH}^-}[\text{OH}^-] = \frac{[\text{In'}\text{OH}]}{[\text{In}^+]} \times K_{\text{inb}} \times \frac{f_{\text{In}^-}\text{OH}}{f_{\text{In}^+}}$$

$$= \frac{[\text{Form with "alkaline" colour}]}{[\text{Form with "acid" colour}]} \times K_{\text{inb}} \times \frac{f_{\text{In}^-}\text{OH}}{f_{\text{In}^+}} \quad (16)$$

where $K_{\text{inb}}$ is the apparent dissociation constant of the base. Remembering that $K_a = f_{\text{In}^+}[\text{H}^+] \times f_{\text{OH}^-}[\text{OH}^-]$, we may write:

$$f_{\text{H}^+}[\text{H}^+] = \frac{K_a}{K_{\text{inb}}} \times \frac{[\text{In}^+]}{[\text{In'}\text{OH}]} \times \frac{f_{\text{In}^+}}{f_{\text{In}^-}\text{OH}} \ldots (17)$$

The equation is of the same form as (12), since the ratio of the two constants may be replaced by a new constant $K_{\text{inb}}$.

The above theory applies only to a monobasic acid or to a monoacid base. Complications arise if two such changes are possible, and the transition range may be increased.

The apparent ionisation constant of an indicator may be determined approximately by finding either the $p\text{H}$ of a solution (Section I, 17) containing it when it shows its middle tint, or by finding the range of hydrogen-ion concentration in which definite colour changes are observed; the $p\text{H}$ of such a solution lies within the limits $pK_{\text{inb}}$ (or $pK_{\text{inb}}$) $\pm$ 1. A more accurate method depends upon the determination of the fraction of the indicator (e.g., $[\text{In}^-]/[\text{HIn}^+]$) which has changed colour in a series of solutions of known $p\text{H}$ (buffer solutions—Section I, 20); the approximate apparent dissociation constants may then be calculated from equations (12) or (17), the activity coefficients being assumed to be unity. With a one-colour indicator the colour intensity is measured, e.g., by means of a colorimetric or spectrophotometric method, in a series of solutions of equal concentration of indicator and different values of $p\text{H}$. For an indicator of the phenolphthalein type, the standard of comparison will be a solution containing an appreciable excess of alkali: this will correspond to a value of $[\text{In}^-]$ equal to the total indicator concentration. With a two-colour indicator, various modifications must be introduced, which cannot, however, be discussed here. In some cases, e.g., p-nitrophenol and methyl orange, the constants may be determined by conductance measurements or by a study of the hydrolysis of salts. Some approximate values of the apparent dissociation constants of indicators, which we may term indicator constants $K_{\text{inb}}$, are given in Table X. This Table contains a selected list of indicators suitable for volumetric analysis and also for the colorimetric determination of $p\text{H}$ (Section V, 9).

It is necessary to draw attention to the $p\text{H}$ of various types of water which may be encountered in quantitative analysis. Water in equilibrium with the normal atmosphere containing 0.03 per cent by volume of carbon dioxide has a $p\text{H}$ of about 5.7; very carefully prepared conductivity water has a $p\text{H}$ close to 7; water saturated with carbon...
### Table X.—Colour Changes and pH Range of Certain Indicators

<table>
<thead>
<tr>
<th>Indicator (acid)</th>
<th>Chemical Name</th>
<th>pH Range</th>
<th>Colour in Acid Solution</th>
<th>Colour in Alkaline Solution</th>
<th>pK&lt;sub&gt;i&lt;/sub&gt;</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brilliant cresyl blue</td>
<td>Amino-diethylamino-methyl diphenazonium chloride</td>
<td>0-0-1-0</td>
<td>Red-orange</td>
<td>Blue</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cresol red</td>
<td>α-Cresol sulphonephthalein</td>
<td>0-2-1-3</td>
<td>Red</td>
<td>Yellow</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Quinaldine red</td>
<td>α-(p-Dimethylamino-phenyl-ethylene)-quinoline ethiodide</td>
<td>1-0-2-0</td>
<td>Colourless</td>
<td>Red</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Thymol blue (acid)</td>
<td>Thymol-sulphonephthalein</td>
<td>1-2-2-8</td>
<td>Red</td>
<td>Yellow</td>
<td>1-7</td>
<td>—</td>
</tr>
<tr>
<td>Tropaeolin O</td>
<td>Diphenylamino-p-benzene-sodium sulphonate</td>
<td>1-3-3-0</td>
<td>Red</td>
<td>Yellow</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Meta-cresol purple</td>
<td>m-Cresol sulphonephthalein</td>
<td>1-2-2-8</td>
<td>Red</td>
<td>Yellow</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Bromo-phenol blue</td>
<td>Tetra-bromophenolphthalein</td>
<td>2-8-4-6</td>
<td>Yellow</td>
<td>Blue</td>
<td>4-0</td>
<td>—</td>
</tr>
<tr>
<td>Methyl yellow</td>
<td>Dimethylaminophenol</td>
<td>2-9-4-0</td>
<td>Red</td>
<td>Yellow</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Dimethylaminophenol</td>
<td>3-1-4-4</td>
<td>Red</td>
<td>Yellow</td>
<td>3-7</td>
<td>—</td>
</tr>
<tr>
<td>Congo red</td>
<td>Diphenyl-bisazo-anthraquinone acid</td>
<td>3-0-5-0</td>
<td>Violet</td>
<td>Red</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Bromo-cresol green</td>
<td>Tetra-bromophenolphthalein</td>
<td>3-8-5-4</td>
<td>Yellow</td>
<td>Blue</td>
<td>4-7</td>
<td>—</td>
</tr>
<tr>
<td>Methyl red</td>
<td>o-Carboxybenzenazo-dimethylamine</td>
<td>4-2-6-3</td>
<td>Red</td>
<td>Yellow</td>
<td>5-1</td>
<td>—</td>
</tr>
<tr>
<td>Chloro-phenol red</td>
<td>Dichloro-phenolphthalein</td>
<td>4-8-6-4</td>
<td>Yellow</td>
<td>Red</td>
<td>6-0</td>
<td>—</td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>p-Nitrophenol</td>
<td>5-0-7-6</td>
<td>Colourless</td>
<td>Yellow</td>
<td>7-1</td>
<td>—</td>
</tr>
<tr>
<td>Bromo-cresol purple</td>
<td>Diphenol</td>
<td>5-2-6-8</td>
<td>Yellow</td>
<td>Purple</td>
<td>6-3</td>
<td>—</td>
</tr>
<tr>
<td>Azolitmin (litmus)</td>
<td>—</td>
<td>5-0-8-0</td>
<td>Red</td>
<td>Blue</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Bromo-thymol blue</td>
<td>Diphenol</td>
<td>6-0-7-6</td>
<td>Yellow</td>
<td>Blue</td>
<td>7-0</td>
<td>—</td>
</tr>
<tr>
<td>Neutral red</td>
<td>Amino-dimethylamino-toluidine</td>
<td>6-8-8-0</td>
<td>Red</td>
<td>Orange</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Phenol red</td>
<td>Phenol-sulphonephthalein</td>
<td>6-8-8-4</td>
<td>Yellow</td>
<td>Red</td>
<td>7-9</td>
<td>—</td>
</tr>
<tr>
<td>Cresol red (base)</td>
<td>o-Cresol sulphonephthalein</td>
<td>7-2-8-8</td>
<td>Yellow</td>
<td>Red</td>
<td>8-3</td>
<td>—</td>
</tr>
</tbody>
</table>
The Theoretical Basis of Quantitative Analysis

TABLE X.—Continued

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Chemical Name</th>
<th>pH Range</th>
<th>Colour in Acid Solution</th>
<th>Colour in Alkaline Solution</th>
<th>pKₐ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Naphthol-phthalein</td>
<td>α-Naphtholphthalein</td>
<td>7.3—8.7</td>
<td>Yellow</td>
<td>Blue</td>
<td>8.4</td>
</tr>
<tr>
<td>Thymol blue (base)</td>
<td>Thymol-sulphone-phthalein</td>
<td>8.0—9.6</td>
<td>Yellow</td>
<td>Blue</td>
<td>8.9</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Phenolphthalein</td>
<td>8.3—10.0</td>
<td>Colourless</td>
<td>Red</td>
<td>9.6</td>
</tr>
<tr>
<td>Turmeric Thymolphthalein</td>
<td>Thymolphthalein</td>
<td>8.0—10.0</td>
<td>Yellow</td>
<td>Orange</td>
<td></td>
</tr>
<tr>
<td>Alizarine yellow R</td>
<td>p-Nitrobenzene-salicylic acid&lt;br&gt;(see above)</td>
<td>10.1—12.0</td>
<td>Yellow</td>
<td>Orange red</td>
<td></td>
</tr>
<tr>
<td>Brilliant cresyl blue (base)</td>
<td>p-Sulphobenzene-azo-resorcinol</td>
<td>10.8—12.0</td>
<td>Blue</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>Tropaeolin O</td>
<td>2:4:6-Triphenyl-methyl-nitroamine</td>
<td>10.8—13.0</td>
<td>Colourless</td>
<td>Orange-brown</td>
<td></td>
</tr>
</tbody>
</table>

Dioxide under a pressure of one atmosphere has a pH of about 3.7 at 25°C. The analyst may therefore be dealing, according to the conditions that prevail in the laboratory, with water having a pH between the two extremes pH 3.7 and pH 7. Hence for indicators which show their alkaline colours at pH values above 4.5, the effect of carbon dioxide introduced during a titration, either from the atmosphere or from the titrating solutions, must be seriously considered. This subject is discussed again later (Section I, 32).

The colour-change intervals of most of the various indicators listed in the table are represented graphically in Fig. I, 27, 2. It will be seen that the pH range between 0 and 13 is covered by the above indicators.

The indicators at present most used in quantitative analysis are methyl orange (as the simple or "screened" forms—see Section I, 29), methyl red and phenolphthalein. The phthalein indicators merit much more attention than has hitherto been given to them; this would be the case if their many advantages, particularly their sharp colour changes and slight sensitivity to carbon dioxide, were more widely realised.

I, 28. Preparation of indicator solutions.—As a rule the stock solutions of the indicators contain 0.5—1 g. of indicator per litre of solvent. If the substance is soluble in water, e.g., if a sodium salt, water is the solvent; in most other cases 70—90 per cent alcohol is employed. It should now be stated that the new synthetic indicators, particularly the sulphonephthaleins and phthaleins which exhibit brilliant colour changes, may be used with confidence in all those cases where the older ones, largely natural products, were formerly employed.

Methyl orange. This indicator is encountered in commerce either as the free acid or as the sodium salt.
Quantitative Inorganic Analysis

Dissolve 0.5 g. of the free acid in 1 litre of water, and filter the cold solution if a precipitate separates.

Dissolve 0.5 g. of the sodium salt in 1 litre of water, add 15.2 ml. of 0.1N-hydrochloric acid, and filter, if necessary, when cold.

Methyl red. Dissolve 1 g. of the free acid in 1 litre of hot water, or dissolve in 600 ml. of alcohol and dilute with 400 ml. of water.

Phenolphthalein. Dissolve 5 g. of the reagent in 500 ml. of alcohol and add 500 ml. of water with constant stirring. Filter, if a precipitate forms.

Alternatively, dissolve 1 g. of the dry indicator in 60 ml. of ethylene-glycol monoethyl ether (cellosolve), b.p. 135°C, and dilute to 100 ml. with distilled water: the loss by evaporation is less with this preparation.

Thymolphthalein. Dissolve 0.4 g. of the reagent in 600 ml. of alcohol and add 500 ml. of water with stirring.

α-Naphtholphthalein. Dissolve 1 g. of the indicator in 500 ml. of alcohol and dilute with 500 ml. of water.

Litmus. Commercial litmus contains, in addition to the colouring matter (azolitmin), varying quantities of calcium carbonate, calcium sulphate, etc. Purification is effected as follows. Digest 10 g. of the commercial substance with 35 ml. of rectified spirit on the water-bath for 1 hour and decant the alcohol; repeat this process twice so that 105 ml. of alcohol are employed in all. Extract the residue several times with water (total volume 175 ml.—the first 25 ml. is discarded as it contains most of the potassium carbonate), and allow to stand for several days. Decant or siphon off the clear extract. This is of suitable concentration for most practical purposes.

As a general rule the use of litmus in quantitative neutralisations should be avoided, for the solution may contain variable amounts of the colouring matter. It is useful for qualitative tests, but then litmus

---

**FIG. 1, 27, 2.**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH 1</th>
<th>pH 2</th>
<th>pH 3</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 9</th>
<th>pH 10</th>
<th>pH 11</th>
<th>pH 12</th>
<th>pH 13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brilliant cresyl blue</td>
<td>B</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>B</td>
<td>Y</td>
<td>B</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cresyl red</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quinoline red</td>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thymol blue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tropaeolin G</td>
<td>D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl red</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Naphtholphthalein</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol red</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxazine yellow B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tropaeolin G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitramine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* B = Blue
* C = Daburines
* O = Orange
* OB = Orange-brown
* P = Purple
* R = Red
* RO = Red-orange
* Y = Yellow

pH units
Theoretical Basis of Quantitative Analysis

paper is to be preferred to the solution. Such indicators as bromo-
cresol purple or bromo-thymol blue, which cover approximately the
same pH range, are excellent substitutes for litmus; the colour changes
are very striking and a pure product can be obtained, so that a uniform
solution is assured.

Azolitmin. This is the pure litmus colouring matter, and consists
largely of the blue potassium salt of (red) azolitmic acid. A solution
is prepared by dissolving 1 g. in 1 litre of water. It is not very much
more sensitive than good litmus solution.

Sulphonephthaleins. These indicators are usually supplied in the
acid form. They are rendered water-soluble by adding sufficient
sodium hydroxide to neutralise the potential sulphonic acid group.
One gram of the indicator is triturated in a clean glass mortar with the
appropriate quantity of 0.1N-sodium hydroxide solution, and then
diluted with water to 1 litre. The following volumes of 0.1N-sodium
hydroxide are required for 1 g. of the indicators: bromo-phenol blue,
16.0 ml.; bromo-cresol green, 14.4 ml.; bromo-cresol purple, 18.6 ml.;
chloro-phenol red, 23.8 ml.; bromo-thymol blue, 16.0 ml.; phenol red,
28.4 ml.; thymol blue, 21.5 ml.; cresol red, 26.2 ml.; meta-cresol
purple, 26.2 ml.

Quinaldinic acid. Dissolve 1 g. in 100 ml. of rectified spirit.

Methyl yellow, neutral red, and congo red. Dissolve 1 g. of the indicator
in 1 litre of 80 per cent alcohol. Congo red may also be dissolved in
water.

p-Nitrophenol. Dissolve 2 g. of the solid in 1 litre of water.

Alizarine yellow R. Dissolve 0.5 g. of the indicator in 1 litre of recti-
fied spirit.

Tropaeolin O and Tropaeolin OO. Dissolve 1 g. of the solid in 1 litre of
water.

Many of the indicator solutions are available commercially already
prepared for use. These should be bought from the actual chemical
manufacturers, who will usually supply full details as to the method of
preparation, concentration of the solution, etc.

I. 29. Mixed indicators.—With some indicators, e.g., methyl orange,
the colour change is not easily detectable, particularly in artificial light.
A sharper and more pronounced colour change may often be obtained
by using a suitable mixture of the indicator and an indifferent dye.
Thus for methyl orange, Moerk (1921) used a mixture of 1 g. of methyl
orange and 2.5 g. of indigo carmine dissolved in 1 litre of water; the
colour change from the alkaline to the acid side is yellowish-green →
grey → violet, the grey stage being reached at pH 4. This indicator is
stored in a brown bottle. Hickman and Linstead (1922) obtained a
somewhat better effect by dissolving a mixture of 1 g. of methyl orange
and 1.4 g. of xylene cyanol FF* in 500 ml. of 50 per cent alcohol;
here the colour change from the alkaline to the acid side is green → grey
→ magenta, the middle (grey) stage being obtained at pH 3.8. The

* The constitution is

\[
\begin{align*}
\text{NaO}_8\text{S} & \quad \text{O} \\
\text{C} & \quad \text{NHC}_4\text{H}_4 \\
\text{OH} & \quad \text{O} \\
\text{OH} & \quad \text{NHC}_4\text{H}_4 \\
\text{CH}_2 & \quad \text{CH}_3
\end{align*}
\]
above is an example of a *screened indicator*, and the solution is sometimes known as "screened" methyl orange.

For some purposes it is desirable to have a sharp colour change over a narrow and selected range of hydrogen-ion concentration; this is not easily seen with an ordinary indicator, since the colour change usually extends over two units of pH. The result may, however, be achieved by the use of a suitable mixture of indicators. Four examples will be given.

(a) A mixture of equal parts of neutral red (0·1 per cent solution in alcohol) and methylene blue (0·1 per cent solution in alcohol) gives a sharp colour change from violet-blue to green in passing from acid to alkaline solution at pH 7. This indicator may be employed to titrate acetic acid with ammonia solution or vice versa. Both acid and base are approximately of the same strength, hence the equivalence point will be at a pH of ca. 7 (Section I, 35); owing to the extended hydrolysis and the flat nature of the titration curve (see Section I, 35), the titration cannot be performed except with an indicator of very narrow range.

(b) A mixture of equal parts of methyl orange or of methyl yellow (0·1 per cent solution in alcohol) and methylene blue (0·1 per cent solution in alcohol) may be used in the titration of the very weak base pyridine and a strong acid; in this case also the titration curve is very flat. This indicator is also useful for other somewhat stronger bases and strong acids.

(c) A mixture of phenolphthalein (2 parts of 0·1 per cent solution in 50 per cent alcohol) and α-naphtholphthalein (1 part of 0·1 per cent solution in 50 per cent alcohol) passes from pale rose through green to violet at pH = 9·6. The mixed indicator is suitable for the titration of phosphoric acid to the dibasic stage \( K_2 = 6·2 \times 10^{-8} \); equivalence point at pH = ca. 8·7.

Phenolphthalein, which was previously used, is not so satisfactory, since its pH range is 8·3–10 and the titration curve is relatively flat (Section I, 36).

(d) A mixture of thymol blue (6 parts of 0·1 per cent aqueous solution) and cresol red (1 part of 0·1 per cent aqueous solution) is violet at pH 8·4, blue at pH 8·3, and rose at pH 8·2. It has been recommended by Simpson (1924) for the titration of carbonate to the bicarbonate stage.

I, 30. Universal or multiple range indicators. By suitably mixing certain indicators the colour change may be made to extend over a considerable portion of the pH range. Such mixtures are usually called "universal indicators." They are not suitable for quantitative titrations, but may be employed for the determination of the approximate pH of a solution by the colorimetric method. Bogen (1927) gives the following details: dissolve 0·1 g. of phenolphthalein, 0·2 g. of methyl red, 0·3 g. of methyl yellow, 0·4 g. of bromothymol blue, and 0·5 g. of thymol blue in 500 ml. of absolute alcohol, and add sufficient sodium hydroxide solution until the colour is yellow. The colour changes are as follows: pH 2, red; pH 4, orange; pH 8, yellow; pH 10, blue.

The following recipe is due to T. B. Smith (1929). Dissolve 0·05 g. of methyl orange, 0·15 g. of methyl red, 0·3 g. of bromo-thymol blue, and 0·35 g. of phenolphthalein in 1 litre of 66 per cent alcohol. The colour changes are: pH up to 3, red; pH 4, orange-red; pH 5, orange;
pH 6, yellow; pH 7, yellowish-green; pH 8, greenish-blue; pH 9, blue; pH 10, violet; pH 11, reddish-violet. Several "universal indicators" are available commercially as solutions and as test papers: a more detailed account will be found in Section V, 9 in connexion with the colorimetric determination of pH.

I, 31. Neutralisation curves.—An insight into the mechanism of neutralisation processes is obtained by studying the changes in the hydrogen-ion concentration during the course of the appropriate titration. The change in pH in the neighbourhood of the equivalence point is of the greatest importance, as it enables us to select an indicator which will give the smallest titration error. The curve obtained by plotting pH as ordinates against the percentage of acid neutralised (or the number of ml. of alkali added) as abscissae is known as the neutralisation (or, more generally, the titration) curve. This may be evaluated experimentally by a determination of the pH at various stages during the titration by an electrometric method (Section VI, 2-4), or it may be computed approximately with the aid of the theoretical principles that we have already studied. We shall, for the present, adopt the latter method.

I, 32. Neutralisation of a strong acid and a strong base.—We shall assume that both the acid and the base are completely dissociated and that the activity coefficients of the ions are unity in order to calculate the change of pH during the course of the neutralisation of the strong acid and the strong base, or vice versa, at the laboratory temperature. For simplicity of calculation we shall start with 100 ml. of, say, N-hydrochloric acid and add N-sodium hydroxide solution. The pH of N-hydrochloric acid is 0. When 50 ml. of the base have been added, 50 ml. of un-neutralised N acid will be present in a total volume of 150 ml.

\[ [H^+] = \frac{100 \times 1}{150} = 6.67 \times 10^{-1}, \text{ or } pH = 0.7 \]

for 75 ml. of base, \[ [H^+] = 25 \times 1 = 7.49 \times 10^{-1}, \text{ or } pH = 0.94 \]

for 90 ml. of base, \[ [H^+] = 10 \times 1 = 1.27 \times 10^{-1}, \text{ or } pH = 1.3 \]

for 98 ml. of base, \[ [H^+] = 2 \times 1 = 2.01 \times 10^{-1}, \text{ or } pH = 2.0 \]

for 99 ml. of base, \[ [H^+] = 1 \times 1 = 5.03 \times 10^{-1}, \text{ or } pH = 2.3 \]

for 99.9 ml. of base, \[ [H^+] = 0.1 \times 1 = 5.01 \times 10^{-1}, \text{ or } pH = 3.3 \]

Upon the addition of 100 ml. of base, the pH will change sharply to 7, the equivalence point, provided carbon dioxide is absent; the resultant solution is equivalent to one of sodium chloride.

With 100·1 ml. of base, \[ [OH^-] = 0.1 \times 100.1 = 5.00 \times 10^{-3}, \text{ or } pH = 3.3 \]

With 101 ml. of base, \[ [OH^-] = 1 \times 101 = 5.00 \times 10^{-3}, \text{ or } pH = 2.3, \text{ and } pH = 11.7 \]

These results show that as the titration proceeds, the pH rises slowly, but between the addition of 99·9 and 100·1 ml. of alkali, the pH of the solution rises from 3·3 to 10·7, i.e., in the vicinity of the equivalence point the rate of change of pH of the solution is very rapid.

The complete results, extended to 200 ml. of alkali, are collected in Table XI; this also includes the figures for 0·1N and 0·01N solutions of acid and base respectively. The additions of alkali have been
Quantitative Inorganic Analysis

extended in all three cases to 200 ml.; it is evident that the range from 200 to 100 ml. and beyond represents the reverse titration of 100 ml. of alkali with the acid in the presence of the non-hydrolysed sodium chloride solution. The data in the table are presented graphically in Fig. 1, 32, 1.

Table XI.—pH during titration of 100 ml. of HCl with NaOH of equal normality

<table>
<thead>
<tr>
<th>Ml. of NaOH Added</th>
<th>N Solution pH</th>
<th>0-1N Solution pH</th>
<th>0-01N Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>75</td>
<td>0.8</td>
<td>1.8</td>
<td>2.8</td>
</tr>
<tr>
<td>90</td>
<td>1.3</td>
<td>2.3</td>
<td>3.3</td>
</tr>
<tr>
<td>99</td>
<td>2.3</td>
<td>3.3</td>
<td>4.3</td>
</tr>
<tr>
<td>99.5</td>
<td>2.6</td>
<td>3.6</td>
<td>4.6</td>
</tr>
<tr>
<td>99.8</td>
<td>3.0</td>
<td>4.0</td>
<td>5.0</td>
</tr>
<tr>
<td>99.9</td>
<td>3.3</td>
<td>4.3</td>
<td>5.3</td>
</tr>
<tr>
<td>100-0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>100-1</td>
<td>10.7</td>
<td>9.7</td>
<td>8.7</td>
</tr>
<tr>
<td>100-2</td>
<td>11.0</td>
<td>10.0</td>
<td>9.0</td>
</tr>
<tr>
<td>100-5</td>
<td>11.4</td>
<td>10.4</td>
<td>9.4</td>
</tr>
<tr>
<td>101</td>
<td>11.7</td>
<td>10.7</td>
<td>9.7</td>
</tr>
<tr>
<td>102</td>
<td>12.0</td>
<td>11.0</td>
<td>10.0</td>
</tr>
<tr>
<td>110</td>
<td>12.7</td>
<td>11.7</td>
<td>10.7</td>
</tr>
<tr>
<td>125</td>
<td>13.2</td>
<td>12.2</td>
<td>11.2</td>
</tr>
<tr>
<td>150</td>
<td>13.5</td>
<td>12.5</td>
<td>11.5</td>
</tr>
<tr>
<td>200</td>
<td>14.0</td>
<td>13.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Fig. I, 32, 1.—Neutralisation Curves of 100 ml. of HCl with NaOH of same Normality (Calculated).
In quantitative analysis we are especially interested in the changes of pH near the equivalence point. This part of Fig. 1, 32, 1 is accordingly shown on a larger scale in Fig. 1, 32, 2, on which are also indicated the colour-change intervals of some of the common indicators.

With N solutions, it is evident that any indicator with an effective range between pH 3 and 10·5 may be used. The colour change will be sharp and the titration error negligible.

With 0·1N solutions, the ideal pH range for an indicator is limited to 4·5–9·5. Methyl orange will exist chiefly in the alkaline form when 99·8 ml of alkali have been added, and the titration error will be 0·2 per cent, which is negligibly small for most practical purposes; it is therefore advisable to add sodium hydroxide solution until the indicator is present completely in the alkaline form. The titration error is also negligibly small with phenolphthalein.

With 0·01N solutions, the ideal pH range is still further limited to 5·5–8·5; such indicators as methyl red, bromothymol blue, or phenol red will be suitable. The titration error for methyl orange will be 1–2 per cent.

The above considerations apply to solutions which do not contain carbon dioxide. In practice, carbon dioxide is usually present (compare Section I, 27); it may be derived from the small quantity of carbonate in the sodium hydroxide and/or from the atmosphere. The gas is in equilibrium with carbonic acid, of which both stages of ionisation are weak. This will introduce a small error when indicators of high pH range (above pH 5) are used, e.g., phenolphthalein or thymolphthalein. More acid indicators, such as methyl orange and methyl...
yellow, are unaffected by carbonic acid. Kolthoff has calculated that the difference in the amounts of sodium hydroxide solution used with methyl orange and phenolphthalein is not greater than 0.15–0.2 ml. of 0.1N-sodium hydroxide when 100 ml. of 0.1N-hydrochloric acid are titrated. A method of eliminating this error, other than that of selecting an indicator with a pH range below pH 5, is to boil the solution while still acid and to continue the titration with the cold solution. Boiling the solution is particularly efficacious when titrating dilute (e.g., 0.01N) solutions.

I, 33. Neutralisation of a weak acid with a strong base.—We shall confine our attention to 0.1N solutions; other concentrations can be treated analogously. Let us study the neutralisation of 100 ml. of 0.1N-acetic acid with 0.1N-sodium hydroxide solution. The pH of the solution at the equivalence point is given by (Section I, 19):

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2} \log c$$

$$= 7 + 2.37 + \frac{1}{2}(-1.30) = 8.72$$

For other concentrations, we may employ the approximate mass action expression:

$$[H^+] \times \frac{[C_2H_3O_2^-]}{[H\cdot C_2H_2O_2]} = K_a \quad \ldots \quad (1)$$

or

$$[H^+] = \frac{[H\cdot C_2H_2O_2]}{[C_2H_3O_2^-]} \times K_a$$

or

$$pH = \log \frac{[\text{Salt}]}{[\text{Acid}]} + pK_a \quad \ldots \quad (2)$$

The concentration of the acid at any point is taken as equal to the concentration of the acid that has not yet been neutralised, and the concentration of the salt is assumed equal to the concentration of alkali added. These approximations are not valid at the beginning of the neutralisation, but since we are interested only in the pH change near the stoichiometric point, the subsequent argument is unaffected.

The initial pH of 0.1N-acetic acid is computed from equation (1); the dissociation of the acid is relatively so small that it may be neglected in expressing the concentration of acetic acid. Hence from equation (1):

$$[H^+] \times \frac{[C_2H_3O_2^-]}{[H\cdot C_2H_2O_2]} = 1.82 \times 10^{-5}$$

or

$$[H^+]^2/0.1 = 1.82 \times 10^{-5}$$

or

$$[H^+] = \sqrt{1.82 \times 10^{-3}} = 1.35 \times 10^{-3}$$

or

$$pH = 2.87$$

When 50 ml. of 0.1N-alkali have been added,

$$[\text{Salt}] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$$

and

$$[\text{Acid}] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$$

$$pH = \log \left(\frac{3.33 \times 10^{-2}}{3.33 \times 10^{-2}}\right) + 4.74 = 4.74$$

The pH values at other points on the titration curve are similarly calculated. After the equivalence point has been passed, the solution contains excess of OH- ions which will repress the hydrolysis of the salt; the pH may be assumed, with sufficient accuracy for our purpose, to be that due to the excess of base present, so that in this region the titration curve will almost coincide with that for 0.1N-hydrochloric acid (Fig. I, 32, 1 and Table XI). All the results are collected in Table XII, and are depicted graphically in Fig. I, 33, 1. The results
The Theoretical Basis of Quantitative Analysis

for the titration of 100 ml. of 0.1N solution of a weaker acid (\(K_a = 1 \times 10^{-7}\)) with 0.1N-sodium hydroxide at the laboratory temperature are also included.

For 0.1N-acetic acid and 0.1N-sodium hydroxide, it is evident from

TABLE XII.—Neutralisation of 100 ml. of 0.1N-Acetic Acid (\(K_a = 1.82 \times 10^{-5}\)) and of 100 ml. of 0.1N-HA (\(K_a = 1 \times 10^{-7}\)) with 0.1N-Sodium Hydroxide

<table>
<thead>
<tr>
<th>ML of 0.1N-NaOH Used.</th>
<th>0.1N-Acetic Acid pH.</th>
<th>0.1N-HA ((K_a = 1 \times 10^{-7})) pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.9</td>
<td>4.0</td>
</tr>
<tr>
<td>10</td>
<td>3.8</td>
<td>6.0</td>
</tr>
<tr>
<td>25</td>
<td>4.3</td>
<td>6.5</td>
</tr>
<tr>
<td>50</td>
<td>4.7</td>
<td>7.0</td>
</tr>
<tr>
<td>90</td>
<td>5.7</td>
<td>8.0</td>
</tr>
<tr>
<td>99.0</td>
<td>6.7</td>
<td>9.0</td>
</tr>
<tr>
<td>99.5</td>
<td>7.0</td>
<td>9.3</td>
</tr>
<tr>
<td>99.8</td>
<td>7.4</td>
<td>9.7</td>
</tr>
<tr>
<td>99.9</td>
<td>7.7</td>
<td>9.8</td>
</tr>
<tr>
<td>100.0</td>
<td>8.7</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Fig. I, 32, 1.—Neutralisation Curves of 0.1N-Acetic Acid and of 0.1N-Acid (\(K_a = 1 \times 10^{-7}\)) with 0.1N-Sodium Hydroxide (Calculated).

the titration curve that neither methyl orange nor methyl red can be used as indicators. The equivalence point is at \(pH = 8.7\), and it is necessary to use an indicator with a \(pH\) range on the slightly alkaline side, such as phenolphthalein, thymolphthalein, or thymol blue (\(pH\) range, as base, 8.0-9.6). For the acid with \(K_a = 10^{-7}\), the equivalence point is at \(pH = 10\), but here the rate of change of \(pH\) in the neighbourhood
of the stoichiometric point is very much less pronounced, owing to considerable hydrolysis. Phenolphthalein will commence to change colour after about 92 ml. of alkali have been added, and this change will occur to the equivalence point; thus the end point will not be sharp and the titration error will be appreciable. With thymolphthalein, however, the colour change covers the pH range 9·3-10·5; this indicator may be used, the end point will be more sharp than for phenolphthalein, but nevertheless somewhat gradual, and the titration error will be about 0·2 per cent. Acids that have dissociation constants less than $10^{-7}$ cannot be satisfactorily titrated in $0·1N$ solution with a simple indicator.

In general, it may be stated that weak acids ($K_a > 5 \times 10^{-6}$) should be titrated with phenolphthalein, thymolphthalein, or thymol blue as indicators.

**I, 34. Neutralisation of a weak base with a strong acid.**—We may illustrate this case by the titration of 100 ml. of $0·1N$-ammonium hydroxide ($K_b = 1·8 \times 10^{-5}$) with $0·1N$-hydrochloric acid at the ordinary laboratory temperature. The pH of the solution at the equivalence point is given by the equation (Section I, 19):

$$pH = \tfrac{1}{2}K_w - \tfrac{1}{2}pK_b - \tfrac{1}{2} \log c = 7 - 2·37 - \tfrac{1}{2}(-1·30) = 5·28$$

For other concentrations, the pH may be calculated in the following manner. Using the approximate mass action expression:

$$(1) \quad [\text{NH}_4^+]/[\text{OH}^-][\text{NH}_4\text{OH}] = K_b$$

or

$$(2) \quad [\text{OH}^-] = [\text{NH}_4\text{OH}] \times K_b/[	ext{NH}_4^+]$$

or

$$(3) \quad pOH = \log [\text{Salt}]/[\text{Base}] + pK_b$$

or

$$(4) \quad pH = pK_w - pK_b - \log [\text{Salt}]/[\text{Base}]$$

The concentration of the base at any point is assumed equal to the concentration of the base that has not been neutralised, and the concentration of the salt is taken as equal to the concentration of acid added. These approximations are not valid at the beginning of the neutralisation, but the error thus introduced is small. After the equivalence point has been reached, the solution contains excess of $H^+$ ions, hydrolysis of the salt will be repressed, and the subsequent pH changes may be assumed, with sufficient accuracy for our purpose, to be those due to the excess of acid present, so that in this region the titration curve will almost coincide with that for $0·1N$-sodium hydroxide (Fig. I, 32, 1 and Table XI).

The results computed in the above manner are given in Table XIII, and are represented graphically in Fig. I, 34, 1. The results for the titration of 100 ml. of a $0·1N$ solution of a weaker base ($K_b = 1 \times 10^{-7}$) are also included.

It is clear that neither thymolphthalein nor phenolphthalein can be employed in the titration of $0·1N$-ammonium hydroxide. The equivalence point is at pH 5·1, and it is necessary to use an indicator with a pH range on the slightly acid side (3·6-5·), such as methyl orange, methyl red, bromo-phenol blue, or bromo-cresol green. The last-named indicators may be utilised for the titration of all weak bases ($K_b > 5 \times 10^{-6}$) with strong acids.
Table XIII.—Neutralisation of 100 ml. of 0·1N-Ammonium Hydroxide ($K_a = 1.8 \times 10^{-6}$) and of 100 ml. of 0·1N-BOH ($K_a = 1 \times 10^{-7}$) with 0·1N-Hydrochloric Acid

<table>
<thead>
<tr>
<th>Ml. of 0·1N-HCl Added.</th>
<th>0·1N-Ammonium Hydroxide pH.</th>
<th>0·1N-BOH ($K_a = 1 \times 10^{-7}$) pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>11·1</td>
<td>10·0</td>
</tr>
<tr>
<td>10</td>
<td>10·2</td>
<td>8·0</td>
</tr>
<tr>
<td>25</td>
<td>9·8</td>
<td>7·5</td>
</tr>
<tr>
<td>50</td>
<td>9·3</td>
<td>7·0</td>
</tr>
<tr>
<td>90</td>
<td>8·3</td>
<td>6·1</td>
</tr>
<tr>
<td>99·0</td>
<td>7·3</td>
<td>5·0</td>
</tr>
<tr>
<td>99·5</td>
<td>7·0</td>
<td>4·7</td>
</tr>
<tr>
<td>99·8</td>
<td>6·6</td>
<td>4·3</td>
</tr>
<tr>
<td>99·9</td>
<td>6·3</td>
<td>4·0</td>
</tr>
<tr>
<td>100·0</td>
<td>5·3</td>
<td>4·0</td>
</tr>
</tbody>
</table>

For the weak base ($K_a = 1 \times 10^{-7}$), bromo-phenol blue or methyl orange may be used; no sharp colour change will be obtained with bromo-cresol green or with methyl red, and the titration error will be considerable.

I. 35. Neutralisation of a weak acid with a weak base.—This case is exemplified by the titration of 100 ml. of 0·1N-acetic acid ($K_a = 1.8 \times 10^{-5}$) with 0·1N-ammonium hydroxide ($K_a = 1.8 \times 10^{-5}$). The pH at the equivalence point is given by (Section I, 19):

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

$$= 7.0 + 2.37 - 2.37 = 7.0$$
The calculation of the neutralisation curve is a little more difficult.* The titration curve for the neutralisation of 100 ml. of 0.1N-acetic acid with 0.1N-ammonium hydroxide at the laboratory temperature is shown by the dotted line in Fig. I, 33, 1. The chief feature of the curve is that the change of $pH$ near the equivalence point and, indeed, during the whole of the neutralisation curve is very gradual. There is no sudden change in $pH$, and hence no sharp end point can be found with any simple indicator. A mixed indicator, which exhibits a sharp colour change over a very limited $pH$ range, may sometimes be found which is suitable. Thus for acetic acid–ammonia solution titrations, neutral red—methylene blue indicator may be used (see Section I, 29). On the whole, it is best to avoid titrations involving both a weak acid and a weak base.

I, 36. Neutralisation of a polybasic acid with a strong base.—The shape of the titration curve will depend upon the relative magnitudes of the various dissociation constants. It is assumed that titrations take place at the ordinary laboratory temperature in solutions of concentration of 0.1N or stronger. For a dibasic acid, if the difference between the primary and secondary dissociation constants is very large ($K_1/K_2 > 10,000$), the solution behaves like a mixture of two acids with constants $K_1$ and $K_2$ respectively; the considerations given previously may be applied. Thus for sulphurous acid, $K_1 = 1.7 \times 10^{-2}$ and $K_2 = 1.0 \times 10^{-7}$, it is evident that there will be a sharp change of $pH$ near the first equivalence point, but for the second stage the change will be less pronounced, yet just sufficient for the use of, say, thymolphthalein as indicator (see Fig. I, 33, 1). For carbonic acid, however, for which $K_1 = 4.3 \times 10^{-7}$ and $K_2 = 5.6 \times 10^{-11}$, only the first stage will be just discernible in the neutralisation curve (see Fig. I, 33, 1); the second stage is far too weak to exhibit any point of inflexion and there is no suitable indicator available for direct titration. As indicator for the primary stage, thymol blue may be used (see Section I, 34), although a mixture of thymol blue (3 parts) and cresol red (1 part) (see Section I, 29) is more satisfactory; with phenolphthalein the colour change will be somewhat gradual and the titration error may be several per cent.

It can be shown † that the $pH$ at the first equivalence point for a dibasic acid is given by

$$[H^+] = \sqrt{\frac{K_1K_2c}{K_1 + c}}$$

Provided that the first stage of the acid is weak and that $K_1$ can be neglected by comparison with $c$, the concentration of salt present, this expression reduces to $[H^+] = \sqrt{K_1K_2}$, or $pH = \frac{1}{2}pK_1 + \frac{1}{2}pK_2$.

With a knowledge of the $pH$ at the stoichiometric point and also of the course of the neutralisation curve, it should be an easy matter to select the appropriate indicator for the titration of any dibasic acid for which $K_1/K_2$ is at least $10^4$. For many dibasic acids, however, the two dissociation constants are too close together and it is not possible to differentiate between the two stages. If $K_2$ is not less than about $10^{-7}$, all

---

* For details, see, for example, S. Glasstone, The Electrochemistry of Solutions. Third Edition, pp. 224 et seq. (Methuen, 1945.)

† See, for example, ibid., pp. 232 et seq.
the replaceable hydrogen may be titrated, e.g., sulphuric acid (primary stage—a strong acid), oxalic acid, malonic, succinic, and tartaric acids (for dissociation constants, see Table II, Section I, 4).

Similar remarks apply to tribasic acids. These may be illustrated by reference to orthophosphoric acid, for which \( K_1 = 7.5 \times 10^{-3} \), \( K_2 = 6.2 \times 10^{-8} \), and \( K_3 = 5 \times 10^{-13} \). Here \( K_1/K_2 = 1.2 \times 10^6 \) and \( K_2/K_3 = 1.2 \times 10^6 \), so that the acid will behave as a mixture of three monobasic acids with the dissociation constants given above. Neutralisation proceeds almost completely to the end of the primary stage before the secondary stage is appreciably affected, and the secondary stage proceeds almost to completion before the tertiary stage is apparent. The \( \text{pH} \) at the first equivalence point is given approximately by \( \frac{1}{2} pK_1 + \frac{1}{2} pK_2 = 4.6 \), and at the second equivalence point by \( \frac{1}{2} pK_2 + \frac{1}{2} pK_3 = 9.7 \); in the very weak third stage, the curve is very flat and no indicator is available for direct titration. The third equivalence point may be computed approximately from the equation (Section I, 19):

\[
\text{pH} = \frac{1}{2} pK_1 + \frac{1}{2} pK_2 + \frac{1}{2} \log c = 7.0 - 0.15 + (-0.5) = 7.2 - 6 \text{ in } 0.1N \text{ solution}
\]

For the primary stage (phosphoric acid as a monobasic acid), methyl orange, bromo-cresol green, or congo red may be used as indicators. The secondary stage of phosphoric acid is very weak (see acid \( K_1 = 1 \times 10^{-7} \) in Fig. I, 33, 1) and the only suitable simple indicator is thymolphthalein (see Section I, 34); with phenolphthalein the error may be several per cent. A mixed indicator composed of phenol-
phthalein (2 parts) and α-naphtholphthalein (1 part) is the most satisfactory for the determination of the end point of phosphoric acid as a dibasic acid (see Section I, 29). The experimental neutralisation curve of 50 ml. of 0·1M-orthophosphoric acid with 0·1N-potassium hydroxide, determined by electrometric titration, is shown in Fig. I, 36, 1.

There are a number of tribasic acids, e.g., citric acid with $K_1 = 9.2 \times 10^{-4}$, $K_2 = 2.7 \times 10^{-5}$, $K_3 = 1.3 \times 10^{-6}$, the three dissociation constants of which are too close together and for which the three stages cannot consequently be differentiated. If $K_3 > ca. 10^{-7}$, all the replaceable hydrogen may be titrated; the indicator will be determined by the value of $K_3$.

I, 37. Titration of solutions of hydrolysed salts. Displacement titration.—The examples which are encountered in practice are largely the salts formed from a strong base and a very weak acid, such as potassium cyanide, borax, and sodium carbonate, or the salts derived from a strong acid and a very weak base, for example, aniline hydrochloride. We shall therefore confine our attention to examples of these salts. Both types will be largely hydrolysed in solution.

Titration of potassium cyanide with a strong acid.—Let us consider first the titration of 100 ml. of 0·2N-potassium cyanide with 0·2N-hydrochloric acid at the laboratory temperature. The salt is completely dissociated:

$$KCN \rightleftharpoons K^+ + CN^-$$

The hydrolysis of the salt is represented by:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

The reaction upon the addition of hydrochloric acid is simply the combination between the $R^+$ ions from the acid and the $OH^-$ ions produced by hydrolysis:

$$H^+ + OH^- = H_2O$$

The net result is that the weak hydrocyanic acid has been displaced by the stronger hydrochloric acid:

$$KCN + HCl = HCN + KCl$$

the process is therefore often referred to as a displacement titration. The $pH$ at the true end point can be calculated from the dissociation constant and the concentration of the weak acid at the equivalence point, Thus in our example the volume is doubled at the equivalence point, hence the concentration of hydrocyanic acid is 0·1N. $K_a$ for hydrocyanic acid is $7.2 \times 10^{-10}$, i.e.,

$$[H^+] \times [CN^-]/[HCN] = 7.2 \times 10^{-10}$$

hence $[H^+] = \sqrt{7.2 \times 10^{-10} \times 0.1}$, since $[H^+] = [CN^-]$

or

$$pH = 5.1$$

If 100·1 ml. of hydrochloric acid are added, the $pH$ will be 4, with 100·2 ml. the $pH$ will be 3·7, with 101 ml. the $pH$ will be 3, etc. There will be a fairly abrupt decrease of $pH$ in the neighbourhood of the equivalence point. If the titration error is not to exceed 0·2 per cent, any indicator covering the $pH$ range 3·7-5·1 (and slightly beyond this) may be used; suitable indicators are bromo-cresol green, methyl orange, bromo-phenol blue, and methyl red.
Titration of borax with a strong acid.—With borax, similar considerations apply. The net result of the displacement titration is given by:

\[ \text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} = 2\text{NaCl} + 4\text{H}_3\text{BO}_3 \]

Boric acid behaves as a weak monobasic acid with a dissociation constant of \( 6 \times 10^{-10} \). The pH at the equivalence point in the titration of 0.2N-borax with 0.2N-hydrochloric acid is that due to 0.1N-boric acid, i.e., 5.1. Further addition of hydrochloric acid will cause a sharp decrease of pH as in the case of potassium cyanide. Similar indicators may therefore be used.

Titration of sodium carbonate with a strong acid.—The solution of sodium carbonate may be titrated to the bicarbonate stage (i.e., with one equivalent of acid), when the net reaction is:

\[ \text{Na}_2\text{CO}_3 + \text{HCl} = \text{NaHCO}_3 + \text{NaCl} \]

The equivalence point for the primary stage of ionisation of carbonic acid is at \( pH = (\frac{1}{2}pK_1 + \frac{1}{2}pK_2) = 8.3 \), and we have seen (Section I, 34) that \textit{inter alia} thymol blue and, less satisfactorily, phenolphthalein, or a mixed indicator may be employed to detect the end point.

Sodium carbonate solution may also be titrated until all the carbonic acid is displaced (two equivalents of acid). The net reaction is then:

\[ \text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{CO}_3 \]

The same end point is reached by titrating sodium bicarbonate solution with hydrochloric acid:

\[ \text{NaHCO}_3 + \text{HCl} = \text{NaCl} + \text{H}_2\text{CO}_3 \]
The end point with 100 ml. of 0·2N-sodium bicarbonate and 0·2N-
hydrochloric acid may be deduced exactly as described above for
potassium cyanide. The pH at the equivalence point is very approxi-
mately 3·8 \((K_b, for \text{H}_2\text{CO}_3 = 4·3 \times 10^{-7}; \text{the secondary ionisation and}
the loss of carbonic acid, due to escape of carbon dioxide, have been
neglected). Suitable indicators are therefore methyl yellow, methyl
orange, congo red, and bromo-phenol blue. The experimental titra-
cion curve, determined with the hydrogen electrode, for 100 ml. of
0·1N-sodium carbonate and 0·1N-hydrochloric acid is shown in
Fig. 1, 37, 1.

Salts of weak bases and strong acids, e.g., aniline hydrochloride
\((K_b = 4·0 \times 10^{-10})\), may be treated in an analogous manner.

1, 38. Choice of indicators in neutralisation reactions.—As a general
rule it may be stated that for a titration to be feasible, there should
be a change of approximately two units of pH at or near the stoichio-
metric point produced by the addition of a small volume of the reagent.
The pH at the equivalence point may be computed by means of the
equations given in Section I, 19 (see also below); the pH at either side
of the equivalence point (0·1–1 ml.) may be calculated as described in
the preceding sections, and the difference will indicate whether the
change is large enough to permit a sharp end point to be determined.
Alternatively, the pH change on both sides of the equivalence point
may be noted from the neutralisation curve determined by electrometric
titration (Sections VI, 2–4). If the pH change is satisfactory, an
indicator should be selected that changes at or near the equivalence
point.

For convenience of reference, we shall summarise the conclusions
already deduced from theoretical principles.

Strong acid and strong base. For 0·1N solutions or stronger, any
indicator may be used which has a range between the limits pH 4·5 and
pH 9·5. With 0·01N solutions, the pH range is somewhat smaller
(5·5–8·5). If carbon dioxide is present, the solution should either be
boiled whilst still acid and the solution titrated when cold, or an
indicator with a range below pH 5 be employed.

Weak acid and a strong base. The pH at the equivalence point is cal-
culated from the equation:

\[
pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2} \log c
\]

The pH range for acids with \(K_a > 10^{-5}\) is 7–10·5; for weaker acids
\((K_a > 10^{-6})\) the range is reduced (8–10). The pH range 8–10·5 will
cover most of the examples likely to be encountered; this permits of
the use of thymol blue, thymolphthalein, or phenolphthalein.

Weak base and strong acid. The pH at the equivalence point is
computed from the equation:

\[
pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2} \log c
\]

The pH range for bases with \(K_b > 10^{-5}\) is 3–7, and for weaker bases
\((K_b > 10^{-6})\) 3–5. Suitable indicators will be methyl red, methyl
orange, methyl yellow, bromo-cresol green, and bromo-phenol blue.

Weak acid and weak base. There is no sharp rise in the neutralisation
curve and, generally, no simple indicator can be used. The titration
should therefore be avoided, if possible. The approximate pH at the equivalence point can be computed from the equation:

\[ p\text{H} = \frac{1}{2}pK_a + \frac{1}{2}pK_b - \frac{1}{2}pK_c \]

It is sometimes possible to employ a mixed indicator which exhibits a colour change over a very limited pH range, for example, neutral red-methylene blue for ammonia solution and acetic acid.

As a general rule, wherever an indicator does not give a sharp end point, it is advisable to prepare an equal volume of a comparison solution containing the same quantity of indicator and of the final products and other components of the titration as in the solution under test, and to titrate to the colour shade thus obtained.

**THEORY OF PRECIPITATION AND COMPLEX-FORMATION PROCESSES**

I, 39. Precipitation reactions.—The most important precipitation processes in volumetric analysis utilise silver nitrate as the reagent (argentimetric processes). Our discussion of the theory will therefore be confined to argentimetric processes; the same principles can, of course, be applied to other precipitation reactions. Let us consider the changes in ionic concentration which occur during the titration of 100 ml. of 0·1N-sodium chloride with 0·1N-silver nitrate. The solubility product of silver chloride at the laboratory temperature is \(1·2 \times 10^{-10}\). The initial concentration of chloride ions, \([\text{Cl}^-]\), is 0·1g. equivalent per litre, or \(p\text{Cl}^- = 1\) (see Section I, 17). When 50 ml. of 0·1N-silver nitrate have been added, 50 ml. of 0·1N-sodium chloride remain in a total volume of 150 ml.: thus \(\text{[Cl}^-\text{]} = 50 \times 0·1/150 = 3·33 \times 10^{-2}\), or \(p\text{Cl}^- = 1·48\. With 90 ml. of silver nitrate solution \([\text{Cl}^-\text{]} = 10 \times 0·1/190 = 5·3 \times 10^{-3}\), or \(p\text{Cl}^- = 2·28\. Now \(\text{[Ag}^+\text{]} \times \text{[Cl}^-\text{]} = 1·2 \times 10^{-10} = S_{\text{AgCl}}\)]
or \(p\text{Ag}^+ + p\text{Cl}^- = 9·92 = p\text{AgCl}\)

In the last calculation, \(p\text{Cl}^- = 1·48\), hence \(p\text{Ag}^+ = 9·92 - 1·48 = 8·44\). In this manner, the various concentrations of chloride and silver ions can be computed up to the equivalence point. At the equivalence point:

\[ \text{Ag}^+ = \text{Cl}^- = \sqrt{S_{\text{AgCl}}} \]
\[ p\text{Ag}^+ = p\text{Cl}^- = \frac{1}{2}p\text{AgCl} = 9·92/2 = 4·96 \]

and a saturated solution of silver chloride with no excess of silver or chloride ions is present.

With 100·1 ml. of silver nitrate solution, \([\text{Ag}^+\text{]} = 0·1 \times 0·1/200·1 = 5 \times 10^{-5}\), or \(p\text{Ag}^+ = 4·30\); \(p\text{Cl}^- = p\text{AgCl} - p\text{Ag}^+ = 9·92 - 4·30 = 5·62\).*

* This is not strictly true, since the dissolved silver chloride will contribute silver and chloride ions to the solution; the actual concentration is ca. 1 \(\times 10^{-5}\) g.-ions per litre. If the excess of silver ions added is greater than 10 times this value, i.e., \(>10\sqrt{S_{\text{AgCl}}}\), the error introduced by neglecting the ionic concentration produced by the dissolved salt may be taken as negligible for the purpose of the ensuing discussion.
Quantitative Inorganic Analysis

The values computed in this way up to the addition of 110 ml. of 0.1N-silver nitrate are collected in Table XIV. Similar values for the

**TABLE XIV.**—Titration of 100 ml. of 0.1N-NaCl and 100 ml. of 0.1N-KI respectively with 0.1N-AgNO₃ (SₐgCl = 1.2 × 10⁻¹⁰; SₐgI = 1.7 × 10⁻¹⁶)

<table>
<thead>
<tr>
<th>Ml. of 0.1N-AgNO₃ Added.</th>
<th>Titration of Chloride.</th>
<th>Titration of Iodide.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pCl⁻</td>
<td>pAg⁺</td>
</tr>
<tr>
<td>0</td>
<td>1.0</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>1.5</td>
<td>8.4</td>
</tr>
<tr>
<td>90</td>
<td>2.3</td>
<td>7.6</td>
</tr>
<tr>
<td>95</td>
<td>2.6</td>
<td>7.3</td>
</tr>
<tr>
<td>98</td>
<td>3.0</td>
<td>6.0</td>
</tr>
<tr>
<td>99</td>
<td>3.3</td>
<td>6.6</td>
</tr>
<tr>
<td>99.5</td>
<td>3.7</td>
<td>6.2</td>
</tr>
<tr>
<td>99.8</td>
<td>4.0</td>
<td>5.9</td>
</tr>
<tr>
<td>99.9</td>
<td>4.3</td>
<td>5.6</td>
</tr>
<tr>
<td>100.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>100.1</td>
<td>5.6</td>
<td>4.3</td>
</tr>
<tr>
<td>100.2</td>
<td>5.9</td>
<td>4.0</td>
</tr>
<tr>
<td>100.5</td>
<td>6.3</td>
<td>3.6</td>
</tr>
<tr>
<td>101</td>
<td>6.6</td>
<td>3.3</td>
</tr>
<tr>
<td>102</td>
<td>6.9</td>
<td>3.0</td>
</tr>
<tr>
<td>105</td>
<td>7.3</td>
<td>2.6</td>
</tr>
<tr>
<td>110</td>
<td>7.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

titration of 100 ml. of 0.1N-potassium iodide with 0.1N-silver nitrate are included in the same table (SₐgI = 1.7 × 10⁻¹⁶).

![Graph](image)

**Fig. 1, 39, 1.**—Titration Curves of 100 ml. of 0.1N-NaCl and of 100 ml. of 0.1N-KI respectively with 0.1N-AgNO₃ (Calculated).

It will be seen by inspecting the silver-ion exponents in the neighbourhood of the equivalence point (say, between 99.8 and 100.2 ml.)
that there is a marked change in the silver-ion concentration, although
the change is more pronounced for silver iodide than for the silver
chloride, since the solubility product of the latter is about $10^6$ larger
than for the former. This is shown more clearly in the titration curve
in Fig. I, 39, 1, which represents the changes of $pAg^+$ in the range
between 10 per cent before and 10 per cent after the stoichiometric
point in the titration of 0.1N-chloride and 0.1N-iodide respectively
with 0.1N-silver nitrate. An almost identical curve is obtained by
potentiometric titration with the silver electrode (see Sections VI,
2-4); the $pAg^+$ values may be computed from the e.m.f. figures
exactly as in the calculation of $pH$.

I, 40. Complex formation reactions.—An example of this type of
reaction is the titration of cyanide with silver nitrate solutions, a
method first proposed by Liebig (1851). When a solution of silver
nitrate is added to a solution containing cyanide ions (e.g., an alkali
cyanide) a white precipitate is formed when the two liquids first come
into contact with one another, but on stirring it re-dissolves owing to
the formation of a stable complex cyanide, the alkali salt of which is
soluble:

$$\text{AgNO}_3 + 2\text{KCN} \rightleftharpoons \text{K}[\text{Ag(CN)}_2] + \text{KNO}_3$$

or

$$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag(CN)}_2]^-$$

When the above reaction is complete, further addition of silver nitrate
solution yields the insoluble silver argentocyanide (often termed silver
cyanide):

$$\text{Ag}^+ + [\text{Ag(CN)}_2]^- \longrightarrow \text{Ag}[\text{Ag(CN)}_2]$$

The end point of the reaction is therefore indicated by the formation
of a permanent precipitate or turbidity.

Let us attempt to investigate the suitability of this reaction for
quantitative work and to calculate the titration error involved. The
instability constant (Section I, 12; Table V), i.e.,

$$[\text{Ag}^+] \times [\text{CN}^-]^2 / ([\text{Ag(CN)}_2]^-)$$

is $1.0 \times 10^{-21}$ at the ordinary temperature. Let us suppose, for
purposes of illustration, that an amount of potassium cyanide solution
equivalent to 10 ml. of 0.1N-silver nitrate is employed, and that the
volume at the end point is 100 ml. The concentration of the complex
$K[\text{Ag(CN)}_2]$ will then be 0.01M. Here the $\text{Ag}^+$ and $\text{CN}^-$ ions present
will be derived from the dissociation of the complex $[\text{Ag(CN)}_2]^-$. ion.
At the stoichiometric point:

$$[\text{CN}^-] = 2[\text{Ag}^+] = 2x$$

hence

$$\frac{[\text{Ag}^+] \times [\text{CN}^-]^2}{([\text{Ag(CN)}_2]^-)} = 1.0 \times 10^{-21} = \frac{x \times (2x)^2}{0.01}$$

or

$$x = \sqrt[3]{2.5 \times 10^{-24}} = 1.36 \times 10^{-8}$$

or

$$[\text{Ag}^+] = 1.36 \times 10^{-8}, \text{ and } [\text{CN}^-] = 2.72 \times 10^{-8}$$

The solubility product of silver argentocyanide, $[\text{Ag}^+] \times ([\text{Ag(CN)}_2]^-)$,
Quantitative Inorganic Analysis

is \(2.25 \times 10^{-12}\), hence precipitation of this substance will commence when:

\[
\frac{[Ag^+] \times [\text{Cl}^-]}{S_{AgCl}} > \frac{[Ag(\text{CN})_2^-] \times [\text{CN}^-]}{S_{Ag(\text{CN})_2^-}} > \frac{[Ag^+]^2 \times [\text{CrO}_4^{2-}]}{S_{Ag[\text{CrO}_4]}}
\]

The silver-ion concentration at the theoretical end point is \(1.36 \times 10^{-8}\), hence precipitation will occur just before this. The difference is so small, however, that for all practical purposes the titration error is negligible; moreover, in practice, the theoretical end point will be exceeded in order to produce enough precipitate to be visible.

The above method yields satisfactory results if the reagent is added very slowly near the end point, but is not applicable to ammoniacal solutions owing to the removal of the silver ions by the formation of the soluble complex \([Ag(NH_3)_2]^+\) (see Section I. 12). An alternative procedure is to work in ammoniacal solution in the presence of a little alkali iodide (G. Dénigès, 1895): the end point is marked by the formation of turbidity of silver iodide (see Sections I. 11, 12).

I. 41. Determination of end points in precipitation and in complex formation reactions.—Many methods are utilised in determining end points in these reactions, but only the most important will be mentioned here.

A. Formation of a coloured precipitate. This may be illustrated by the Mohr procedure (1856) for the determination of chloride and bromide. In the titration of a neutral solution of, say, chloride ions with silver nitrate solution, a small quantity of potassium chromate solution is added to serve as indicator. At the end point the chromate ions combine with silver ions to form the sparingly soluble, red silver chromate.

The theory of the process is as follows. We have here a case of fractional precipitation (Section I. 11), the two sparingly soluble salts being silver chloride (S.P. \(1.2 \times 10^{-10}\)) and silver chromate (S.P. \(1.7 \times 10^{-12}\)). Let us consider an actual example encountered in practice, viz., the titration of, say, 0.1N-silver nitrate with 0.1N-sodium chloride in the presence of a few ml. of dilute potassium chromate solution. Silver chloride is the less-soluble salt and, furthermore, the initial chloride concentration is high, hence silver chloride will be precipitated. At the first point where red silver chromate is just precipitated, we shall have both salts in equilibrium with the solution, hence:

\[
[Ag^+] \times [\text{Cl}^-] = S_{AgCl} = 1.2 \times 10^{-10}
\]

\[
[Ag^+]^2 \times [\text{CrO}_4^{2-}] = S_{Ag[\text{CrO}_4]} = 1.7 \times 10^{-12}
\]

\[
\frac{[Ag^+]}{[\text{Cl}^-]} = \frac{S_{AgCl}}{\sqrt{S_{Ag[\text{CrO}_4]}}} = \frac{1.2 \times 10^{-10}}{\sqrt{1.7 \times 10^{-12}}} = 0.2 \times 10^{-5}
\]

At the equivalence point \([\text{Cl}^-] = \sqrt{S_{AgCl}} = 1.1 \times 10^{-5}\). If silver chromate is to precipitate at this chloride-ion concentration:

\[
[\text{CrO}_4^{2-}] = \left(\frac{[\text{Cl}^-]}{0.2 \times 10^{-5}}\right)^2 = \left(\frac{1.1 \times 10^{-5}}{0.2 \times 10^{-5}}\right)^2 = 1.4 \times 10^{-8}
\]

or the potassium chromate solution should be 0.014M. It should be
noted that a slight excess of silver nitrate solution must be added before the red colour of silver chromate is visible. In practice, a more dilute solution (0·002–0·004M) of potassium chromate is generally used, since a chromate solution of concentration 0·01–0·02M imparts a distinct deep orange colour to the solution, which renders the detection of the first appearance of silver chromate somewhat difficult. We can readily calculate the error thereby introduced, for if \[ [\text{CrO}_4^{2-}] = (\text{say}) \ 0·003, \] silver chromate will be precipitated when:

\[
[\text{Ag}^+] = \sqrt{\frac{S_{\text{Ag}_2\text{CrO}_4}}{[\text{CrO}_4^{2-}]}} = \sqrt{\frac{1·7 \times 10^{-12}}{3 \times 10^{-4}}} = 2·4 \times 10^{-5}
\]

If the theoretical concentration of indicator is used:

\[
[\text{Ag}^+] = \sqrt{\frac{1·7 \times 10^{-12}}{1·4 \times 10^{-5}}} = 1·1 \times 10^{-5}
\]

The difference is \(1·3 \times 10^{-5}\) g.-equivalent per litre. If the volume of the solution at the equivalence point is 150 ml., then this corresponds to \(1·3 \times 10^{-5} \times 150 \times 10^4/1000 = 0·02\) ml. of 0·1N-silver nitrate. This is the theoretical titration error, and is therefore negligible. In actual practice another factor must be considered, viz., the small excess of silver nitrate solution which must be added before the eye can detect the colour change in the solution; this is of the order of one drop or ca. 0·05 ml. of 0·1N-silver nitrate.

The titration error will increase with increasing dilution of the solution being titrated and is quite appreciable (ca. 0·6 per cent) in dilute, say, 0·01N, solutions when the chromate concentration is of the order 0·002–0·004M. This is most simply allowed for by means of an indicator blank determination, e.g., by measuring the volume of standard silver nitrate solution required to give a perceptible coloration when added to distilled water containing the same quantity of indicator as is employed in the titration. This volume is subtracted from the volume of standard solution used.

It must be mentioned that the titration should be carried out in neutral solution or in very faintly alkaline solution, i.e., within the pH range 6·5–9. In acid solution, the following reaction occurs:

\[
2\text{CrO}_4^{2-} + 2\text{H}^+ \underset{\text{eq}}{\rightleftharpoons} 2\text{HCrO}_4^{-} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}
\]

\(\text{HCrO}_4^{-}\) is a weak acid, consequently the chromate-ion concentration is reduced and the solubility product of silver chromate may not be exceeded. In markedly alkaline solutions, silver hydroxide (S.P. \(2·3 \times 10^{-8}\)) might be precipitated. A simple method of making an acid solution neutral is to add an excess of pure calcium carbonate.

B. Formation of a soluble coloured compound. This procedure is exemplified by the method of Volhard (1878) for the titration of silver in the presence of free nitric acid with standard potassium or ammonium thiocyanate solution. The indicator is a solution of ferric nitrate or of ferric ammonium alum. The addition of the thiocyanate solution produces first a precipitate of silver thiocyanate (S.P. \(7·1 \times 10^{-12}\)):

\[
\text{Ag}^+ + \text{CNS}^- \rightleftharpoons \text{AgCNS}
\]

When this reaction is complete, the slightest excess of thiocyanate
produces a reddish-brown coloration, due to the formation of the complex ferri-thiocyanate ion.*

\[
\text{Fe}^{3+} + 6\text{CNS}^- \rightleftharpoons [\text{Fe(CNS)}_6]^{3-} \\
\text{(or } 2\text{Fe}^{3+} + 6\text{CNS}^- \rightleftharpoons \text{Fe}[\text{Fe(CNS)}_6] \rightleftharpoons \text{Fe}^{3+} + [\text{Fe(CNS)}_6]^{3-})
\]

This method may be applied to the determination of chlorides, bromides, and iodides in acid solution. Excess of standard silver nitrate solution is added, and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:

\[
\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl} \\
\text{Ag}^+ + \text{CNS}^- \rightleftharpoons \text{AgCNS}
\]

The two sparingly soluble salts will be in equilibrium with the solution, hence:

\[
\frac{[\text{Cl}^-]}{[\text{CNS}^-]} = \frac{S_{\text{AgCl}}}{S_{\text{AgCNS}}} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 170
\]

When the excess of silver has reacted, the thiocyanate may react with the silver chloride, since silver thiocyanate is the less-soluble salt until the ratio \([\text{Cl}^-]/[\text{CNS}^-]\) in the solution is 170:

\[
\text{AgCl} + \text{CNS}^- \rightleftharpoons \text{AgCNS} + \text{Cl}^-
\]

This will take place before reaction occurs with the ferric ions in the solution, and there will consequently be a considerable titration error. It is therefore absolutely necessary to prevent the reaction between the thiocyanate and the silver chloride. This may be effected in several ways, of which the first is probably the most reliable: (i) the silver chloride is filtered off, and the filtrate and washings are titrated; (ii) the silver chloride is coagulated, and thus rendered less reactive by boiling, and the mixture is cooled and titrated; (iii) the addition of a few ml. of ether or, preferably, of 1 ml. of nitrobenzene, which causes coagulation, before back titration.

With bromides, we have the equilibrium:

\[
\frac{[\text{Br}^-]}{[\text{CNS}^-]} = \frac{S_{\text{AgBr}}}{S_{\text{AgCNS}}} = \frac{3.5 \times 10^{-13}}{7.1 \times 10^{-13}} = 0.5
\]

The titration error is small, and no difficulties arise in the determination of the end point. Silver iodide (S.P. \(1.7 \times 10^{-16}\)) is less soluble than the bromide; the titration error is negligible, but the ferric-iron indicator should not be added until excess of silver is present, since the dissolved iodide reacts with the ferric iron:

\[
2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2
\]

C. Use of adsorption indicators. K. Fajans (1923–24) has introduced a new type of indicator for precipitation reactions as a result of his studies on the nature of adsorption. The action of these indicators is due to the fact that at the equivalence point the indicator is adsorbed by the precipitate, and during the process of adsorption a change

* According to Bent and French (1941) the coloration is due to the \(\text{FeCNS}^{2+}\) ion:

\[
\text{Fe}^{3+} + \text{CNS}^- \rightleftharpoons \text{FeCNS}^{2+}
\]
occurs in the indicator which leads to a substance of different colour; they have therefore been termed adsorption indicators. The substances employed are either acid dyes, such as those of the fluorescein series, e.g., fluorescein and eosin which are utilised as the sodium salts, or basic dyes, such as those of the rhodamine series (e.g., rhodamine 6G), which are applied as the halogen salts.

The theory of the action of these indicators is based upon the properties of colloids (see Section I, 56). When silver nitrate solution is titrated with a solution of a chloride, the precipitated silver chloride adsorbs chloride ions (a precipitate has a tendency to adsorb its own ions); this may be termed the primarily adsorbed layer, and it will hold by secondary adsorption oppositely charged ions present in solution (shown diagrammatically in Fig. I, 4I, 1, a). As soon as the stoichiometric point is reached, silver ions are present in excess; these will now be primarily adsorbed, and nitrate ions will be held by secondary adsorption (Fig. I, 4I, 1, b). If fluorescein is also present in the solution, the negative fluorescein ion, which is much more strongly adsorbed than the nitrate ion, is immediately adsorbed, and will reveal its presence in the precipitate, not by its own colour, which is that of the solution, but by the formation of the red (or pink) silver fluoresceinate on the surface with first trace of excess of silver ions. An alternative view is that during the adsorption of the fluorescein ion a re-arrangement of the structure of the ion occurs with the formation of a coloured substance. It is important to notice that the colour change takes place at the surface of the precipitate. If chloride is now added, the suspension will remain pink until chloride ions are present in excess, the adsorbed silver will then be converted into silver chloride, which will then primarily adsorb chloride ions. The fluorescein ions secondarily adsorbed will pass back into solution, to which they impart a greenish-yellow colour.

The following conditions will govern the choice of a suitable indicator:

(i) The precipitate should separate as far as possible in the colloidal condition. Large quantities of neutral salts, particularly of polyvalent ions, should be avoided owing to their coagulating effect. The solution should not be too dilute, as the amount of precipitate formed will be small and the colour change far from sharp with certain indicators.

(ii) The indicator ion must be of opposite charge to the ion of the precipitating agent.
(iii) The indicator ion should not be adsorbed before the particular compound has been completely precipitated, but it should be strongly adsorbed immediately after the equivalence point. The indicator ion should not be too strongly adsorbed by the precipitate; if this occurs, the adsorption of the indicator ion may be a primary process and will take place before the equivalence point, e.g., eosin (tetrabromofluorescein) in the chloride–silver titration.

For the titration of chlorides, fluorescein may be used. This indicator is a weak acid \( (K_a = ca. 1 \times 10^{-4}) \) and cannot be employed in strongly acid solutions. Titration should be carried out in neutral or in feebly acid (acetic acid) solutions; acid solutions may be treated with a slight excess of sodium acetate. Alternatively, dichloro-fluorescein, which is a stronger acid, may be utilised in slightly acid solutions \( (pH > 4.4) \); this indicator has a further advantage in that it is applicable in very dilute solutions.

For the titration of bromides, iodides, and thiocyanates with silver, eosin is a suitable indicator; the colour on the precipitate is magenta. The best results for iodides are obtained with dimethyldi-iodofluorescein, which gives a blue-red colour on the precipitate. The titration of silver solutions with bromide as the precipitating agent is best effected with rhodamine 6G, the precipitate assuming a violet colour at the end point; a sharp end point is obtained with this indicator in the presence of nitric acid up to a concentration of 2N. Cyanides may be titrated with standard silver solutions using diphenylcarbazide as the adsorption indicator (see Section I, 40); the precipitate is pale-violet at the end point.

Phenosafranine (0·2 per cent aqueous solution) has been used as an indicator for the titration of chloride and bromide solutions. The dyestuff is a green crystalline solid, which yields a bright red aqueous solution. During the titration of chloride or bromide ions with silver nitrate solution most of the indicator is adsorbed on the precipitate in its red form; at the equivalence point the colour of the adsorbed indicator changes suddenly to blue (bromides) and lilac (chlorides). This indicator is less affected by the presence of foreign ions than are the adsorption indicators already described, can be employed in the presence of nitric acid up to a 0·5N concentration, but cannot be used in the presence of sulphuric acid because of a bleaching effect upon the colour. It will be noted that the mechanism of the action of phenosafranine is different from other adsorption indicators (Fajans, 1938).

Rhodamine 6G, the hydrochloride of a basic dye (0·05 per cent aqueous solution), is a good indicator for the titration of silver ions with a standard bromide solution in dilute nitric acid solution (the acidity should not exceed 0·5N). As long as silver ions are present in excess, the indicator cation is not noticeably adsorbed by silver bromide. At the equivalence point or after a very slight excess of bromide has been added, the precipitate adsorbs the dye strongly and acquires a blue-violet colour. Partial coagulation of the silver bromide usually occurs shortly before the end point, but the solid remains uncoloured.

D. Turbidity method. The appearance of a turbidity is sometimes utilised to mark the end point of a reaction, as in Liebig’s method for cyanides (see Section I, 40). A method which should be included here
is the equal turbidity procedure introduced by Gay Lussac (1832) for the determination of silver with chloride. At the end point of the titration of, say, sodium chloride with silver nitrate solution, a solution of sodium nitrate which is saturated with silver chloride is obtained. If the clear supernatant liquid is withdrawn, and equal volumes treated with equivalent strengths of silver nitrate and sodium chloride solutions respectively, then equal turbidities of silver chloride should be produced. If equal turbidities are not found, the titration is continued with sodium chloride or silver nitrate to the point of equal turbidities.

This method yields very accurate results in experienced hands, and a refined modification is still employed for the determination of silver in alloys in the mints of certain governments. For ordinary work, however, any of the methods described above will be found more suitable for the average student. It must, however, be pointed out that nephelometric methods are employed in atomic-weight determinations and, indeed, owe their introduction to T. W. Richards, who first used a simple, but effective, nephelometer in connexion with his researches on the atomic weight of silver. A detailed account of modern nephelometric technique is given in Section V, 8.

I, 42. THEORY OF OXIDATION-REDUCTION REACTIONS

Reference has already been made in Section I, 23 to the fact that oxidation may be defined as the loss of electrons, and reduction as the gain of electrons by an atom or group of combined atoms. Thus in the reduction of ferric chloride by stannous chloride:

\[ 2\text{FeCl}_3 + \text{SnCl}_2 = 2\text{FeCl}_2 + \text{SnCl}_4 \]

or

\[ 2\text{Fe}^{III} + \text{Sn}^{II} = 2\text{Fe}^{II} + \text{Sn}^{IV} \]

for every gram-atom of ferric iron (56 g.) reduced 96,500 coulombs or one Faraday of electricity is lost by the iron, and for every gram-atom of stannous tin (119 g.) oxidised, the latter gains \(2 \times 96,500\) coulombs or two Faradays.*

According to modern theory, an electric current is essentially a transfer of electrons. It should therefore be possible to obtain direct proof of the transfer of electricity in the oxidation-reduction reaction under suitable experimental conditions. This may be shown by the following experiment (Fig. 1, 42, 1). Solutions of stannous chloride and of ferric chloride, each acidified with dilute hydrochloric acid in order to increase the conductivity, are placed in separate beakers \(A\) and \(B\), and the two solutions are connected by means of a "salt bridge".

* It follows from Faraday’s laws (Section I, 64) that each gram-equivalent weight of an ion is associated with a charge of one Faraday of electricity. A change of charge of one thus corresponds to the gain or loss of one Faraday per formula weight of the substance.
containing sodium chloride. The latter consists of a U-tube filled with a solution of a conducting electrolyte, such as sodium chloride, and stoppered at each end with a plug of cotton wool in order to minimise diffusion. It connects the two parts of the redox system, and prevents mixing. The electrolyte in solution in the salt bridge is always selected so that it does not react chemically with either of the solutions which it connects. Platinum-foil electrodes are introduced into each of the solutions, and the two electrodes are connected to a milli-voltmeter \( V \). When the circuit is closed it will be found that the (negative) current in the external circuit passes from the stannous chloride solution to the ferric chloride solution \(^*\). After a time, stannic ions can be detected in \( A \) and ferrous ions in \( B \).

In the preceding experiment the flow of current is due to the e.m.f. produced by the chemical change in the redox reaction. It can also be shown that an electric current, say from a storage battery, will give rise to oxidation–reduction reactions. Thus, if in Fig. 1, 42, 1 beaker \( A \) contains ferrous ammonium sulphate acidified with dilute sulphuric acid, and beaker \( B \) ferric chloride likewise acidified with dilute sulphuric acid, the salt bridge dilute sulphuric acid, and the millivoltmeter \( V \) replaced by a 6-volt battery, then after some time ferric ions can be detected in \( A \) and ferrous ions in \( B \).

It is a well-known fact that oxidants and reductants vary considerably in strength. Information of a quantitative character as to the relative strengths (compare relative strengths of weak acids and bases as expressed by their dissociation constants in Table II) would be of considerable practical value. A method which suggests itself at once is the measurement of the e.m.f. of redox reactions under standard conditions. This is indeed the method which is employed, but before this can be understood by the student, it will be necessary to consider the subject of electrode potentials.

1, 43. Electrode potentials.—When a metal is immersed in a solution containing its own ions, say, zinc in zinc sulphate solution, a potential difference \( E \) is established between the metal and the solution. The potential difference \( E \) for an electrode reaction, \( M = M^{n+} + ne^- \), is given by the expression:

\[
E = \frac{RT}{nF} \log a_+ + E_0
\]

(1)

where \( F \) is the Faraday constant, \( T \) is the absolute temperature, \( F \) the Faraday, \( n \) the valency of the ions, \( a_+ \) the activity of the ions in the solution, and \( E_0 \) is a constant dependent upon the metal. Equation (1) can be simplified by introducing the known values of \( R \) and \( F \), and converting the natural logarithms to base 10 by multiplying by 2.3026; it then becomes:

\[
E = \frac{0.0001982T}{n} \log a_+ + E_0
\]

(2)

For a temperature of 25° C. \( (T = 298°) \):

\[
E = \frac{0.0591}{n} \log a_+ + E_0
\]

(3)

* The arrows in Fig. 1, 42, 1 indicate the direction of the flow of electrons (negative current). The conventional (positive) current flows in the opposite direction outside the cell, \( \rightarrow \), from the positive pole (electrode dipping in FeCl₃ solution) to the negative pole (electrode dipping in SnCl₂ solution).

† For a derivation of this equation, see any good text-book of physical chemistry.
The Theoretical Basis of Quantitative Analysis

For most purposes in quantitative analysis, it is sufficiently accurate to substitute $a_+$ by $c_+^*$, the ion concentration (in g.-ions per litre):

$$
E = \frac{0.0591}{n} \log c_+^* + E_0 
$$

The latter is often known as the Nernst equation.

For a non-metal, which yields negative ions, equation (3) becomes:

$$
E = E_0 - \frac{0.0591}{n} \log a_- 
$$

where $a_-$ is the activity of the negative ions. Here also, we may introduce the approximation of substituting $c_-$ for $a_-$. If in equation (4), $c_+^*$ is put equal to unity, $E$ is equal to $E_0$. $E_0$ is called the standard or normal potential of the metal.

In order to determine the potential difference between an electrode and a solution, it is necessary to have another electrode and a solution, the potential difference between which is known. The two electrodes can then be combined to form a voltaic cell, the e.m.f. of which can be directly measured. The e.m.f. of the cell is the arithmetical sum or difference of the electrode potentials (depending upon the sign of these two potentials); the value of the unknown potential can then be calculated. In practice, the standard electrode potential used for comparative purposes is the molar or normal hydrogen electrode (see also Section VI, 2). This consists of a piece of platinum foil, coated with platinum black by an electrolytic process, and immersed in a solution of hydrochloric acid, normal with respect to hydrogen ions (more correctly, in a solution of hydrochloric acid containing hydrogen ions of unit activity). Hydrogen gas at a pressure of one atmosphere is passed over the foil through the side tube $C$ (Fig. 1, 43, 1) and escapes through the small openings $B$ in the surrounding glass tube $A$; the foil is thus kept saturated with the gas. Connexion between the platinum foil sealed into the tube $D$ with an outer circuit is made with mercury in $D$. The platinum black has the remarkable property of adsorbing large quantities of hydrogen, and it permits the change from the gaseous to the ionic form and the reverse process to occur without hindrance; it therefore behaves as though it were composed entirely of hydrogen, that is, as a hydrogen electrode. Under fixed conditions, viz., of atmospheric pressure and normal concentration of hydrogen ions in the solution in contact with the electrode, the hydrogen electrode possesses a definite potential at all temperatures. By connecting the normal hydrogen electrode with a metal electrode (a metal in contact with a molar solution of its ions) by means of a salt (say, potassium chloride) bridge, the normal, molar, or standard electrode potential may be determined. Other electrodes, particularly the calomel electrode...
Quantitative Inorganic Analysis

and the silver–silver chloride electrode, the potentials of which have been determined by direct reference to the normal hydrogen electrode, are often used in practice owing to convenience in manipulation. These are discussed in Section VI, 2.

We may therefore define the standard or normal electrode potential of an element as the e.m.f. produced when a half-cell consisting of the element immersed in a molar solution of its ions (more correctly, in a solution of its ions possessing unit activity) is coupled with a molar hydrogen electrode, the potential of which is assumed equal to zero. The more important standard electrode potentials at 25° C. are collected in Table XV; the sign of the potential here adopted is that of the charge on the electrode.

<table>
<thead>
<tr>
<th>Element</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/Li⁺</td>
<td>-2.959</td>
</tr>
<tr>
<td>K/K⁺</td>
<td>-2.924</td>
</tr>
<tr>
<td>Ca/Ca⁺</td>
<td>-2.76</td>
</tr>
<tr>
<td>Na/Na⁺</td>
<td>-2.715</td>
</tr>
<tr>
<td>Mg/Mg⁺</td>
<td>-1.55</td>
</tr>
<tr>
<td>Al/Al⁺⁺</td>
<td>-1.33</td>
</tr>
<tr>
<td>Mn/Mn⁺⁺</td>
<td>-1.1</td>
</tr>
<tr>
<td>Zn/Zn⁺⁺</td>
<td>-0.762</td>
</tr>
<tr>
<td>Cr/Cr⁺⁺</td>
<td>-0.557</td>
</tr>
<tr>
<td>Fe/Fe⁺⁺</td>
<td>-0.441</td>
</tr>
<tr>
<td>Cd/Cd⁺⁺</td>
<td>-0.401</td>
</tr>
<tr>
<td>Co/Co⁺⁺</td>
<td>-0.28</td>
</tr>
<tr>
<td>Ni/Ni⁺⁺</td>
<td>-0.23</td>
</tr>
<tr>
<td>Sn/Sn⁺⁺</td>
<td>-0.136</td>
</tr>
<tr>
<td>Pb/Pb⁺⁺</td>
<td>-0.122</td>
</tr>
<tr>
<td>Pt(H₂)/H⁺</td>
<td>0.000</td>
</tr>
<tr>
<td>Bi/Bi⁺⁺</td>
<td>+0.226</td>
</tr>
<tr>
<td>Cu/Cu⁺⁺</td>
<td>+0.344</td>
</tr>
<tr>
<td>Hg/Hg⁺⁺</td>
<td>+0.799</td>
</tr>
<tr>
<td>Ag/Ag⁺⁺</td>
<td>+0.799</td>
</tr>
<tr>
<td>Pd/Pd⁺⁺</td>
<td>+0.82</td>
</tr>
<tr>
<td>Au/Au⁺⁺</td>
<td>+1.36</td>
</tr>
</tbody>
</table>

When metals are arranged in the order of their standard electrode potentials, the so-called electrochemical series of the metals is obtained. The greater the negative value of the potential, the greater is the tendency of the metal to pass into the ionic state. A metal with a more negative potential will displace any other metal below it in the series from solutions of its salts. Thus magnesium, aluminium, zinc, or iron will displace copper from solutions of its salts; lead will displace copper, mercury, or silver; copper will displace silver.

The standard electrode potential is a quantitative measure of the readiness of the element to lose electrons. It is therefore a measure of the strength of the element as a reducing agent; the more negative the potential of the element, the more powerful is its action as a reductant.

1, 44. Concentration cells.—The electrode potential varies with the concentration of the ions in the solution. Hence by bringing two electrodes of the same metal, but immersed in solutions containing different concentrations of the ions, into contact, a cell may be formed. Such a cell is termed a concentration cell. The e.m.f. of the cell will be the algebraic difference of the two potentials, if a salt bridge be inserted to eliminate the liquid–liquid junction potential. It may be calculated as follows. At 25° C.:

\[ E = \frac{0.0591}{n} \log c_1 + E_0 - \left( \frac{0.0591}{n} \log c_2 + E_0 \right) \]

\[ = \frac{0.0591}{n} \log \frac{c_1}{c_2}, \text{ where } c_1 > c_2 \]
As an example we may consider the cell:

\[
\begin{align*}
\text{Ag} & | \text{AgNO}_3 \text{aq.} \quad [\text{Ag}^+] = 0.00475M \quad || \quad \text{AgNO}_3 \text{aq.} \quad [\text{Ag}^+] = 0.043M \quad \text{Ag} \\
E_2 & \\
E_1 &
\end{align*}
\]

Assuming that there is no potential difference at the liquid junction:

\[
E = E_1 - E_2 = -\frac{0.0591}{1} \log \frac{0.043}{0.00475} = 0.056 \text{ volt}
\]

I. 45. Calculation of the e.m.f. of a voltaic cell.—An interesting application of electrode potentials is to the calculation of the e.m.f. of a voltaic cell. One of the simplest of galvanic cells is the Daniell cell. It consists of a rod of zinc dipping into zinc sulphate solution and a strip of copper in copper sulphate solution; the two solutions are generally separated by placing one inside a porous pot and the other in the surrounding vessel. The cell may be represented as:

\[
\begin{align*}
\text{Zn} & | \text{ZnSO}_4 \text{aq.} \ || \text{CuSO}_4 \text{aq.} \ | \text{Cu}
\end{align*}
\]

At the zinc electrode, zinc ions pass into solution, leaving an equivalent negative charge on the metal. Copper ions are deposited at the copper electrode, rendering it positively charged. By completing the external circuit, the current (electrons) passes from the zinc to the copper. The chemical reactions in the cell are as follows:

(a) zinc electrode, \( \text{Zn} \rightarrow \text{Zn}^+ + 2\epsilon \);
(b) copper electrode, \( \text{Cu}^+ + 2\epsilon \rightarrow \text{Cu} \)

The net chemical reaction is:

\[
\text{Zn} + \text{Cu}^+ = \text{Zn}^+ + \text{Cu}
\]

The potential difference at each electrode may be calculated by the formula given above, and the e.m.f. of the cell is the algebraic difference of the two potentials, the correct sign being applied to each.

As an example we may calculate the e.m.f. of the Daniell cell with molar concentrations of zinc ions and cupric ions:

\[
E = E_{\text{Cu}^{2+}} - E_{\text{Zn}^2+} = 0.34 - (-0.76) = 1.10 \text{ volts}
\]

The small potential difference produced at the contact between the two solutions (the so-called liquid-junction potential) is neglected.

I, 46. Oxidation-reduction cells.—Reduction is accompanied by a gain of electrons, and oxidation by a loss of electrons. In a system containing both an oxidising agent and its reduction product, there will be an equilibrium between them and electrons. If an inert electrode, such as platinum, is placed in a redox system, for example, one containing ferric and ferrous ions, it will assume a definite potential indicative of the position of equilibrium. If the oxidation tendency predominates, the system will take electrons from the platinum, leaving the latter positively charged; if, however, the system has reducing properties, electrons will be given up to the metal, which will then acquire a negative charge. The magnitude of the potential will thus be a measure of the oxidising or reducing properties of the system.
To obtain comparative values of the "strengths" of oxidising agents, it is necessary, as in the case of the electrode potentials of the metals, to measure under standard experimental conditions the potential difference between the platinum and the solution relative to a standard of reference. The primary standard is the molar or normal hydrogen electrode (Section I, 43), and its potential is taken as zero. The standard experimental conditions for the redox system are those in which the ratio of the concentration of the oxidant to that of the reductant is unity. Thus for a ferrous-ferric chloride electrode, the redox cell would be:

\[
\text{Pt} \mid \text{Fe}^{++/3+} \mid \text{H}^+ \mid \text{H}_2\text{(Pt)}
\]

The potential measured in this way is called the standard oxidation potential. A selection of these is given in Table XVI. The sign of the potential is that of the electrode.

**Table XVI.—Standard Oxidation Potentials at 25° C.**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrode Reaction</th>
<th>(E^*) (volts)</th>
</tr>
</thead>
</table>
| \(\text{MnO}_7^-, \text{MnO}_4/\text{Pt}\) | \(
\begin{align*}
\text{MnO}_7^- + 4\text{H}^+ + 3\text{e}^- & \rightarrow \text{MnO}_4^- + 2\text{H}_2\text{O} \\
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- & \rightarrow \text{Mn}^{++} + 4\text{H}_2\text{O}
\end{align*}
\) | +1.59 |
| \(\text{MnO}_5^-, \text{Mn}^{++}/\text{Pt}\) | \(
\begin{align*}
\text{MnO}_5^- + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{Mn}^{++} + 3\text{H}_2\text{O}
\end{align*}
\) | +1.52 |
| \(\text{Br}_2, \text{Br}^-/\text{Pt}\) | \(
\begin{align*}
\text{Br}_2 + 2\text{e}^- & \rightarrow 2\text{Br}^-
\end{align*}
\) | +1.45 |
| \(\text{Ce}^{+++}, \text{Ce}^{+++/4+}/\text{Pt}\) | \(
\begin{align*}
\text{Ce}^{+++} + \text{e}^- & \rightarrow \text{Ce}^{+++/4+}
\end{align*}
\) | +1.36 |
| \(\text{Cr}_2\text{O}_7^-/, \text{Cr}^{+++/4+}/\text{Pt}\) | \(
\begin{align*}
\text{Cr}_2\text{O}_7^- + 14\text{H}^+ + 6\text{e}^- & \rightarrow 2\text{Cr}^{+++/4+} + 7\text{H}_2\text{O}
\end{align*}
\) | +1.30 |
| \(\text{Cl}_2, \text{Cl}^-/\text{Pt}\) | \(
\begin{align*}
\text{Cl}_2 + 2\text{e}^- & \rightarrow 2\text{Cl}^-
\end{align*}
\) | +1.07 |
| \(\text{I}_2, \text{I}^-/\text{Pt}\) | \(
\begin{align*}
\text{I}_2 + 2\text{e}^- & \rightarrow 2\text{I}^-
\end{align*}
\) | +0.77 |
| \(\text{Fe}^{+++}, \text{Fe}^{+++/2+}/\text{Pt}\) | \(
\begin{align*}
\text{Fe}^{+++} + \text{e}^- & \rightarrow \text{Fe}^{+++/2+}
\end{align*}
\) | +0.56 |
| \(\text{H}_2\text{AsO}_4, \text{H}_2\text{AsO}_3/\text{Pt}\) | \(
\begin{align*}
\text{H}_2\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HAsO}_3 + 2\text{H}_2\text{O}
\end{align*}
\) | +0.53 |
| \(\text{Fe(CN)}_6^{3-}, \text{Fe(CN)}_6^{4-}/\text{Pt}\) | \(
\begin{align*}
\text{Fe(CN)}_6^{3-} + \text{e}^- & \rightarrow \text{Fe(CN)}_6^{4-}
\end{align*}
\) | +0.30 |
| \(\text{Cu}^{+++/2+}, \text{Cu}^{+/+/3+}/\text{Pt}\) | \(
\begin{align*}
\text{Cu}^{+++/2+} + 2\text{e}^- & \rightarrow \text{Cu}^{+/+/3+}
\end{align*}
\) | +0.35 |
| \(\text{Sn}^{+++}, \text{Sn}^{+++/2+}/\text{Pt}\) | \(
\begin{align*}
\text{Sn}^{+++} + 2\text{e}^- & \rightarrow \text{Sn}^{+++/2+}
\end{align*}
\) | +0.15 |
| \(\text{H}^+, \text{H}_2\text{Pt}\) | \(
\begin{align*}
\text{H}^+ + 2\text{e}^- & \rightarrow \text{H}_2
\end{align*}
\) | 0.00 |
| \(\text{Cd}^{+++/2+}, \text{Cd}^{+/+/3+}/\text{Pt}\) | \(
\begin{align*}
\text{Cd}^{+++/2+} + 2\text{e}^- & \rightarrow \text{Cd}^{+/+/3+}
\end{align*}
\) | +0.40 |
| \(\text{Cr}^{+++}, \text{Cr}^{+++/2+}/\text{Pt}\) | \(
\begin{align*}
\text{Cr}^{+++} + \text{e}^- & \rightarrow \text{Cr}^{+++/2+}
\end{align*}
\) | +0.41 |
| \(\text{S, S}^{--}/\text{Pt}\) | \(
\begin{align*}
\text{S} + 2\text{e}^- & \rightarrow \text{S}^{--}
\end{align*}
\) | +0.51 |
| \(\text{Zn}^{+++/2+}, \text{Zn}^{+/+/3+}/\text{Pt}\) | \(
\begin{align*}
\text{Zn}^{+++/2+} + 2\text{e}^- & \rightarrow \text{Zn}
\end{align*}
\) | +0.76 |

* The symbol Pt throughout this table must be interpreted as any inert unattacatable electrode. The potential refers to a solution 1M in H⁺.

The oxidation potentials enable us to predict which ions will oxidise or reduce other ions at molar concentrations. The most powerful oxidising agents are those at the upper end of the table, and the most powerful reducing agents at the lower end. Thus permanganate ions can oxidise \(\text{Cl}^-, \text{Br}^-, \text{I}^-, \text{Fe}^{+++}, \text{Fe(CN)}_6^{3-}\); ferric ions can oxidise \(\text{H}_2\text{AsO}_3\) and \(\text{I}^-\), but not \(\text{Cr}_2\text{O}_7^-\) or \(\text{Cl}^-\) ions. It must be emphasised that oxidation potentials do not give any information as to the speed of the reaction; in some cases, as in the oxidation of arsenious acid by ceric ions, the presence of a catalyst is necessary in order that the reaction may proceed with reasonable velocity.
I, 47. Calculation of the oxidation potential.—A reversible oxidation-reduction reaction may be written in the form (oxidant = substance in oxidised state, reductant = substance in reduced state):

\[
\text{Reductant} \rightleftharpoons \text{Oxidant} + n\epsilon
\]

The electrode potential which is established when an inert or unattackable electrode is immersed in a solution containing both oxidant and reductant is given by the expression:

\[
E_T = E^0 + \frac{RT}{nF} \log \frac{a_{Ox}}{a_{Red}} \quad \ldots \ldots \quad (1)
\]

where \(E_T\) is the observed potential of the redox electrode at \(T^0\) relative to the standard or normal hydrogen electrode taken as zero, \(E^0\) is the standard oxidising potential, \(n\) the number of electrons gained by the oxidant in being converted into the reductant, and \(a_{Ox}\) and \(a_{Red}\) are the activities of the oxidant and reductant respectively.

Since activities are often difficult to determine directly, they may be replaced by concentrations; the error thereby introduced is usually of no great importance. The equation therefore becomes:

\[
E_T = E^0 + \frac{RT}{nF} \log \frac{c_{Ox}}{c_{Red}} \quad \ldots \ldots \quad (1')
\]

Substituting the known values of \(R\) and \(F\), and changing from natural to common logarithms (by multiplying by 2.3026), we have for a temperature of 25°C (\(T' = 298^\circ\)):

\[
E_{298} = E^0 + \frac{0.0591}{n} \log \frac{[Ox]}{[Red]} \quad \ldots \ldots \quad (1'')
\]

If the concentrations (or, more accurately, the activities) of the oxidant and reductant are equal, \(E_{298} = E^0\), i.e., the standard oxidation potential. It follows from this expression that, for example, a ten-fold change in the ratio of the concentrations of the oxidant to the reductant will produce a change in the potential of the system of 0.0591/n volts.

I, 48. Equilibrium constants of oxidation-reduction reactions.—The general equation for an oxidation-reduction electrode may be written:

\[
pA + qB + rC \ldots \ldots + N\epsilon \rightleftharpoons sX + tY + uZ + \ldots \ldots
\]

The potential is given by:

\[
E = E^0 + \frac{RT}{nF} \log \frac{a_x^s \cdot a_y^t \cdot a_z^u \ldots \ldots}{a_A^p \cdot a_B^q \cdot a_C^r \ldots \ldots}
\]

where \(a\) refers to activities, and \(n\) to the number of electrons involved in the oxidation-reduction reaction. This expression reduces to the following for a temperature of 25°C. (Concentrations are substituted for activities in order to permit of its facile application in practice):

\[
E = E^0 + \frac{0.0591}{n} \log \frac{c_x^s \cdot c_y^t \cdot c_z^u \ldots \ldots}{c_A^p \cdot c_B^q \cdot c_C^r \ldots \ldots}
\]

It is, of course, possible to calculate the influence of the change of
concentration of certain constituents of the system by the use of the latter equation. Consider, for example, the permanganate reaction:

$$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{++} + 4\text{H}_2\text{O}$$

$$E = E^\circ + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{++}]}$$

(at 25°C C.)

The concentration (or activity) of the water is taken as constant, since it is assumed that the reaction takes place in dilute solution, and the concentration of the water does not change appreciably as the result of the reaction. The equation may be written in the form:

$$E = E^\circ + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{++}]} + \frac{0.0591}{5} \log [\text{H}^+]$$

This enables us to calculate the effect of change in the ratio $[\text{MnO}_4^-]/[\text{Mn}^{++}]$ at constant hydrogen-ion concentration, other factors being maintained constant. In this particular case difficulties are experienced in the latter calculation owing to the fact that the reduction products of the permanganate ion vary at different hydrogen-ion concentrations. In other cases no such difficulties arise, and the calculation may be employed with confidence. Thus in the reaction:

$$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$$

$$E = E^\circ + \frac{0.0591}{2} \log \frac{[\text{H}_3\text{AsO}_4]}{[\text{H}_3\text{AsO}_3]}$$

(at 25°C C.) or

$$E = E^\circ + \frac{0.0591}{2} \log \frac{[\text{H}_3\text{AsO}_4]}{[\text{H}_3\text{AsO}_3]} + \frac{0.0591}{2} \log [\text{H}^+]^2$$

We are now in a position to calculate the equilibrium constants of oxidation-reduction reactions, and thus to determine whether such reactions can find application in quantitative analysis. Let us consider first the simple reaction:

$$\text{Cl}_2 + 2\text{Fe}^{++} \rightleftharpoons 2\text{Cl}^- + 2\text{Fe}^{+++}$$

The equilibrium constant is given by:

$$\frac{[\text{Cl}^-]^2 \times [\text{Fe}^{+++}]^2}{[\text{Cl}_2] \times [\text{Fe}^{++}]} = K$$

The reaction may be regarded as taking place in a voltaic cell, the two half-cells being a $\text{Cl}_2,2\text{Cl}^-$ electrode and a $\text{Fe}^{+++},\text{Fe}^{++}$ electrode. The reaction is allowed to proceed to equilibrium; the total voltage or e.m.f. of the cell will then be zero, i.e., the potentials of the two electrodes will be equal:

$$E^\circ_{\text{Cl}_2,2\text{Cl}^-} + \frac{0.059}{2} \log \frac{[\text{Cl}_2]}{[\text{Cl}^-]^2} = E^\circ_{2\text{Fe}^{++},\text{Fe}^{+++}} + \frac{0.059}{1} \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}$$

Now $E^\circ_{\text{Cl}_2,2\text{Cl}^-} = 1.36$ volts and $E^\circ_{2\text{Fe}^{++},\text{Fe}^{+++}} = 0.75$ volts, hence

$$\log \frac{[\text{Fe}^{+++}]^2}{[\text{Fe}^{++}]} = 0.61 \times 20.67 = 0.02965 = \log K$$

or

$$K = 4.7 \times 10^{20}$$

* More accurately, activities should be employed. The square brackets denote molecular concentrations.
The large value of the equilibrium constant signifies that the reaction will proceed from left to right almost to completion, i.e., a ferrous salt is almost completely oxidised by chlorine.

Consider now the more complex reaction:

\[ \text{MnO}_4^- + 5\text{Fe}^{++} + 8\text{H}^+ \rightleftharpoons \text{Mn}^{++} + 5\text{Fe}^{+++} + 4\text{H}_2\text{O} \]

The equilibrium constant \( K \) is given by:

\[ K = \frac{[\text{Mn}^{++}] [\text{Fe}^{+++}]^5}{[\text{MnO}_4^-] [\text{Fe}^{++}]^5} \]

The term \( 4\text{H}_2\text{O} \) is omitted, since the reaction is carried out in dilute solution, and the water concentration may be assumed constant. The hydrogen-ion concentration is taken as molar. The complete reaction may be divided into two half-cell reactions corresponding to the partial equations:

\[ \text{MnO}_4^- + 8\text{H}^+ + 5\epsilon \rightleftharpoons \text{Mn}^{++} + 4\text{H}_2\text{O} \quad \ldots \quad (1) \]

\[ \text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++} + \epsilon \quad \ldots \quad (2) \]

For (1) as an oxidation-reduction electrode, we have:

\[ E = E^0 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{++}]} \times \frac{[\text{H}^+]^8}{[\text{H}_2\text{O}]} \]

\[ = 1.52 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{++}]} \times \frac{[\text{H}^+]^8}{[\text{H}_2\text{O}]} \]

The partial equation (2) may be multiplied by 5 in order to balance (1) electrically:

\[ 5\text{Fe}^{++} \rightleftharpoons 5\text{Fe}^{+++} + 5\epsilon \quad \ldots \quad (2') \]

For (2') as an oxidation-reduction electrode:

\[ E = E^0 + \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5} \]

\[ = 0.77 + \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5} \]

Combining the two electrodes into a cell, the e.m.f. will be zero when equilibrium is attained, i.e.,

\[ 1.52 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{++}]} \times \frac{[\text{H}^+]^8}{[\text{H}_2\text{O}]} = 0.77 + \frac{0.059}{5} \log \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5} \]

or

\[ \log \frac{[\text{Mn}^{++}]}{[\text{MnO}_4^-]} \times \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5} \times \frac{[\text{H}^+]^8}{[\text{H}_2\text{O}]} = \frac{5(1.52 - 0.77)}{0.059} = 63.5 \]

\[ K = \frac{[\text{Mn}^{++}]}{[\text{MnO}_4^-]} \times \frac{[\text{Fe}^{+++}]^5}{[\text{Fe}^{++}]^5} \times \frac{[\text{H}^+]^8}{[\text{H}_2\text{O}]} = 3 \times 10^{63} \]

This result clearly indicates that the reaction proceeds virtually to completion. It is a simple matter to calculate the residual ferrous-ion concentration in any particular case. Thus suppose we titrate 10 ml. of 0.1\( N \)-potassium permanganate with an approximately 0.1\( N \) solution of ferrous ions in the presence of molar concentration of hydrogen ions. Let the volume of the solution at the equivalence point be 100 ml. Then \([\text{Fe}^{+++}] = 0.01N \), since it is known that the reaction is practically complete, \([\text{Mn}^{++}] = \frac{1}{5} \times [\text{Fe}^{+++}] = 0.002N \), and \([\text{Fe}^{++}] = x \). Let the
excess of permanganate solution at the end point be one drop or 0.05 ml.; its concentration will be $0.05 \times 0.1/100 = 5 \times 10^{-5}N = [\text{MnO}_4^-]$. Substituting these values in the equation:

$$K = \frac{(2 \times 10^{-3}) \times (1 \times 10^{-2})^5}{(5 \times 10^{-5}) \times x^5 \times 1^5} = 3 \times 10^{63}$$

or

$$x = [\text{Fe}^{3+}] = 5 \times 10^{-15}N$$

For the general oxidation-reduction reaction:

$$a \text{Ox}_I + b \text{Red}_{II} \rightleftharpoons b \text{Ox}_{II} + a \text{Red}_I \quad \ldots \quad (1)$$

$$K = \frac{[\text{Red}_I]^a \times [\text{Ox}_{II}]^b}{[\text{Red}_{II}]^b \times [\text{Ox}_I]^a}$$

It can readily be shown that the concentrations at the stoichiometric point, when equivalent quantities of the two substances $\text{Ox}_I$ and $\text{Red}_{II}$ are allowed to react, are given by:

$$\frac{[\text{Red}_I]}{[\text{Ox}_I]} = \frac{[\text{Ox}_{II}]}{[\text{Red}_{II}]} = \frac{a+b}{a+b} \sqrt{K} \quad \ldots \quad (2)$$

This expression enables us to calculate the exact concentration at the equivalence point in any redox reaction of the type (1), and therefore the feasibility of a titration for quantitative analysis. Consider again the interaction between, say, 0.1N solutions of potassium permanganate and a ferrous salt in the presence of molar sulphuric acid. The equilibrium constant of the reaction is $3 \times 10^{63}$. At the equivalence point:

$$\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = \frac{5+1}{5} \sqrt{3 \times 10^{63}} = \frac{6}{5} \times 10^{63} = 4 \times 10^{60}$$

Since the ferric-ion concentration will then be ca. 0.05N, it is evident that for all practical purposes the reaction is a quantitative one.

It is clear from what has already been stated that standard oxidation potentials may be employed to determine whether redox reactions are sufficiently complete for their possible use in quantitative analysis. It must be emphasised, however, that these calculations provide no information as to the speed of the reaction, upon which the application of that reaction in practice will ultimately depend. This question must form the basis of a separate experimental study, which may include the investigation of the influence of temperature, variations of $pH$ and of the concentrations of the reactants, and the influence of catalysts. Thus, theoretically, potassium permanganate should quantitatively oxidise oxalic acid in aqueous solution. It is found, however, that the reaction is extremely slow at the ordinary temperature, but is more rapid at about 80° C., and also increases in velocity when a little manganous ion has been formed, the latter apparently acting as a catalyst.

It is of interest to consider the calculation of the equilibrium constant of the general redox reaction (1), viz.:

$$a \text{Ox}_I + b \text{Red}_{II} \rightleftharpoons b \text{Ox}_{II} + a \text{Red}_I$$

The complete reaction may be regarded as composed of two oxidation-reduction electrodes. $a \text{Ox}_I$, $a \text{Red}_I$ and $b \text{Ox}_{II}$, $b \text{Red}_{II}$, combined to-
The Theoretical Basis of Quantitative Analysis

gather into a cell; at equilibrium, the potentials of both electrodes are the same:

\[ E_1 = E_1^o + \frac{0.0591}{n} \log \frac{[\text{OxI}]}{[\text{RedI}]} \]
\[ E_2 = E_2^o + \frac{0.0591}{n} \log \frac{[\text{OxII}]}{[\text{RedII}]} \]

At equilibrium, \( E_1 = E_2 \), hence:

\[ E_1^o + \frac{0.0591}{n} \log \frac{[\text{OxI}]}{[\text{RedI}]} = E_2^o + \frac{0.0591}{n} \log \frac{[\text{OxII}]}{[\text{RedII}]} \]

or

\[ \log \frac{[\text{OxI}]}{[\text{RedI}]} \times \frac{[\text{RedII}]}{[\text{OxII}]} = \log K = \frac{n}{0.0591} (E_1^o - E_2^o) \quad (3) \]

This equation may be employed to compute the equilibrium constant of any redox reaction, provided the two standard potentials \( E_1^o \) and \( E_2^o \) are known; from the value of \( K \) thus obtained, the feasibility of the reaction in analysis may be ascertained.

I. 49. Change of the electrode potential during the titration of an oxidant and a reductant. Oxidation-reduction curve.—In Sections I, 33–36 we calculated the change in pH during the titration of an acid and a base, and we utilised the neutralisation curve thus obtained in order (a) to specify the most suitable indicator for use in the process, and (b) to compute the titration error in the quantitative neutralisation. We shall now attempt to carry out parallel calculations for oxidation-reduction processes. Let us study first a simple case which involves only the valency change of ions, and is theoretically independent of the hydrogen-ion concentration. A suitable example, for purposes of illustration, is the titration of 100 ml. of 0.1N-ferrous iron with 0.1N-ceric cerium:

\[ \text{Ce}^{+++} + \text{Fe}^{++} \rightleftharpoons \text{Ce}^{+++} + \text{Fe}^{++} \]

The quantity corresponding to pH is the ratio \([\text{Ox}]/[\text{Red}]\). We are concerned here with two systems, the ferrous-ferric ion electrode (1), and the cerous-ceric ion electrode (2).

For (1) at 25° C.:

\[ E_1 = E_1^o + \frac{0.0591}{1} \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} = +0.75 + 0.0591 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} \]

For (2), at 25° C.:

\[ E_2 = E_2^o + \frac{0.0591}{1} \log \frac{[\text{Ce}^{+++}]}{[\text{Ce}^{+++}]} = +1.45 + 0.0591 \log \frac{[\text{Ce}^{+++}]}{[\text{Ce}^{+++}]} \]

The equilibrium constant of the reaction is given by (Section I, 48):

\[ \log K = \frac{[\text{Ce}^{+++}]}{[\text{Ce}^{+++}]} \times \frac{[\text{Fe}^{++}]}{[\text{Fe}^{++}]} \]

\[ = \frac{1}{0.0591} (1.45 - 0.75) \]

\[ = 11.84 \]

or

\[ K = 7 \times 10^{11} \]

The reaction is therefore virtually complete.
During the addition of the ceric solution up to the equivalence point, its only effect will be to oxidise the ferrous iron (since \( K \) is large) and consequently change the ratio \([\text{Fe}^{3+}]/[\text{Fe}^{2+}]\). When 10 ml. of the oxidising agent have been added, \([\text{Fe}^{3+}]/[\text{Fe}^{2+}] = 10/90 \) (approx.), and \( E_1 = 0.75 + 0.0591 \log 10/90 = 0.75 + 0.056 = 0.81 \) volt:

- with 50 ml. of the oxidising agent, \( E_1 = E_1^o = 0.75 \) volt
- with 90 ml., \( E_1 = 0.75 + 0.0591 \log 90/10 = 0.81 \) volt
- with 99 ml., \( E_1 = 0.75 + 0.0591 \log 99/1 = 0.87 \) volt
- with 99.9 ml., \( E_1 = 0.75 + 0.0591 \log 99.9/0.1 = 0.93 \) volt

These results are plotted graphically in Fig. 1, 49, 1.

At the equivalence point (100·0 ml.) \([\text{Fe}^{3+}]/[\text{Ce}^{3+}] = [\text{Ce}^{4+}]/[\text{Fe}^{2+}]\), and the electrode potential is given by:

\[
\frac{E_1^o + E_2^o}{2} = \frac{0.75 + 1.45}{2} = 1.10 \text{ volts}
\]

The subsequent addition of the ceric solution will merely increase the ratio \([\text{Ce}^{4+}]/[\text{Ce}^{3+}]\). Thus:

- with 100·1 ml., \( E_1 = 1.45 + 0.0591 \log 1.1/100 = 1.27 \) volts
- with 101 ml., \( E_1 = 1.45 + 0.0591 \log 1/100 = 1.33 \) volts
- with 110 ml., \( E_1 = 1.45 + 0.0591 \log 10/100 = 1.39 \) volts
- with 190 ml., \( E_1 = 1.45 + 0.0591 \log 90/100 = 1.45 \) volts

These results are plotted graphically in Fig. 1, 49, 1.

* For a deduction of this expression and a discussion of the approximations involved, see Kolthoff and Furman, *Potentiometric Titrations*, 1926, p. 100. It can similarly be shown (loc. cit. p. 107) that for the reaction:

\[
a \text{Ox}_1 + b \text{ Red}_2 \rightleftharpoons b \text{ Ox}_2 + a \text{ Red}_1
\]

the potential at the equivalence point is given by:

\[
E = \frac{bE_1^o + aE_2^o}{a + b}
\]

where \( E_1^o \) refers to \( \text{Ox}_1, \text{Red}_1 \), and \( E_2^o \) to \( \text{Ox}_2, \text{Red}_2 \).
It is of interest to calculate the ferrous-ion concentration in the neighbourhood of the equivalence point. When 99.9 ml. of the ceric solution have been added, \([\text{Fe}^{++}] = 0.1 \times 0.1/199.9 = 5 \times 10^{-5}\), or \(p\text{Fe}^{++} = 4.3\). The concentration at the equivalence point is given by (Section I, 48):

\[
\frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]} = K = 7 \times 10^{11} = 8.5 \times 10^5
\]

Now \([\text{Fe}^{+++}] = 0.05 N\), hence \([\text{Fe}^{++}] = 5 \times 10^{-2}/8.5 \times 10^5 = 6 \times 10^{-8} N\), or \(p\text{Fe}^{++} = 7.2\). Upon the addition of 100.1 ml. of ceric solution, the oxidation potential (vide supra) is 1.27 volts. The \([\text{Fe}^{+++}]\) is practically unchanged at \(5 \times 10^{-8} N\), and we may calculate \([\text{Fe}^{++}]\) with sufficient accuracy for our purpose from the equations:

\[
E = E^\circ + 0.0591 \log \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}
\]

\[
1.27 = 0.75 + 0.0591 \log \frac{5 \times 10^{-2}}{[\text{Fe}^{++}]}
\]

or

\[
[\text{Fe}^{++}] = 1 = 10^{-10}
\]

\(p\text{Fe}^{++} = 10\)

Thus \(p\text{Fe}^{++}\) changes from 4.3 to 10 between 0.1 per cent before and 0.1 per cent after the stoichiometric point. These quantities are of importance in connexion with the use of indicators for the detection of the equivalence point.

It is evident that the abrupt change of the potential in the neighbourhood of the equivalence point is dependent upon the standard potentials of the two oxidation-reduction systems that are involved, and therefore upon the equilibrium constant of the reaction; it is independent of the concentrations unless these are extremely small. The change in oxidation potential for a number of typical oxidation-reduction systems is exhibited graphically in Fig. 1, 49, 2. For the \(\text{MnO}_4^-\), \(\text{Mn}^{++}\) system and others which are dependent upon the pH of the solution, the hydrogen-ion concentration is assumed to be molar; lower acidities give lower potentials. The value at 50 per cent oxidised form will, of course, correspond to the standard oxidation potential. As an indication of the application of the curves, we may take the titration of ferrous iron with potassium dichromate. The titration curve would follow that of the ferrous-ferric system until the end point was reached, then it would rise steeply and continue along the curve for the dichromate-chromic system; the potential at the equivalence point can be computed as already described.
I, 50. Indicators for the detection of the end point in oxidation-reduction titrations.—A. Internal oxidation-reduction indicators. We have already seen (Sections I, 32-34) that acid-base indicators are employed to mark the sudden change in pH during acid-base titrations. Similarly an oxidation-reduction indicator should mark the sudden change in the oxidation potential in the neighbourhood of the equivalence point in an oxidation-reduction titration. The ideal oxidation-reduction indicator will be one with an oxidation potential intermediate between that of the solution titrated and that of the titrant, and which exhibits a sharp, readily detectable colour change. The subject is still in its infancy, and thus far only a few such indicators have been discovered.

An oxidation-reduction indicator is a compound which has different colours in the oxidised and reduced forms:

\[ \text{In}_{\text{ox}} \leftrightarrow n \text{e} \rightarrow \text{In}_{\text{red}} \]

The oxidation and reduction of the indicator should be reversible. Many organic dyestuffs belong to this class; the leuco compounds obtained on reduction are usually colourless, and are converted by oxidation into the coloured dyes. If such an indicator is added to any redox system, for example, one containing ferric and ferrous ions, the following equilibrium will be present:

\[ \text{Fe}^{+++} + \text{In}_{\text{red}} \rightleftharpoons \text{Fe}^{++} + \text{In}_{\text{ox}} \]

If the quantity of indicator added is small, it will have little effect on the main ferric-ferrous system, and it will adjust itself so that its potential is the same as that of the solution in which it is placed. The colour of the indicator system will depend upon this potential. When the concentrations of \( \text{In}_{\text{ox}} \) and \( \text{In}_{\text{red}} \) are equal, the colour will be intermediate between those of the two extreme states, and the potential is equal to the standard potential of the indicator \( E^\circ_{\text{In}} \).

It can be shown that if the potential is about 0.05 volt greater than \( E^\circ_{\text{In}} \), the indicator will be about 90 per cent oxidised, and its colour will be indistinguishable to the eye from that of the oxidised form (compare Section I, 27); if the potential is \( (E^\circ_{\text{In}} - 0.05) \) volt, then about 90 per cent of the indicator will be in the reduced form and it will exhibit its almost completely reduced colour. Thus the colour change for a redox indicator will be over the potential range \( (E^\circ_{\text{In}} + 0.05) \) to \( (E^\circ_{\text{In}} - 0.05) \) volts. For a sharp colour change at the end point, \( E^\circ_{\text{In}} \) should differ by at least 0.15 volt from the other systems involved in the reaction.

One of the best oxidation-reduction indicators is the ortho-phenanthroline ferrous ion. The base ortho-phenanthroline combines readily in solution with ferrous salts in the molecular ratio 3 base : 1 ferrous ion forming the intensely red tri-ortho-phenanthroline ferrous ion; with strong oxidising agents the ferric complex ion is formed, which has a pale blue colour. The colour change is a very striking one:

\[ \text{[Fe(C}_{12}\text{H}_8\text{N}_2\text{O}_3]}^{+++} \rightleftharpoons \text{[Fe(C}_{12}\text{H}_8\text{N}_2\text{O}_3]}^{+++} + \epsilon \]

The oxidation potential is 1.14 volts. The indicator is of great value in the titration inter alia of ferrous salts and other substances with ceric sulphate solutions. It is prepared by dissolving ortho-phenanthroline hydrate (molecular weight = 198.1) in the calculated quan-
tity of 0·02M acid-free ferrous sulphate, and is therefore tri-ortho-
phenanthroline ferrous sulphate. One drop is usually sufficient in a
titration: this is equivalent to less than 0·01 ml. of 0·1N oxidising
agent, and hence the indicator blank is negligible. The only disadvan-
tage of this indicator is that it is somewhat expensive. It may be
replaced in many titrations by the less costly N-phenylanthranilic acid
(see Section III, 73), which has an oxidation potential of 1·08 volts.
Xylene cyanol FF \(E^\circ_{\text{in}} > 1·0 \text{ volt}\) may also be employed.

Mention should be made of one of the earliest internal indicators.
This is a 1 per cent solution of diphenylamine in concentrated sulphuric
acid, and was introduced by Knop (1924) for the titration of ferrous
salts with potassium dichromate solution. To obtain a satisfactory
end point (an intense blue-violet coloration), phosphoric acid must be
present; this forms a complex with the ferric ions, thereby reducing
the concentration of the latter, and consequently the actual potential
of the ferric-ferrous system is reduced well below the normal value of
0·75 volt. The action of diphenylamine (I) as an indicator depends upon
its oxidation first into colourless diphenylbenzidine (II), which is the
real indicator and is reversibly further oxidised to diphenylbenzidine-
violet (III). Under certain conditions there is formed as an inter-
mediate product a very slightly soluble green compound which is
usually considered to be a molecular compound of diphenylbenzidine
and diphenylbenzidine-violet.

\[
\begin{align*}
\text{NH} & \quad \text{NH} \\
\text{II} & \\
\text{NH} & \quad \text{NH} \\
\text{III} & + 2\text{H}^+ + 2\epsilon
\end{align*}
\]

A solution of diphenylbenzidine in concentrated sulphuric acid acts
similarly to diphenylamine. The oxidation potential of the system
II, III is 0·76 volt. It is therefore evident that a lowering of the
potential of the ferrous–ferric system is necessary, as already mentioned,
in order to obtain a sharp colour change. The disadvantage of diphenyl-
amine and of diphenylbenzidine is their slight solubility in water.
This has been overcome by the use of the soluble barium or sodium
diphenylamine sulphonate, which are employed in 0·2 per cent solution.
The oxidation potential \(E^\circ_{\text{in}}\) is slightly higher (0·83 volt), and the
oxidised form has a reddish-violet colour resembling that of potassium
permanganate, but the colour slowly disappears on standing; phos-
phoric acid must still be present in order to lower the oxidation potential
of the system. The addition of phosphoric acid may be avoided by the
use of ortho-phenanthroline ferrous ion, N-phenylanthranilic acid, or
xylene cyanol FF as indicators.

A list of selected oxidation–reduction indicators, together with their
colour changes and oxidation potentials in acid medium, is given in
Table XVII.
TABLE XVII.—SOME OXIDATION–REDUCTION INDICATORS

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Oxidised Form</th>
<th>Reduced Form</th>
<th>$E^2$ (at pH = 0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indigo monosulphonate</td>
<td>Blue</td>
<td>Colourless</td>
<td>0.26</td>
</tr>
<tr>
<td>Pheno-safranine</td>
<td>Red</td>
<td>Colourless</td>
<td>0.28</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Blue</td>
<td>Colourless</td>
<td>0.62</td>
</tr>
<tr>
<td>1-Naphthol-2-sodium sulphonate indophenol</td>
<td>Red</td>
<td>Colourless</td>
<td>0.54</td>
</tr>
<tr>
<td>2 : 6-Dibromophenol indo-phenol</td>
<td>Blue</td>
<td>Colourless</td>
<td>0.67</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>Violet</td>
<td>Colourless</td>
<td>0.76</td>
</tr>
<tr>
<td>Diphenylbenzidine</td>
<td>Violet</td>
<td>Colourless</td>
<td>0.76</td>
</tr>
<tr>
<td>Diphenylamine sulphonic acid</td>
<td>Red-violet</td>
<td>Colourless</td>
<td>0.85</td>
</tr>
<tr>
<td>Lissamine green (erio green)</td>
<td>Orange</td>
<td>Green</td>
<td>0.99</td>
</tr>
<tr>
<td>Ergotamine</td>
<td>Orange</td>
<td>Greenish-yellow</td>
<td>1.00</td>
</tr>
<tr>
<td>N-Phenylanthranilic acid</td>
<td>Purple-red</td>
<td>Colourless</td>
<td>1.08</td>
</tr>
<tr>
<td>o-Phenanthroline</td>
<td>Blue</td>
<td>Red</td>
<td>1.08</td>
</tr>
<tr>
<td>o-Phenanthroline ferrous sulphate</td>
<td>Blue</td>
<td>Red</td>
<td>1.14</td>
</tr>
<tr>
<td>Nitro-o-phenanthroline</td>
<td>Magenta</td>
<td>Red</td>
<td>1.25</td>
</tr>
<tr>
<td>Nitro-o-phenanthroline ferrous sulphate</td>
<td>Magenta</td>
<td>Red</td>
<td>1.25</td>
</tr>
</tbody>
</table>

At this stage reference may be made to potential mediators, i.e., substances which undergo reversible oxidation-reduction and reach equilibrium rapidly. If we have a mixture of two ions, say $M^{++}$ and $M^+$, which reaches equilibrium slowly with an inert electrode, and a very small quantity of a ceric salt is added, then the reaction:

$$M^+ + Ce^{+++} \rightarrow M^{++} + Ce^{+++}$$

takes place until the tendency of $M^+$ to be oxidised to $M^{++}$ is exactly balanced by the tendency of $Ce^{+++}$ to be oxidised to $Ce^{++++}$, that is, until the $M^{++}, M^+$ and $Ce^{+++}, Ce^{++++}$ potentials are equal. A platinum or other inert electrode rapidly attains equilibrium with the cerous and ceric ions, and will soon register a stable potential which is also due to the $M^{++} + e = M^+$ system. If the potential mediator is employed in small amount, then a negligible quantity of $M^+$ is converted into $M^{++}$ when equilibrium is reached, and the measured potential may be regarded as that of the original system. Potential mediators are, of course, useful in the measurement of the oxidation-reduction potentials of redox systems; in this connexion mention may be made of the use of potassium iodide ($= iodo-iode$ system) in the arsenate-arsenite system in acid solution and of ceric carbonate ($= ceric-cerous$ system) in the arsenate-arsenite system in alkaline solution. It is evident that redox indicators (e.g., ortho-phenanthroline ferrous ion) may act as potential mediators.

The reagent may serve as its own indicator. This is well illustrated by potassium permanganate. One drop (0.05 ml.) of excess of, say, 0.1 N-potassium permanganate will impart a visible pink coloration to several hundred ml. of solution, even in the presence of slightly coloured ions, such as ferric ions. The colour of ceric sulphate and of iodine
solutions have also been employed in the detection of end points, but the colour change is not so marked as for potassium permanganate; here, however, sensitive internal indicators (ortho-phenanthroline ferrous ion or N-phenylanthranilic acid and starch respectively) are available.

This method has the drawback that an excess of oxidising agent is always present at the end point. For work of the highest accuracy, the indicator blank may be determined and allowed for, or the error may be considerably reduced by performing the standardisation and determination under similar experimental conditions.

C. External indicators. The best-known example of an external indicator in a redox process is the spot-test method for the titration of ferrous iron with standard potassium dichromate solution. Near the equivalence point, drops of the solution are removed and brought into contact with dilute, freshly prepared potassium ferricyanide solution on a spot plate. The end point is reached when the drop first fails to give a blue coloration. Another example is provided by the titration of zinc ions with standard potassium ferrocyanide solution; here a solution of uranyl acetate or nitrate is the external indicator, and titration is continued until a drop of the solution just imparts a brown colour to the indicator. External indicators are gradually being superseded by the more satisfactory internal oxidation-reduction indicators: thus in the first example ortho-phenanthroline ferrous ion or N-phenylanthranilic acid is suitable, whilst for the second diphenylamine or diphenylbenzidine may be used.

D. Potentiometric methods. These are discussed briefly in the following Section; a more detailed treatment is given in Chapter VI. Potentiometric methods can frequently be applied where no satisfactory indicator is available.

I. 51. Potentiometric titration.—The various visual methods, dependent largely upon the use of indicators, for the detection of the end point in titrations have already been discussed. We shall now deal with a physico-chemical method which may be applied not only to those cases where suitable indicators are available, but also to those in which the visual-indicator method fails or is of limited accuracy, e.g., for coloured or for very dilute solutions; the procedure is termed potentiometric titration. This method may often be employed for the determination of two or more constituents in a single operation. Thus a mixture of iodide and chloride may be titrated with silver nitrate solution; the first point of inflexion is the equivalence point of the iodide reaction and the second inflexion point is that for the chloride reaction (compare Fig. 1, 39, 1).

The theory of potentiometric titration is very similar to that already given for ordinary titrations. It has been shown (Section I. 43) that the potential of a metal electrode in a solution of its own ions at $25^\circ$ C. is given by the expression:

$$E_{25} = E^\circ + \frac{0.0591}{n} \log c_i^+ . . . . . (1)$$

where $E^\circ$ is the standard potential of the metal, $n$ the valency of the ions, and $c_i^+$ is the ionic concentration (strictly, this should be the ionic activity). If we write $c_i^+$ in the exponential form, i.e.,

$$-\log [Me^{n+}] = pMe^{n+}$$
the equation becomes:

$$E_{25^\circ} = E^\circ - \frac{0.0591}{n} \log \frac{pMe^{n+}}{Me^{n+}}$$  \hspace{1cm} (1')

The expression for a hydrogen electrode at 25° C. is:

$$E_{25^\circ} = E_H^\circ - 0.0591 \times pH$$  \hspace{1cm} (2)

where $E_H^\circ$ is the standard potential of the normal hydrogen electrode. For an oxidation-reduction electrode, the expression is:

$$E_{25^\circ} = E^\circ + \frac{0.0591}{n} \log \frac{[Ox]}{[Red]}$$  \hspace{1cm} (3)

where $E^\circ$ is the standard oxidation potential, $n$ the number of electrons gained by the oxidant in being converted into the reductant, and $[Ox]$ and $[Red]$ are the concentrations (strictly, the activities) of the oxidant and reductant respectively.

The determination of $E$ is the essence of potentiometric titration: this may be used either to measure the ionic (or $[Ox]/[Red]$) concentration of a solution, or, what is more important for our present purpose, to follow the changes in ionic concentration or of the ratio $[Ox]/[Red]$ during the course of a titration.

Since $E_H^\circ$, the normal potential for hydrogen, viz., the potential of the hydrogen electrode immersed in a solution of hydrogen ions of unit activity at one atmosphere pressure, is taken arbitrarily as zero at all temperatures, expression (2) reduces to:

$$E = - 0.0591 \times pH \text{ (at 25° C.)*}$$

on this scale. On theoretical grounds, therefore, the determination of the hydrogen-ion concentration is the simplest case to deal with, and is discussed in Section VI, 2.

**I. 52. OTHER PHYSICO-CHEMICAL METHODS OF ANALYSIS**

Under instrumental titrimetry are included the methods of:

(i) potentiometric titration (Chapter VI);
(ii) conductometric titration (Chapter VII); and
(iii) amperometric titration (Chapter IX).

Other instrumental methods of analysis which find extensive application for inorganic compounds include the following:

(iv) colorimetric analysis and spectrophotometry (these, and also turbidimetry, nephelometry, and fluorimetry, are discussed in Chapter V: a brief account of the principles and applications of flame photometry is given below);
(v) polarography (Chapter VIII); and
(vi) emission spectrography.

**Flame photometry.** One method for obtaining the emission spectrum of an element consists in the atomisation of its solution and spraying

* At any other temperature $T$, this becomes:

$$E = - 0.0001982T \times pH$$

where $T$ is the absolute temperature.
it into an oxy-acetylene or oxy-coal-gas flame; this procedure now constitutes standard spectrographic technique. Flame photometry utilises the same means of spectrum excitation, but the subsequent measurement of emission intensity is simplified by the introduction of light filters and direct-reading photocell-galvanometer combinations. A flame photometer is a device for measuring the intensity of the light emitted by elements when excited in a flame. In the simplest form of flame photometer, light filters are introduced to select those regions of the spectrum which contain suitable spectral lines of the particular element concerned and simultaneously to cut out any radiation emitted by other elements present in the solution. This selection may, of course, be achieved more precisely (but with additional cost) by means of monochromators, as in the case of the flame-photometer attachment for use with the Beckman spectrophotometer (Fig. V, 7, 29).* Most commercial flame photometers measure the intensity of one line at a time, and consequently it is necessary to maintain the characteristics of the flame source constant throughout each series of determinations. This is accomplished by regulation of the air, gas (natural gas, coal gas, or acetylene), and oxygen pressures and rates of flow, which incidentally controls the rate of introduction of the sample into the flame. For the most trustworthy results the unknown is compared with standard samples of approximately the same concentration. Qualitative analysis can be made by atomising the solution into the burner and checking the light emitted for the wavelengths characteristic of the elements being sought. More than forty elements, and particularly the alkali metals, can be excited in a hot flame and can be investigated qualitatively and quantitatively by a flame photometer. The samples to be analysed must, of course, be brought into solution.

In the Beckman flame spectrophotometer the samples are atomised and introduced into a very hot oxy-gas flame through a specially designed burner. The spectrophotometer isolates the desired spectral lines and measures their intensities relative to a blank or standard. It consists essentially of an atomiser, spray chamber, burner, and control unit. Samples to be analysed are brought either into aqueous or non-aqueous solution and placed beneath the atomiser; the sample spray is consumed in a special burner fed with illuminating-gas and oxygen. The fuel is burned at many small ports located round the larger holes, which feed the spray to the flame. This arrangement provides a broad, uniform flame which does not require precise optical alignment with the monochromator of the Model DU spectrophotometer. The hot portion of the flame is focused on the slit of the monochromator; the available light is increased by a stainless-steel mirror behind the flame. The results may be read directly from the dial of the photometer in terms of the line intensities expressed in arbitrary units, or the instrument may be calibrated to read in parts per million. Some typical results which have been obtained with the Beckman instrument are collected in the following summary in order to give some idea of the applicability and range of the method. The particular element determined, the approximate minimum detectable amount in parts per million, and the spectral lines in Angstrom units employed for measurement are given in that order: B, 5, 5481; Ca, 0-3, 6182, 6203; Cs,

* A flame-photometer attachment is being developed for the Hilger Uvispek (Fig. V, 7, 18).
Quantitative Inorganic Analysis

The flame photometer has been suggested for the simultaneous determination of all the alkali metals in mixtures, the determination of most of the rare earths in mixtures, the determination of traces of strontium and calcium in barium, of silver in gold, of copper in mercury, of cobalt in nickel, and also for the analysis of many alloys containing iron, cobalt, nickel, copper, manganese, and chromium.

Emission spectrography. The emission spectra of elements may be produced by the following methods of excitation: the flame, an A.C. or D.C. arc, and the high-voltage spark. The spectra are characteristic of the elements irrespective of their state of chemical combination. Only a brief introduction to the subject can be given here, because of the limitation of space and also because the cost of the equipment for quantitative analysis is beyond the means of the average teaching institution. The essential features of a typical spectrograph (the Hilger medium quartz spectrograph) will be evident from Fig. I, 52, 1; the actual instrument is shown in Fig. I, 52, 2. The light produced from the specimen by any of the means of excitation enumerated above is received by a narrow slit and passes through a lens system to...
a prism which deviates each radiation from a direct path by an amount depending upon its wavelength. A second lens system forms an image of the narrow slit upon a photographic plate for each radiation in the order determined by the prism. Hence with a substance giving a number of discrete radiations, there will be a corresponding spectrum of slit images or spectrum lines. Identification of their wavelengths as a function of their positions will provide identification of the elements giving rise to them. Many sensitive lines appear in the ultra-violet; the whole optical system is therefore constructed of quartz, since ultra-violet radiations are absorbed by glass. Usually the visible and ultra-violet spectrum is photographed upon suitable plates or films.

The intensities of the various lines of an element are different, and, in general, the intensity of a given line is proportional to the concentration of the element. Upon reducing the concentration of the element the weakest lines will disappear first, and ultimately a concentration is reached at which only the most persistent lines remain; these lines have been called persistent lines or raies ultimes (R.U.) and are, of course, the most useful in detecting small concentrations of impurities.

Emission spectrography as a qualitative method, particularly for detecting trace elements, possesses a sensitivity which is beyond most chemical tests and, moreover, a single photographic determination will reveal at once every element present in the specimen. For quantitative work spectrochemical analysis is, within its special limitations, a rapid and trustworthy method for the determination of small percentages of components; under present conditions, the procedure is limited to minor elements (proportion less than 10 per cent), and its accuracy tends to increase as the quantity of the element being determined diminishes. Quantitative methods depend, in principle, upon the relative intensities of the radiations from the main element and from the minor elements to be determined. This generally involves measurement of the blackening of photographed spectrum lines in reasonably close proximity, say, by means of a microphotometer which measures this function photo-electrically; the comparison line may be that of another element present at a constant concentration ("internal standard" method). Frequently standard samples containing known amounts of the elements being determined are employed for comparison.

The applications of emission spectrography include:

(i) the examination of a single metal or an alloy for its impurities;
(ii) the analysis of an alloy for its general composition, including a search for minor components and traces of impurities;
(iii) the analysis of ash of organic substances and other materials (e.g., natural waters) amenable to similar treatment; and
(iv) the detection of contaminants in food.

The chief advantages of the spectrographic method of analysis are:

(a) The procedure is specific for the element being determined, although difficulties occasionally arise when a line of another element overlaps that of the unknown.
(b) The method is time-saving; a quantitative determination of traces of the elements in a sample, especially an alloy or a metal, may be made without any preliminary treatment. Most metals
and some non-metals (e.g., phosphorus, silicon, arsenic, carbon, and boron) may be determined.

(c) A permanent record may be obtained on a photographic plate.

(d) It may be (and is usually) applied to the determination of traces of impurities where conventional methods of analysis are difficult, fail, or give less-accurate results.

The apparent disadvantages are:

(a) The necessary equipment is costly, and its successful use requires considerable experience.

(b) The accuracy is not as high as gravimetric, volumetric, and some colorimetric methods. With a good instrument an accuracy of 5 per cent of the material present may be obtained for most elements; this is usually sufficient when dealing with elements present in small proportion.
I. SELECTED BIBLIOGRAPHY ON THEORY OF VOLUMETRIC ANALYSIS AND SOME PHYSICO-CHEMICAL METHODS OF ANALYSIS

THEORY OF GRAVIMETRIC ANALYSIS

I, 54. Gravimetric analysis.-Gravimetric analysis or quantitative analysis by weight is the process of isolating and weighing an element or a definite compound of the element in as pure a form as possible. The element or compound is separated from a weighed portion of the substance being examined. A large proportion of the determinations of gravimetric analysis is concerned with the transformation of the element or radical to be determined into a pure stable compound which can be readily converted into a form suitable for weighing. The weight of the element or radical may then be readily calculated from a knowledge of the formula of the compound and the atomic weights of the constituent elements.

The separation of the element or of the compound containing it may be effected in a number of ways, the most important of which are: (a) precipitation methods, (b) volatilisation or evolution methods, (c) electro-analytical methods, and (d) miscellaneous physical methods. It is proposed to utilise these four as the basis for the classification of gravimetric methods, and to discuss the theory of each in turn.

It may be mentioned at this stage that the great advantage of gravimetric over volumetric analysis is that the constituent may be seen and examined for the presence of impurities and a correction applied, if necessary; the disadvantage of gravimetric methods is that they are generally more time-consuming.

I, 55. PRECIPITATION METHODS

These are perhaps the most important with which we are concerned in gravimetric analysis. The constituent being determined is precipitated from solution in a form which is so slightly soluble that no appreciable loss occurs when the precipitate is separated by filtration and weighed. Thus in the determination of silver, a solution of the substance is treated with an excess of sodium or potassium chloride solution, the precipitate is filtered off, well washed to remove soluble salts, dried at 130-150° C., and weighed as silver chloride. Frequently the constituent being estimated is weighed in a form other than that in which it was precipitated. Thus magnesium is precipitated, as magnesium ammonium phosphate Mg(NH₄)₂PO₄·6H₂O, but is weighed, after ignition, as the pyrophosphate Mg₃P₂O₇. The following table contains the forms in which the compounds of the common elements are usually weighed: this includes the electro-analytical methods discussed in Section I, 64 et seq. The factors which determine a successful analysis by precipitation are:

(a) The precipitate must be so insoluble that no appreciable loss occurs when it is collected by filtration. In practice this usually means that the quantity remaining in solution does not exceed the minimum detectable by the ordinary analytical balance, viz., 0.1 mg.

(b) The physical nature of the precipitate must be such that it
# The Theoretical Basis of Quantitative Analysis

## Table XVIII.

Forms in which Elements and Radicals are Commonly Precipitated and Weighed in Gravimetric Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Precipitated as</th>
<th>Weighed as</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ag</strong></td>
<td>1. AgCl; 2. Ag.</td>
<td>1. AgCl; 2. Ag.*</td>
</tr>
<tr>
<td><strong>Hg</strong></td>
<td>1. HgS; 2. Hg zinc thiocyanate; 3. Cu ethylenediamine mercuri-iodide; 4. Hg para-periodate.</td>
<td>1. HgS; 2. Hg[Zn(CNS)]₂; 3. [Cu en₃][HgI₄]; 4. Hg₅(IO₃)₂.</td>
</tr>
<tr>
<td><strong>As</strong></td>
<td>1. As₂S₃; 2. Mg(NH₄)AsO₄·6H₂O; 3. NH₄UO₂AsO₄·3H₂O</td>
<td>1. As₂S₃; 2. Mg(NH₄)AsO₄·6H₂O or as Mg₃As₂O₇; 3. U₃O₈.</td>
</tr>
<tr>
<td><strong>Sb</strong></td>
<td>1. Sb₂S₃; 2. Sb pyrogallate.</td>
<td>1. Sb₂S₃ or Sb₂O₅; 2. Sb(C₆H₅O₂N).</td>
</tr>
<tr>
<td><strong>Se</strong></td>
<td>1. Se.</td>
<td>1. Se.</td>
</tr>
<tr>
<td><strong>Te</strong></td>
<td>1. Te; 2. TeO₂.</td>
<td>1. Te; 2. Te.</td>
</tr>
<tr>
<td><strong>Au</strong></td>
<td>1. Au.</td>
<td>1. Au.</td>
</tr>
</tbody>
</table>

* Those elements (and PbO₂) marked with an asterisk are electrolytic determinations.
<table>
<thead>
<tr>
<th>Element</th>
<th>Precipitated as</th>
<th>Weighed as</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>1. Be(OH)_2; 2. Be tannin complex.</td>
<td>I. BoO; 2. BeO.</td>
</tr>
<tr>
<td>Fe</td>
<td>1. Fe(OH)_3; 2. Fe cupferron complex; 3. Basic Fe benzoate; 4. Fe &quot;oxinate.&quot;</td>
<td>1. Fe_2O_3; 2. Fe_2O_3; 3. Fe_2O_3; 4. Fe(C_6H_5ON)_3.</td>
</tr>
<tr>
<td>Co</td>
<td>1. Co α-nitroso-β-naphthololate; 2. Co anthranilate; 3. Co phenylthiodyantolate complex; 4. Co pyridine thiocyantate; 5. Co.</td>
<td>1. CoSO_4 or as Co; 2. Co(C_7H_4O_2N)_2; 3. CoO_4 (impure) and then as 1 or 2; 4. [Co(C_5H_5N)_2]CNS; 5. Co.*</td>
</tr>
<tr>
<td>Zn</td>
<td>1. Zn(NH_₄)PO_4·6H_2O; 2. ZnS; 3. Zn quinaldinate; 4. Zn pyridine thiocyantate; 5. Zn anthranilate; 6. Zn 8-hydroxyquinaldinate (&quot;2-methyl-oxinate&quot;); 7. Zn.</td>
<td>1. Zn(NH_₄)PO_4 or as Zn_2P_2O_7; 2. ZnS or as 1; 3. Zn(C_10H_8O_3N)_2H_2O; 4. [Zn(C_3H_2N)_2]CNS; 5. Zn(UH_4O_6N)_2; 6. Zn(C_10H_8O_6N)_2; 7. Zn.*</td>
</tr>
<tr>
<td>Mn</td>
<td>1. Mn(NH_₄)PO_4·4H_2O.</td>
<td>1. Mn_2P_4O_8 or as Mn(NH_₄)PO_4·4H_2O.</td>
</tr>
<tr>
<td>V</td>
<td>1. Hg_2VO_5; 2. Ag_3VO_5.</td>
<td>1. V_2O_5; 2. Ag_5VO_4.</td>
</tr>
<tr>
<td>U (UO_₂)</td>
<td>1. (NH_₄)₂UO_₂; 2. Uranyl &quot;oxinate&quot;; 3. U (ous) cupferron complex.</td>
<td>1. U_2O_₈; 2. UO_₃(C_6H_4ON)_2C_6H_4O_2N; 3. UO_₃.</td>
</tr>
<tr>
<td>Th</td>
<td>1. Th(CO_2)_3; 2. Th sebacate; 3. Th(IO_₃)_3.</td>
<td>1. ThO_₂; 2. ThO_₂; 3. ThO_₃.</td>
</tr>
<tr>
<td>Ce</td>
<td>1. Ce(IO_₃)_₄.</td>
<td>1. CeO_₂.</td>
</tr>
</tbody>
</table>
### Table XVIII—Continued

<table>
<thead>
<tr>
<th>Element</th>
<th>Precipitated as</th>
<th>Weighed as</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>1. Tl₂CrO₄; 2. Tl₂[Co(NO₃)₆].</td>
<td>1. Tl₂CrO₄; 2. Tl₂[Co(NO₃)₆].</td>
</tr>
<tr>
<td>Mg</td>
<td>1. Mg(NH₄)PO₄.6H₂O; 2. Mg &quot;oxininate&quot;; 3. Mg 8-hydroxy-quinaldinate (&quot;2-methyloxinate&quot;).</td>
<td>1. Mg(NH₄)PO₄.6H₂O or as Mg₂F₄O; 2. Mg(C₆H₈ONH)₂.2H₂O or as Mg(C₆H₈ON)₃; 3. Mg(C₆H₈ON)₂.2H₂O.</td>
</tr>
<tr>
<td>Na</td>
<td>1. Na₂SO₄; 2. Na zinc uranyl acetate; 3. Na magnesium uranyl acetate.</td>
<td>1. Na₂SO₄; 2. NaZn(UO₂)₂(C₂H₆O₂)₆.3H₂O; 3. NaMg(UO₂)₂(C₂H₆O₂)₆.6·5H₂O.</td>
</tr>
<tr>
<td>Li</td>
<td>1. Li₂SO₄; 2. by extraction as LiCl.</td>
<td>1. Li₂SO₄; 2. LiCl.</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1. (NH₄)₂[PtCl₆].</td>
<td>1. (NH₄)₂[PtCl₆].</td>
</tr>
</tbody>
</table>

### Anions

| Cl⁻, Br⁻ | 1. AgCl, AgBr. | 1. AgCl, AgBr. |
| I⁻       | 1. AgI; 2. PuI₃. | 1. AgI; 2. PuI₃. |
| CN⁻      | 1. AgCN. | 1. AgCN. |
| F⁻       | 1. PbClF; (C₆H₈ONH)₃SnF. 2. CaF₃; 3. PbClF; 2. CaF₃; 3. (C₆H₈ONH)₃SnF. | 1. PbClF; 2. CaF₃; 3. (C₆H₈ONH)₃SnF. |
| ClO₃⁻    | 1. AgCl. | 1. AgCl. |
| ClO₄⁻    | 1. AgCl; 2. KClO₄. | 1. AgCl; 2. KClO₄. |
| IO₃⁻     | 1. AgI. | 1. AgI. |
TABLE XVIII—Continued

<table>
<thead>
<tr>
<th>Element</th>
<th>Precipitated as</th>
<th>Weighed as</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄⁻</td>
<td>1. Mg(NH₄)₂PO₄·6H₂O; 2. (NH₄)₃[FeMo₆O₁₅]</td>
<td>1. Mg(NH₄)₂PO₄·6H₂O or as Mg₃P₂O₇;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. (NH₄)₃[FeMo₆O₁₅] or as P₃O₁₀·24MoO₇.</td>
</tr>
<tr>
<td>HPO₄⁻·H₂PO₄⁻</td>
<td>1. Hg₂Cl₂; 2. Mg(NH₄)₂PO₄·6H₂O.</td>
<td>1. Hg₂Cl₂; 2. Mg(NH₄)₂PO₄·6H₂O or as Mg₃P₂O₇.</td>
</tr>
<tr>
<td>C₂O₄⁻</td>
<td>1. CaC₂O₄·H₂O.</td>
<td>1. CaC₂O₄·H₂O, or CaCO₃ or CaO.</td>
</tr>
<tr>
<td>SiO₂⁻·²H₂O</td>
<td>1. SiO₂·²H₂O.</td>
<td>1. SiO₂.</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>1. Nitron nitrate.</td>
<td>1. Ca₃0H₁₃N₄·HNO₃.</td>
</tr>
</tbody>
</table>

can be readily separated from the solution by filtration, and can be washed free of soluble impurities. These conditions require that the particles are of such size that they do not pass through the filtering medium, and that the particle size is unaffected (or, at least, not diminished) by the washing process.

(c) The precipitate must be convertible into a pure substance of definite chemical composition; this may be effected either by ignition or by a simple chemical operation, such as evaporation, with a suitable liquid.

Factor (a), which is concerned with the completeness of precipitation, has already been dealt with in connexion with the solubility product principle (Sections 1, 8 and 9). Therein are discussed the influence upon the solubility of the precipitate of a salt with a common ion, of salts with no common ion, of acids and bases, and of temperature.

It was assumed throughout that the compound which separated out from the solution was chemically pure, but this is not always the case. The purity of the precipitate depends *inter alia* upon the substances present in solution both before and after the addition of the reagent, and also upon the exact experimental conditions of precipitation. In order to understand the influence of these and other factors, it will be necessary to give a short account of the properties of colloids.

I, 56. The colloidal state.—The colloidal state of matter is distinguished by a certain range of particle size, as a consequence of which certain characteristic properties become apparent. Before discussing these, mention must be made of the various units which are employed in expressing small quantities. The most important of these are:

\[ 1\mu = 10^{-3}\ mm. \]
\[ 1\mu = 1\mu = 1\times 10^{-6}\ mm. \]

1 Ångström unit = 1 Å. = 10⁻¹⁰ metre = 10⁻⁷ mm. = 0.1 µm.

Colloidal properties are, in general, exhibited by substances of particle size ranging between 0.1 µ and 1 µ. Ordinary quantitative filter-paper will retain particles up to a diameter of about 10⁻² mm. or 10 µ, so that colloidal solutions in this respect behave like true solutions (size of molecules is of the order of 0.1 µ or 10⁻⁸ cm.). The limit of
vision under the microscope is about 0.2 \( \mu \). If a powerful beam of light is passed through a colloidal solution and the solution is viewed at right angles to the incident light, a scattering of light is observed. This is the so-called Tyndall effect. True solutions, i.e., those with particles of molecular dimensions, do not exhibit a Tyndall effect, and are said to be "optically empty." Use is made of the Tyndall effect in the ultra-microscope; here the Tyndall cone or beam is observed in a microscope which is situated at right angles to the path of the incident light. The diffraction images are thus seen, and it is possible to observe the light scattered by each particle separately. The limit of visibility under the ultra-microscope is about 10 \( \mu \).

By the use of X-rays the nature of the smallest unit of colloidal substances may be ascertained. It has been found that most substances consist of minute crystalline particles; a few, such as silica and stannic oxide, are amorphous. An intermediate stage is also possible: a gradual development of crystalline particles may occur with some amorphous substances upon "ageing" or with suitable treatment, such as hot digestion with water or solutions of electrolytes (Section 1, 58).

An important consequence of the smallness of the size of the particles is that the ratio of surface to weight is extremely large. Phenomena which depend upon the size of the surface, such as adsorption, will therefore play an important part with substances in the colloidal state. Table XIX clearly shows the influence of particle size in connexion with a 1-cm. cube decimally divided.

### Table XIX.—Increase in Number and Total Surface of Particles as a One Centimetre Cube is Decimally Divided

<table>
<thead>
<tr>
<th>Number of Particles</th>
<th>Length of Edge in cm.</th>
<th>Total Surface in sq. cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \times 10^8 )</td>
<td>( 1 \times 10^{-8} )</td>
<td>( 6 \times 10^2 )</td>
</tr>
<tr>
<td>( 1 \times 10^{12} )</td>
<td>( 10^{-4} ) (= 1 ( \mu ))</td>
<td>( 6 \times 10^4 )</td>
</tr>
<tr>
<td>( 1 \times 10^{15} )</td>
<td>( 10^{-6} )</td>
<td>( 6 \times 10^6 )</td>
</tr>
<tr>
<td>( 1 \times 10^{21} )</td>
<td>( 10^{-7} ) (= 1 ( \text{mil} ))</td>
<td>( 6 \times 10^7 ) (= 1.48 acres)</td>
</tr>
<tr>
<td>( 1 \times 10^{24} )</td>
<td>( 10^{-8} ) (= 1 ( \text{Å} ))</td>
<td>( 6 \times 10^8 )</td>
</tr>
</tbody>
</table>

The characteristic properties of colloidal particles are:

(a) they exhibit a Tyndall effect when viewed with proper illumination;

(b) they may be separated from true solutions of substances by means of a collodion or parchment membrane, i.e., by the process of dialysis;

(c) they may be regarded as possessing electrical charges since they migrate under the influence of a suitable potential gradient.

For convenience, we may divide colloids into two main groups, designated as suspensoids and emulsoids.* The chief properties of each class are summarised in the following table, although it must be emphasised that the distinction is not an absolute one, since some gelatinous precipitates (e.g., aluminium and other metallic hydroxides) have properties intermediate between those of suspensoids and emulsoids.

### Suspensoids (or Lyophobic Colloids)

1. The solutions (or sols) are only slightly viscous. Examples: sols of metals, silver halides, metallic sulphides, etc.
2. A comparatively minute concentration of an electrolyte results in flocculation. The change is, in general, irreversible; water has no effect upon the flocculated solid.
3. Suspensoids, ordinarily, have an electric charge of definite sign, which can be changed only by special methods.
4. The ultra-microscope reveals bright particles in vigorous motion (Brownian movement).

### Emulsoids (or Lyophilic Colloids)

1. The solutions are very viscous; they set to jelly-like masses known as gels. Examples: sols of silicic acid, stannic oxide, gelatin.
2. Comparatively large concentrations of electrolytes are required to cause precipitation ("salting out"). The change is, in general, reversible, and is affected by the addition of a solvent (water).
3. Most emulsoids change their charge readily, e.g., they are positively charged in acid medium and negatively charged in an alkaline medium.
4. Only a diffuse light cone is exhibited under the ultra-microscope.

---

The process of dispersing a gel or a flocculated solid to form a sol is called peptisation. The stability of colloidal solutions is intimately associated with the electrical charge on the particles. Thus in the formation of an arsenious sulphide sol by precipitation with hydrogen sulphide in acid solution, sulphide ions are primarily adsorbed (since every precipitate has a tendency to adsorb its own ions), and in order to maintain the electro-neutrality of the solution, an equivalent quantity of hydrogen ions is secondarily adsorbed. The hydrogen ions or other ions which are secondarily adsorbed have been termed counter ions. Thus the so-called electrical double layer is set up between the particles and the solution. An arsenious sulphide particle is represented diagrammatically in Fig. 1, 56, 1. The colloidal particle of arsenious sulphide has a negatively charged surface, with positively charged counter ions which impart a positive charge to the liquid immediately surrounding it. If an electric current is passed through the solution, the negative particles will move towards the anode, although by virtue of the fact that the colloidal particle consists of an aggregate of arsenious sulphide molecules, its mobility will be less than that of ordinary anions.

If the electrical double layer is destroyed, the sol is no longer stable, and the particles will flocculate, since the concentration is in excess of the solubility product. Thus if barium chloride solution is added, barium ions are preferentially adsorbed by the particles; the orientation of the surface is disturbed and the charge disappears. After flocculation, it is found that the dispersion medium is acid owing to the liberation of the hydrogen counter ions. It appears that ions of opposite charge to those primarily adsorbed on the surface are necessary for
The Theoretical Basis of Quantitative Analysis

The minimum amount of electrolyte necessary to cause flocculation of the colloid is called the flocculation or coagulation value. It has been found that the latter depends primarily upon the valency of the ions of the opposite charge to that on the colloidal particles; the nature of the ions has some influence also. This is clearly shown by the results collected in Table XX.

### Table XX.—Coagulation Values in Milli-mols of Coagulating Ion per Litre

<table>
<thead>
<tr>
<th>Salt</th>
<th>Coag. Value</th>
<th>Salt</th>
<th>Coag. Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃</td>
<td>0·062</td>
<td>K⁺Fe(CN)₆</td>
<td>0·067</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>0·074</td>
<td>K₂Fe(CN)₆</td>
<td>0·096</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>0·136</td>
<td>K₂SO₄</td>
<td>0·22</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0·249</td>
<td>K₂Cr₂O₇</td>
<td>0·33</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>0·391</td>
<td>K₂CrO₇</td>
<td>0·24</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0·717</td>
<td>K₂CO₃</td>
<td>31</td>
</tr>
<tr>
<td>Ba(NO₃)₂</td>
<td>0·687</td>
<td>KB₉O₄</td>
<td>47</td>
</tr>
<tr>
<td>KCl</td>
<td>49·5</td>
<td>KCNS</td>
<td>103</td>
</tr>
<tr>
<td>NaCl</td>
<td>51·0</td>
<td>KCl</td>
<td>138</td>
</tr>
<tr>
<td>LiCl</td>
<td>58·4</td>
<td>KNO₃</td>
<td>131</td>
</tr>
<tr>
<td>KNO₃</td>
<td>50·0</td>
<td>KBr</td>
<td>154</td>
</tr>
<tr>
<td>HCl</td>
<td>30·8</td>
<td>KI</td>
<td>154</td>
</tr>
</tbody>
</table>

If two sols of opposite sign are mixed, mutual coagulation usually occurs owing to the neutralisation of charges. The above remarks apply largely to suspensoids. Emulsoids are generally much more difficult to coagulate than suspensoids. If an emulsoid sol, e.g., of gelatin, is added to a suspensoid sol, e.g., of gold, then the suspensoid sol appears to be strongly protected against the flocculating action of electrolytes. It is probable that the particles of the emulsoid sol are adsorbed by the suspensoid and impart their own properties to the latter. The emulsoid is known as a protective colloid. This explains the relative stability produced by the addition of a little gelatin of the otherwise unstable gold sols. For this reason also, organic matter, which might form a protective colloid, is generally destroyed before proceeding with an inorganic analysis.

During the flocculation of a colloid by an electrolyte, the ions of opposite sign to that of the colloid are adsorbed to a varying degree on the surface; the higher the valency of the ion, the more strongly is it adsorbed. In all cases, the precipitate will be contaminated by surface adsorption. Upon washing the precipitate with water, part of the adsorbed electrolyte is removed, and a new difficulty may arise. The electrolyte concentration in the supernatant liquid may fall below the coagulation value, and the precipitate will pass into colloidal solution again. This phenomenon, which is known as peptisation, is of great importance in quantitative analysis. By way of illustration, let us consider the precipitation of silver by excess of chloride ions in acid solution and the subsequent washing of the coagulated silver chloride with water; the adsorbed hydrogen ions will be removed by the washing process and a portion of the precipitate will pass through the filter. If, however, washing is carried out with dilute nitric acid, no peptisation occurs. For this reason, precipitates are always washed with a suitable
solution of an electrolyte which does not interfere with the subsequent steps in the estimation.

The adsorptive properties of colloids find a number of applications in analysis, e.g., in the removal of phosphates by hydrated stannic oxide in the presence of nitric acid, in the use of adsorption indicators (Section I, 48), in the qualitative detection and colorimetric estimation of elements and radicals with many organic reagents (for example, aluminium with "aluminon", Section V, 18).

I, 57. Supersaturation and precipitate formation.—The solubility of a substance at any given temperature in a given solvent is the amount of the substance dissolved by a known weight of that solvent when the substance is in equilibrium with the solvent. The solubility depends upon the particle size, when these are smaller than about 0·01 mm, in diameter; the solubility increases greatly the smaller the particles, owing to the increasing role played by surface effects (compare Table XIX). (The definition of solubility given above refers to particles larger than 0·01 mm.) A supersaturated solution is one that contains a greater concentration of solute than corresponds to the equilibrium solubility at the temperature under consideration. Supersaturation is therefore an unstable state which may be brought to a state of stable equilibrium by the addition of a crystal of the solute ("seeding" the solution) or of some other substance, or by mechanical means such as shaking or stirring. The difficulty of precipitation of magnesium ammonium phosphate will at once come to mind as an example of supersaturation.

According to von Weimarn (1913, 1925) supersaturation plays an important part in determining the particle size of a precipitate. He has deduced that the initial velocity of precipitation is proportional to \( \frac{(Q - S)}{S} \), where \( Q \) is the total concentration of the substance that is to precipitate, and \( S \) is the equilibrium solubility; \( (Q - S) \) will denote the supersaturation at the moment precipitation commences. The expression applies approximately only when \( Q \) is large as compared with \( S \). The influence of the degree of supersaturation is well illustrated by von Weimarn's results for the formation of barium sulphate from solutions of barium thiocyanate and manganese sulphate respectively. These are collected in Table XXI below. The results clearly show that the particle size of a precipitate decreases with increasing concentration of the reactants. For the production of a crystalline precipitate, for which the adsorption errors will be least and filtration will be easiest, \( (Q - S)/S \) should be as small as possible. There is obviously a practical limit to reducing \( (Q - S)/S \) by making \( Q \) very small, since for a precipitation to be of value in analysis, it must be complete in a comparatively short time and the volumes of solutions involved must not be too large. There is, however, another method which may be used, viz., that of increasing \( S \). For example, barium sulphate is about fifty times more soluble in 2N-hydrochloric acid than in water; if 0·1N solutions of barium chloride and sulphuric acid are prepared in 2N boiling hydrochloric acid and the solutions mixed, a typical crystalline precipitate of barium sulphate is slowly formed.

The applications of the above conceptions* are to be found in the following recognised procedures in gravimetric analysis:

1. Precipitation is usually carried out in hot solutions, since the solubility generally increases with rise in temperature.

2. Precipitation is effected in dilute solution and the reagent is added slowly and with thorough stirring. The slow addition results in the first particles precipitated acting as nuclei for the deposition of new particles as they are formed.

3. A suitable reagent is often added to increase the solubility of the precipitate and thus lead to larger primary particles.

<p>| TABLE XXI.—SEPARATION OF BaSO₄ AT VARIOUS DEGREES OF SUPERSATURATION (VON WEIMANN) |
|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Concentration of Reagents</th>
<th>(Q — S)/S</th>
<th>Type of Precipitate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7N</td>
<td>175,000</td>
<td>A gelatinous precipitate is formed, and practically the whole of the water is adsorbed; the containing vessel can be inverted without the contents running out. The gel is unstable, and growth of the large crystals at the expense of small ones is very rapid; after a few hours the precipitate becomes opaque.</td>
</tr>
<tr>
<td>3N</td>
<td>75,000</td>
<td>Gelatinous films formed; become turbid after one minute.</td>
</tr>
<tr>
<td>N</td>
<td>25,000</td>
<td>Primary precipitate is curdy and of colloidal dimensions. Particles appear as points at a magnification of 1500 ×.</td>
</tr>
<tr>
<td>0-05N</td>
<td>1,300</td>
<td>Primary precipitate consists of feathery and star-shaped crystal skeletons.</td>
</tr>
<tr>
<td>0-005N</td>
<td>125</td>
<td>Precipitate consists of compact crystal skeletons.</td>
</tr>
<tr>
<td>ca. 0-001N</td>
<td>25</td>
<td>Solution becomes opalescent during first 5 minutes, and precipitation continues for 2-3 hours. After that time crystals have a length of 0-005 mm.</td>
</tr>
<tr>
<td>ca. 0-002N</td>
<td>5</td>
<td>Precipitate appears after about a month. At the end of six months, the length of the largest crystals is about 0-03 mm. and their breadth 0-015 mm.</td>
</tr>
</tbody>
</table>

1. 58. The purity of the precipitate. Co-precipitation.—When a precipitate separates from a solution, it is not always perfectly pure; it may contain varying amounts of impurities dependent upon the nature of the precipitate and the conditions of precipitation. The contamination of the precipitate by substances which are normally soluble in the mother liquor is termed co-precipitation. We must distinguish between two important types of co-precipitation. The first is concerned with adsorption at the surface of the particles exposed to the solution, and the second relates to the occlusion of foreign substances during the process of crystal growth from the primary particles. With regard to surface adsorption, this will, in general, be greatest for gelatinous precipitates and least for those of pronounced macrocrystalline character. Precipitates with ionic lattices appear to conform to the Paneth—Fajans—Hahn adsorption rule, which states that “those ions whose compounds with the oppositely charged constituent of the lattice are slightly soluble in the solution in question are well adsorbed by the ionic lattice.” Thus silver iodide adsorbs silver acetate much more strongly than silver nitrate under comparable.
conditions, since the former is the less soluble. The deformability of
the adsorbed ions and the electrolytic dissociation of the adsorbed
compound also have a considerable influence; the smaller the disso-
ciation of the compound, the greater is the adsorption. Thus hydrogen
sulphide, a weak electrolyte, is strongly adsorbed by metallic sulphides.

The second type of co-precipitation may be visualised as occurring
during the building up of the precipitate from the primary particles.
The latter will be subject to a certain amount of surface adsorption,
and during their coalescence the impurities will either be partially
eliminated if large single crystals are formed and the process takes place
slowly, or, if coalescence is rapid, large crystals composed of loosely
bound small crystals may be produced and some of the impurities may
be entrained within the walls of the large crystals. If the impurity
is isomorphous or forms a solid solution with the precipitate, the amount
of co-precipitation may be very large, since there will be no tendency
for elimination during the "ageing" process. The latter actually
occurs during the precipitation of barium sulphate in the presence of
alkali nitrates; in this particular case X-ray studies have shown that
the abnormally large co-precipitation (which may be as high as 3-5 per
cent if precipitation occurs in the presence of high concentrations of
nitrate) is due to the formation of solid crystals. Fortunately, how­
ever, such cases are comparatively rare in analysis.

Appreciable errors may also be introduced by post-precipitation.
This is the precipitation which occurs on the surface of the first pre­
cipitate after its formation. It occurs with sparingly soluble substances
which form supersaturated solutions; they usually have anion in common
with the primary precipitate. Thus in the precipitation of calcium as
oxalate in the presence of magnesium, magnesium oxalate separates
out gradually upon the calcium oxalate; the longer the precipitate
is allowed to stand in contact with the solution, the greater is the error
due to this cause. A similar effect is observed in the precipitation of
copper or mercuric sulphide in 0.3N-hydrochloric acid in the presence
of zinc ions; zinc sulphide is slowly post-precipitated.

It is convenient to consider now the influence of digestion. This is
usually carried out by allowing the precipitate to stand for 12-24
hours at room temperature, or sometimes by warming the precipitate
for some time, in contact with the liquid from which it was formed :
the object is, of course, to obtain complete precipitation in a form
which can be readily filtered. During the process of digestion or of
the ageing of precipitates, at least two changes occur. The very small
particles, which have a greater solubility than the larger ones, will, after
precipitation has occurred, tend to pass into solution, and will ultimately
re-deposit upon the larger particles; the co-precipitation on the minute
particles is thus eliminated and the total co-precipitation on the ulti­
mate precipitate reduced. The rapidly formed crystals are probably
of irregular shape and possess a comparatively large internal surface;
upon digestion these tend to become more regular in character, thus
resulting in a decrease in the area of the internal surface and a conse­
quent reduction of adsorption. The net result of digestion is usually to
reduce the extent of co-precipitation and to increase the size of the
particles, rendering filtration easier.

I, 59. Conditions of precipitation.—No universal rules for precipita­
tion can be given which are applicable to all cases of precipitation,
but, with the aid of an intelligent application of the facts enumerated in the foregoing paragraphs, a number of fairly general rules may be stated:

1. Precipitation should be carried out in dilute solution, due regard being paid to the solubility of the precipitate, the time required for filtration, and the subsequent operations to be carried out with the filtrate. This will minimise the errors due to co-precipitation.

2. The reagents should be mixed slowly and with constant stirring. This will keep the degree of supersaturation small and will assist the growth of large crystals. A slight excess of the reagent is all that is generally required; in exceptional cases a large excess may be necessary. In some instances the order of mixing the reagents may be important. Precipitation may be effected under conditions which increase the solubility of the precipitate, thus further reducing the degree of supersaturation (compare Section I, 58).

3. Precipitation is effected in hot solutions, provided the solubility and the stability of the precipitate permit. Either one or both of the solutions should be heated to just below the boiling point or other most favourable temperature. At the higher temperature: (a) the solubility is increased with a consequent reduction in the degree of supersaturation, (b) coagulation is assisted and sol formation decreased, and (c) the velocity of crystallisation is increased, thus leading to better-formed crystals.

4. Crystalline precipitates should be digested for as long as practical, preferably overnight, except in those cases where post-precipitation may occur. As a rule, digestion on the steam-bath is desirable. This process decreases the effect of co-precipitation and gives more readily filterable precipitates. Digestion has little effect upon amorphous or gelatinous precipitates.

5. The precipitate should be washed with the appropriate dilute solution of an electrolyte. Pure water may tend to cause peptisation. (For theory of washing, see Section I, 60 below.)

6. If the precipitate is still appreciably contaminated as a result of co-precipitation or other causes, the error may often be reduced by dissolving it in a suitable solvent and then reprecipitating it. The amount of foreign substance present in the second precipitation will be small, and consequently the amount of the entrainment of the precipitate will also be small.

I, 60. Washing of the precipitate.—The experimental aspect of this important subject is dealt with in Section II, 34. Only some general theoretical considerations will be given here. Most precipitates are produced in the presence of one or more soluble compounds, and it is the object of the washing process to remove these as completely as possible. It is evident that only surface impurities will be removed in this way. The composition of the wash solution will depend upon the solubility and chemical properties of the precipitate and upon its tendency to undergo peptisation, the impurities to be removed, and the influence of traces of the wash liquid upon the subsequent treatment of the precipitate before weighing. Water cannot, in general, be employed owing to the possibility of producing partial peptisation of the precipitate and, in many cases, the introduction of small losses as a consequence of the slight solubility of the precipitate. A solution of some electrolyte is employed. This should possess a common ion
with the precipitate in order to reduce solubility errors, and should easily be volatilised in the preparation of the precipitate for weighing. For these reasons, ammonium salts, ammonia solution, and dilute acids are commonly employed. If the filtrate is required in a subsequent determination, the selection is limited to substances which will not interfere in the sequel. Also hydrolysable substances will necessitate the use of solutions containing a salt which will depress the hydrolysis (compare Section I, 18). As examples of washing liquids we may mention very dilute nitric acid for the silver halides, and dilute ammonium oxalate solution for calcium oxalate. Whether the wash liquid is employed hot or at some other temperature will depend primarily upon the solubility of the precipitate; if permissible, hot solutions are to be preferred, because of the greater solubility of the foreign substances and the increased speed of filtration.

Solubility losses are reduced by employing the minimum quantity of wash solution consistent with the removal of impurities. It can be readily shown that washing is more efficiently carried out by the use of many small portions of liquid than with a few large portions, the volume being the same in both instances. Under ideal conditions, where the foreign body is simply mechanically associated with the particles of the precipitate, the following expression may be shown to hold:

\[ x_n = x_0 \left( \frac{u}{u + v} \right)^n \]

where \( x_0 \) is the concentration of impurity before washing, \( x_n \) is the concentration of impurity after \( n \) washings, \( u \) is the volume in ml. of the liquid remaining with the precipitate after draining, and \( v \) is the volume in ml. of the solution used in each washing. It follows from this expression that it is best:

(a) to allow the liquid to drain as far as possible in order to maintain \( u \) at a minimum, and

(b) to use a relatively small volume of liquid and to increase the number of washings. Thus if \( u = 1 \) ml. and \( v = 9 \) ml., five washings would reduce the surface impurity to \( 10^{-6} \) of its original value; one washing with the same volume of liquid, viz., 45 ml., would only reduce the concentration to \( 1/46 \) or \( 2.2 \times 10^{-2} \) of its initial concentration.

In practice, the washing process is not quite so efficient as the above simple theory would indicate, since the impurities are not merely mechanically associated with the surface. Furthermore, solubility losses are not so great as one would expect from the solubility data because the wash solution passing through the filter is not saturated with respect to the precipitate. Frequent qualitative tests must be made upon portions of the filtrate for some foreign ion which is known to be present in the original solution; as soon as these tests are negative, the washing is discontinued.

Quantitative Separations Based upon Precipitation Methods

I. 61. Fractional precipitation.—The simple theory of fractional precipitation has been given in Section I, 11. It was shown that when the solubility products of two sparingly soluble salts having an ion in

common differ sufficiently, then one salt will precipitate almost completely before the other commences to separate. This separation is actually possible for a mixture of chloride and iodide, but in other cases the theoretical predictions must be verified experimentally because of the danger of co-precipitation (Section I, 58) affecting the results. Some separations based upon fractional precipitation, which are of practical importance, will now be considered.

A. Precipitation of sulphones. In order to fully understand the separations dependent upon the sulphide ion, we shall consider first the quantitative relationships involved in a saturated solution of hydrogen sulphide. The following equilibria are present:

\[ \text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^- \]
\[ \text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^- \]

\[ [\text{H}^+] \times [\text{HS}^-]/[\text{H}_2\text{S}] = K_1 = 9.1 \times 10^{-8} \quad (1) \]
\[ [\text{H}^+] \times [\text{S}^-]/[\text{HS}^-] = K_2 = 1.2 \times 10^{-15} \quad (2) \]

The very small value of \( K_2 \) indicates that the secondary dissociation and consequently \([\text{S}^-] \) is exceedingly small. It follows therefore that only the primary ionisation is of importance, and \([\text{H}^+] \) and \([\text{HS}^-] \) are practically equal in value. A saturated aqueous solution of hydrogen sulphide at 25° C., at atmospheric pressure, is approximately 0.1 M. Substituting \([\text{H}^+] = [\text{HS}^-] \) and \([\text{H}_2\text{S}] = 0.1 \) in equation (1), we obtain:

\[ [\text{H}^+] = [\text{HS}^-] = \sqrt{9.1 \times 10^{-8} \times 0.1} = 9.5 \times 10^{-5} \]

Both the equilibrium equations must be satisfied simultaneously; by substitution of these values for \([\text{H}^+] \) and \([\text{HS}^-] \) in equation (2), we obtain:

\[ 9.5 \times 10^{-5} \times [\text{S}^-] = 1.2 \times 10^{-15} \times 9.5 \times 10^{-5} \]

or 
\[ [\text{S}^-] = 1.2 \times 10^{-15} \]

which is the value for \( K_2 \).

If we multiply equations (1) and (2) together, we obtain:

\[ \frac{[\text{H}^+]^2 \times [\text{S}^-]}{[\text{H}_2\text{S}]} = 1.1 \times 10^{-22} \quad (3) \]

or 
\[ [\text{S}^-] = 1.1 \times 10^{-22}/[\text{H}^+]^2 \quad (3') \]

Thus the concentration of the sulphide ion is inversely proportional to the square of the hydrogen-ion concentration. By varying the \( \text{pH} \) of the solution, the \([\text{S}^-] \) may be controlled; in this way separations of metallic sulphones may be effected. Let us first calculate the \([\text{S}^-] \) in a solution of 0.25 M-hydrochloric acid saturated with hydrogen sulphide; this is the concentration employed for the precipitation of the sulphones of the Group II metals in qualitative analysis. The total concentration of \( \text{H}_2\text{S} \) will be approximately the same as in aqueous solution, i.e., 0.1 M: the \([\text{H}^+] \) will be equal to that of the completely dissociated hydrochloric acid, i.e., 0.25 M, but the \([\text{S}^-] \) will be reduced below 1.2 \( \times \) 10\(^{-15}\). Substituting in equations (1) and (2):

\[ [\text{HS}^-] = \frac{9.1 \times 10^{-8} \times [\text{H}_2\text{S}]}{[\text{H}^+]} = \frac{9.1 \times 10^{-8} \times 0.1}{0.25} = 3.6 \times 10^{-8} \]
\[ [\text{S}^-] = \frac{1.2 \times 10^{-15} \times [\text{HS}^-]}{[\text{H}^+]} = \frac{1.2 \times 10^{-15} \times 3.6 \times 10^{-8}}{0.25} = 1.7 \times 10^{-22} \]
Thus by changing the acidity from $9.5 \times 10^{-5}M$ (that present in saturated hydrogen sulphide water) to $0.25M$, the sulphide-ion concentration is reduced from $1.2 \times 10^{-15}$ to $1.7 \times 10^{-22}$.  

With the aid of a table of solubility products of metallic sulphides (see Section I, 9, Table IV), we can calculate whether certain sulphides will precipitate under any given conditions of acidity and also the concentration of the metallic ions remaining in solution. Precipitation of a metallic sulphide $MS$ will occur when $[M^{+}] \times [S^{-}]$ exceeds the solubility product, and the concentration of metallic ions remaining in the solution may be calculated from the equation:

$$[M^{+}] = \frac{S_{MS}}{[S^{-}]} = \frac{S_{MS} \times [H^{+}]^2}{1.1 \times 10^{-22} \times [H_2S]} \quad \ldots \quad (4)$$

As an example we may consider the precipitation of cupric sulphide ($S_{CuS} = 8.5 \times 10^{-46}$) and ferrous sulphide ($S_{FeS} = 1.5 \times 10^{-19}$) from $0.01M$ solutions of the metallic ions in the presence of $0.25M$-hydrochloric acid. For cupric sulphide, the solubility product is readily exceeded ($[S^{-}] = 1.7 \times 10^{-22}$, $[Cu^{+}] = 0.01$ and precipitation will occur until

$$[Cu^{+}] = 8.5 \times 10^{-46} \times [H^{+}]^2 / 1.1 \times 10^{-22} \times [H_2S]$$

$$= 8.5 \times 10^{-45} \times (0.25)^2 \times 1.1 \times 10^{-22} \times 0.1$$

$$= 5 \times 10^{-23}$$

i.e., precipitation is virtually complete. With ferrous sulphide, the solubility product cannot be exceeded and precipitation will not occur under these conditions. If, however, the acidity is sufficiently decreased, and consequently $[S^{-}]$ increases, ferrous sulphide will be precipitated.

The case of zinc sulphide is of especial interest. Various values are given in the literature for its solubility product: the most trustworthy figures vary between $1 \times 10^{-24}$ and $8 \times 10^{-26}$. If we accept the latter figure, then we should expect precipitation to occur in a, say, $0.01M$ solution of zinc ions in the presence of $0.25M$-hydrochloric acid, since the S.P. should be exceeded; furthermore, the residual zinc-ion concentration should be $4.7 \times 10^{-4}$ when computed as described above. In practice, precipitation does not occur at this acidity. This may be partly due to the great tendency that zinc sulphide possesses to remain in supersaturated solution, but is perhaps best explained as follows. The above figure for the solubility product refers to a solution in equilibrium with relatively large particles, whereas for precipitation to occur it is necessary that the S.P. of the particles actually formed should be exceeded. It may well be that under the above experimental conditions these are extremely small, thus possessing a greater solubility (Section I, 56) and a greater solubility product; precipitation will therefore not take place. This view is supported by the fact that post-precipitation of zinc sulphide (compare Section I, 58) will occur upon the surface of other metallic sulphides, such as those of copper and mercury. It is possible to precipitate zinc in acid solution provided the experimental conditions are very carefully controlled, e.g., when the pH of the solution lies between 2 and 3 and ammonium salts are present as coagulants: this is attained by the use of a buffer mixture of formic acid and ammonium formate, sulphuric acid and...
ammonium sulphate or of chloroacetic acid and sodium chloroacetate. It is probable that large particles of zinc sulphide are initially formed under these conditions.

**B. Precipitation and separation of hydroxides at controlled hydrogen-ion concentration or pH.** The underlying theory is very similar to that just given for sulphides. Precipitation will depend largely upon the solubility product of the metallic hydroxide and the hydroxyl-ion concentration, or upon the hydrogen-ion concentration, since \( pH + pOH = pK_a \) (Section I, 17), of the solution.

We have seen that the sulphide-ion concentration of a saturated aqueous solution of hydrogen sulphide may be controlled within wide limits by suitably changing the concentration of hydrogen ions—a common ion—of the solution. In a like manner the hydroxyl-ion concentration of a solution of a weak electrolyte, such as ammonium hydroxide \( (K_b = 1.8 \times 10^{-5}) \), may be regulated by the addition of a common ion, e.g., ammonium ions in the form of the completely dissociated ammonium chloride. The magnitude of the effect is best illustrated by means of an example. In a 0.1M-ammonia solution, the degree of dissociation is given (Section I, 4) approximately by:

\[
\alpha = \sqrt{K/c} = \sqrt{1.8 \times 10^{-5} \times 0.1} = 0.0013
\]

Hence \( [OH^-] = 0.00013 \), \( [NH_4^+] = 0.00013 \), and \( [NH_4OH] = 0.00999 \).

Let us calculate the change in the degree of dissociation and of \([OH^-]\) upon the addition of 0.5 g.-molecule (26.75 g.) of ammonium chloride to 1 litre of the 0.1M-ammonia solution. If \( \alpha' \) is the degree of dissociation in the presence of the added ammonium chloride, then:

\[
[OH^-] = \alpha'c = 0.1\alpha', \quad \text{and} \quad [NH_4OH] = (1 - \alpha')c = 0.1
\]

since \( \alpha' \) may be taken as negligibly small. The addition of the completely dissociated ammonium chloride will of necessity decrease the \([NH_4^+]\) derived from the base and increase \([NH_4OH]\), since \( K_b \) is constant under all conditions. Now, as a first approximation, \( [NH_4^+] = 0.5 \).

Substituting this value in the equation:

\[
\frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = \frac{0.5 \times 0.1\alpha'}{0.1} = 1.8 \times 10^{-5}
\]

\[
\alpha' = 3.6 \times 10^{-5} \quad \text{and} \quad [OH^-] = 3.6 \times 10^{-6}
\]

Thus the addition of half an equivalent weight of ammonium chloride to a 0.1M solution of ammonium hydroxide has decreased the hydroxyl-ion concentration from 0.00013 to 0.0000036, or has changed \( pOH \) from 3.9 to 5.4, i.e., the \( pH \) has changed from 10.1 to 8.6.

An immediate application of the use of the ammonium hydroxide-ammonium chloride mixture may be made to the familiar example of the prevention of precipitation of magnesium hydroxide (S.P. 1.5 \( \times 10^{-11} \)). We can first compute the minimum hydroxyl-ion concentration necessary to prevent precipitation in, say, 0.1M-magnesium solution,

\[
[OH^-] = \sqrt{\frac{S_{Mg(OH)_{2}}}{[Mg^{2+}]}} = \sqrt{1.5 \times 10^{-11} \times 0.1} = 1.22 \times 10^{-5}M
\]

or

\[
pOH = 4.0 \quad \text{and} \quad pH = 14.0 - 4.9 = 9.1
\]

If we employ an ammonium hydroxide solution which is 0.1M, the
Quantitative Inorganic Analysis

Concentration of \([\text{NH}_4^+]\) ion as ammonium chloride or other ammonium salt necessary to prevent the precipitation of magnesium hydroxide can be readily calculated as follows. Substituting in the mass-action equation:

\[
\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = 1.8 \times 10^{-5}
\]

\[
[\text{NH}_4^+] \times 1.22 \times 10^{-5} = 0.1 \times 1.8 \times 10^{-5}
\]

or

\[
[\text{NH}_4^+] = 1.48 \times 10^{-5} \, \text{M}
\]

This corresponds to an ammonium chloride concentration of 1.48 \times 10^{-1} \times 53.5 = 8.2 g. per litre.

We will now consider the conditions necessary for the practically complete precipitation of magnesium hydroxide from a 0.1 M solution of, say, magnesium chloride. A \(p\text{OH}\) slightly in excess of 4.9 (i.e., \(p\text{H} = 9.1\)) might fail to precipitate the hydroxide owing to supersaturation. Let us suppose the hydroxyl-ion concentration is increased ten times, i.e., to \(p\text{OH} 3.9\) or \(p\text{H} 10.1\), then, provided no supersaturation is present:

\[
[Mg^{++}] = \frac{S_{\text{Mg(OH)}_2}}{[\text{OH}^-]^2} = \frac{1.5 \times 10^{-11}}{(1.22 \times 10^{-4})^2} = 0.001 \, \text{M}
\]

i.e., the concentration of the magnesium ions remaining in solution is 0.001 M, or 1 per cent of the magnesium ions would remain unprecipitated. If \(p\text{OH}\) is changed to 2.9 or \(p\text{H} 11.1\), it can be shown in a similar way that the concentration of the magnesium ions left in solution is ca. 1 \times 10^{-5} M, so that the precipitation error is 0.1 per cent, a negligible quantity. We may therefore say that magnesium is precipitated quantitatively at a \(p\text{H}\) of 11.1.

Our knowledge of the solubility products of metallic hydroxides is, however, not very precise, so that it is not always possible to make exact theoretical calculations. The \(p\text{H}\) values at which various hydroxides begin to precipitate from dilute solution are collected in the following table, which is based upon the work of H. T. S. Britton (1925).

<table>
<thead>
<tr>
<th>(p\text{H})</th>
<th>Metal Ion.</th>
<th>(p\text{H})</th>
<th>Metal Ion.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>(\text{Sn}^{++}, \text{Fe}^{+++}, \text{Zr}^{+++})</td>
<td>7</td>
<td>(\text{Fe}^{++})</td>
</tr>
<tr>
<td>4</td>
<td>(\text{Th}^{+++})</td>
<td>8</td>
<td>(\text{Co}^{++}, \text{Ni}^{++}, \text{Cd}^{++})</td>
</tr>
<tr>
<td>5</td>
<td>(\text{Al}^{+++})</td>
<td>9</td>
<td>(\text{Ag}^{+}, \text{Mn}^{++}, \text{Hg}^{++})</td>
</tr>
<tr>
<td>6</td>
<td>(\text{Zn}^{++}, \text{Cu}^{++}, \text{Cr}^{+++})</td>
<td>11</td>
<td>(\text{Mg}^{++})</td>
</tr>
</tbody>
</table>

One of the easiest, and also a widely employed, separation is that of ferric iron from magnesium. This can be readily effected, as we have just seen, by the use of ammonium chloride–ammonium hydroxide buffer mixture. By proper adjustment of the \(p\text{H}\) of the solution it is possible to separate ferric iron and aluminium from zinc, manganese, nickel, cobalt, and the alkaline earths. This regulation of \(p\text{H}\) is achieved by the addition of the appropriate buffer mixture. It is evident from the above table that some separations will be much more
difficult than others: thus the separation of aluminium and chromium is an example of a difficult separation. The use of ammonia solution is not always satisfactory, as it tends to produce, particularly in the case of the trivalent metals, gelatinous precipitates, which are difficult to filter and wash, and also have a marked tendency to adsorb other cations present in solution. For this reason other reagents are employed for the separation of trivalent ions from divalent ions: a few examples will be mentioned below. Reference must, however, be made to the use of the organic bases, such as phenyl-hydrazine, aniline, pyridine, quinoline, etc. Thus phenyl-hydrazine is particularly valuable for separating aluminium from ferrous iron; only the former is precipitated as the hydroxide. The other organic bases are useful in the separation of the rare earths.

In the basic acetate method a buffer solution consisting of acetic acid with sodium or ammonium acetate is employed. The acetates of such weak bases as ferric iron are hydrolysed in hot solution and are completely precipitated as basic acetates; the acetates of the strong bases of the divalent metals are much less hydrolysed and, if the pH is adequately controlled, are not precipitated. The method is quite satisfactory for the separation of ferric iron from divalent metals such as zinc, manganese, cobalt, nickel, and copper; it is fairly satisfactory for mixtures of iron and aluminium, but not so suitable for aluminium alone; it is inapplicable in the presence of chromium.

\[
\text{Fe(C}_2\text{H}_3\text{O}_2)_3 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2\text{C}_2\text{H}_3\text{O}_2 + \text{Fe(OH)}_3 \cdot \text{C}_2\text{H}_3\text{O}_2
\]

A modification is to use a benzoic acid-ammonium benzoate buffer mixture, when a good separation of ferric iron, aluminium, and chromium from the divalent metals is claimed.

Suspensions of carbonates (e.g., of barium, lead, and cadmium) and of oxides (e.g., of zinc, magnesium, and mercury) have been used for the same purpose, since they may be regarded as exerting a buffer action. Their applications are, however, limited; mention may be made of the use of barium or cadmium carbonates for the separation of the trivalent metals of Group IIIA from the divalent metals of Group IIIB.

I. 62. Organic precipitants.—A number of organic compounds are available which combine with inorganic ions or compounds to form sparingly soluble and often coloured compounds. With cations, the metal is held either by primary valencies or by co-ordinate links, or by both. These compounds usually have high molecular weights, so that a small amount of the ions will yield a relatively large amount of the precipitate. The ideal organic precipitant should be specific in character, i.e., it should give a precipitate with only one particular ion. In few cases, however, has this ideal been attained; it is more usual to find that the organic reagent will react with a group of ions, but frequently by a rigorous control of the experimental conditions it is possible to precipitate only one of the ions of the group. Sometimes the precipitated organic compound may be weighed after drying at a suitable temperature; in other cases the composition is not quite definite and the substance is converted by ignition to the oxide of the metal; in a few instances, a volumetric method is employed which utilises the quantitatively precipitated organic complex. Examples of each of these will be given below.
A. Dimethylglyoxime. This reagent (I) was discovered by L. Tschugaeff in 1905 and was applied by O. Brunek in 1907 for the determination of nickel in steel. It gives a bright red precipitate II or \( \text{Ni(C}_4\text{H}_7\text{O}_2\text{N}_2\text{)}_2 \) with nickel salt solutions; precipitation is usually carried out in ammoniacal solution or in a buffer solution containing ammonium acetate and acetic acid. The complex is weighed after drying at 110–120°C. A slight excess of the reagent exerts no action on the precipitate, but a large excess should be avoided because: (a) of the possible precipitation of the dimethylglyoxime itself due to its low solubility in water* and (b) the increased solubility of the precipitate in water–alcohol mixtures.* The interference of iron, aluminium, or bismuth is prevented by the addition of a soluble tartrate or citrate; when much cobalt, zinc, or manganese is present, precipitation should take place in a sodium acetate, rather than an ammonium salt, buffer.

Solutions of palladium (II) salts give a characteristic yellow precipitate in dilute hydrochloric or sulphuric acid solution; the composition is similar to that of nickel, viz., \( \text{Pd(C}_4\text{H}_7\text{O}_2\text{N}_2\text{)}_2 \), and the precipitate can be dried at 110–120°C and weighed. The precipitate is almost insoluble in hot water, but dissolves readily in ammonia and cyanide solutions. Gold is reduced to the metal by the reagent, and platinum (if present in appreciable quantity) is partially precipitated either as a greenish complex compound or as the metal upon boiling the solution. The precipitation of palladium is not complete in the presence of nitrates in solution.

Bismuth, as nitrate or chloride, when treated with the reagent and made strongly alkaline with ammonia solution, gives an intense yellow voluminous precipitate; sulphate and tartrate interfere with this sensitive test for bismuth.

Dimethylglyoxime is only slightly soluble in water (0.40 g. per litre), consequently it is employed as a 1 per cent solution in alcohol. The sodium salt of dimethylglyoxime \( \text{Na}_2\text{C}_4\text{H}_6\text{O}_2\text{N}_2\cdot9\text{H}_2\text{O} \) is available commercially: this is soluble in water and may be employed as 2–3 per cent aqueous solution.

\( \alpha \)-Furildioxoxime (III) has been proposed for the determination of nickel. It gives a red precipitate with nickel salts in ammoniacal

* These possible errors may be avoided by employing disodium dimethyl glyoxime, which is soluble in water—see below.
solution. The complex is less soluble than nickel dimethylglyoxime, and has a smaller nickel content, thus giving a larger weight of precipitate for a given weight of nickel. The great advantage of α-furildioxime is its solubility in water, which precludes the possibility of contaminating the precipitate of the nickel derivative with the free reagent. A 2 per cent aqueous solution is normally used. The reagent is, however, expensive.

B. Cupferron (ammonium salt of N-nitroso-N-phenylhydroxylamine, IV).* This reagent, the ammonium salt of nitrosophenylhydroxylamine, forms insoluble compounds with a number of metals in both weakly acid and strongly acid solutions. It is most useful when employed in strongly acid solutions (5–10 per cent by volume of hydrochloric or sulphuric acid) and then precipitates ferric iron, vanadium, titanium, zirconium, and tin, separating these elements from aluminium, beryllium, chromium, manganese, nickel, cobalt, zinc, uranium (VI), and the alkaline earths. The presence of tartrate and oxalate has no effect upon the precipitation of metals by cupferron.

Cupferron is often used for the removal of an undesired element in the determination of other metals, e.g., iron in the determination of aluminium; also in solutions which have been previously subjected to electrolysis with the mercury cathode to separate, for example, titanium, vanadium, and zirconium.

The reagent is usually employed as a 6 per cent aqueous solution; this should be freshly prepared, since it does not keep satisfactorily for more than a few days. The solid reagent should be stored in amber bottles containing a few lumps of ammonium carbonate. Precipitation is always carried out in the cold, since cupferron is decomposed into nitrosobenzene on heating. Sufficient reagent is added to form the curdy precipitate of the metallic derivative of cupferron and to give a white flocculent precipitate of free nitrosophenylhydroxylamine (needles). Precipitates should be filtered as soon after their formation as possible, since excess of cupferron is not very stable in acid solution. Nitric acid solutions cannot be used for the precipitation, since oxidising agents destroy the reagent. The addition of macerated filter-paper assists the filtration of the precipitate and also the subsequent gradual ignition. The precipitates cannot be weighed after drying, but must be ignited to the corresponding oxide and weighed in this form. The ignition must be done cautiously in a large crucible with a gradual increase in temperature to avoid mechanical loss by gaseous compounds.

Neo-cupferron (ammonium salt of nitroso-naphthyl-hydroxylamine, V) forms less soluble and more bulky precipitates than cupferron. It may be employed for the direct separation of iron and copper in mineral and sea-waters without preliminary concentration.

C. 8-Hydroxyquinoline (oxine, VI). Oxine (C₅H₄ONO₃) forms sparingly soluble derivatives with metallic ions, which have the composition M(C₅H₄ONO₃)₂ if the co-ordination number of the metal is four (e.g.,

* The name cupferron was assigned to the compound by O. Baudisch in 1909, and is derived from the fact that the reagent precipitates both copper and iron. Cupferron precipitates iron completely in strong mineral acid solution, and copper is only quantitatively precipitated in faintly acid solution. The selectivity of the reagent is greatest in strongly acid solution, and hence the popular name cupferron is misleading.
Quantitative Inorganic Analysis

magnesium, zinc, copper, cadmium, lead, and indium), \( M(C_9H_6ON)_3 \) if the co-ordination number is six (e.g., aluminium, iron, bismuth, and gallium), and \( M(C_9H_6ON)_4 \) if the co-ordination number is eight (e.g., thorium and zirconium). There are, however, some exceptions, for example, \( TiO(C_9H_6ON)_2 \), \( MnO(C_9H_6ON)_3 \), \( WO_3(C_9H_6ON)_2 \), and \( UO_2(C_9H_6ON)_2 \). By proper control of the \( pH \) of the solution, by the use of complex-forming reagents and by other methods, numerous separations may be carried out: thus aluminium may be separated from beryllium in an ammonium acetate–acetic acid buffer, and magnesium from the alkaline-earth metals in ammoniacal solution.

8-Hydroxyquinoline is an almost colourless, crystalline solid, m. p. 75–76°; it is almost insoluble in water. The reagent is prepared for use in either of the following ways:

(i) Two grams of A.R. oxine are dissolved in 100 ml. of 2N-acetic acid, and ammonia solution is added dropwise until a turbidity begins to form; the solution is clarified by the addition of a little acetic acid. This solution is stable for long periods, particularly if it is kept in an amber bottle.

(ii) Two grams of A.R. oxine are dissolved in 100 ml. of methyl or ethyl alcohol (this reagent cannot be used for the determination of aluminium) or in acetone. This solution is stable for about ten days if protected from light. It is stated that the alcoholic solution may be employed in cases where precipitation occurs at a high \( pH \), and the acetic acid solution for precipitations at low \( pH \).

The following general conditions for conducting precipitations with 8-hydroxyquinoline may be given:

1. The reagent is added to the cold solution (or frequently at 50–60°) until the yellow or orange-yellow colour of the supernatant liquid indicates that a small but definite excess is present.

2. The precipitate is coagulated by a short period of heating at a temperature not exceeding 70°.

3. The precipitate may be filtered through paper or any variety of filtering-crucible.

4. The filtrate should possess a yellow or orange colour, indicating the presence of excess of precipitant. If a turbidity appears, a portion should be heated; if the turbidity disappears, it may be assumed to be due to excess of reagent crystallising out, and is harmless. Otherwise, more reagent should be added, and the solution filtered again.

5. Washing of the precipitate may often be effected with hot or cold water (according to the solubility of the metal “oxinate”) and is continued until the filtrates become colourless. The use of alcohol is permissible if it is known to have no effect upon the precipitate.

6. The washed precipitate may be dried at 105–110° C. (usually hydrated “oxinate”) or at 130–140° C. (anhydrous “oxinate”). In cases where prolonged heating at 130–140° C. is required, slight decomposition may occur. Frequently ignition to the oxide yields a more suitable form for weighing, but care must be exercised to prevent
loss, since many "oxinates" are appreciably volatile; it is usually best to cover the complex with oxalic acid (1-3 g.) and heat gradually. The determination may also be completed volumetrically by dissolving the precipitate in dilute hydrochloric acid and titrating with a standard solution of potassium bromate as detailed in Section III, 138.

D. α-Benzoinoxime (cupron, VII). This compound yields a green precipitate, CuC₁₂H₁₁₂O₆N, with copper in dilute ammoniacal solution, which may be dried at constant weight at 110°C. Ions which are precipitated by ammonium hydroxide are kept in solution by the addition of tartrate; the reagent is then specific for copper. Copper may thus be separated from cadmium, lead, nickel, cobalt, zinc, aluminium, and small amounts of iron.

From strongly acidic solutions α-benzoinoxime precipitates molybdate and tungstate ions quantitatively; chromate, vanadate, columbate, tannate, and palladium (II) are partially precipitated. The molybdate complex is best ignited at 500-525°C to MoO₃ before weighing; alternatively, the precipitate may be dissolved in ammonia solution and the molybdenum precipitated as lead molybdate, in which form it is conveniently weighed.

α-Benzoinoxime is a white, crystalline solid, m.p. 152°C, which is sparingly soluble in water but fairly soluble in alcohol. The reagent is employed as a 2 per cent solution in rectified spirit.

E. Salicylaldoxime (VIII). This compound is chiefly employed for the determination of copper: a greenish-yellow precipitate Cu(C₇H₆O₂N)₂ is obtained in the presence of acetic acid (the precipitation is complete at pH 2-6), which is weighed after drying at 100-105°C. Ferric iron is carried down with the copper complex in acetic acid solution and interferes seriously, but silver, cadmium, mercury, arsenic, and zinc have no effect. Salicylaldoxime reacts with many other ions, and has found application in the determination of lead, bismuth, zinc, nickel, and palladium. As with similar selective reagents (e.g., oxine), the pH of the solution is an important factor, particularly if it is desired to separate one divalent metal from another. Thus copper is completely precipitated at a pH of 2-6, nickel commences to precipitate at a pH of 3-3, and hence for the separation of copper from nickel the pH must be maintained between 2-6 and 3-3.

A bright yellow, insoluble basic salt is formed with bismuth ions in almost neutral solution, which must be ignited to the oxide Bi₂O₃ for weighing. Lead is quantitatively precipitated as a yellow complex PbC₇H₅O₂N at pH 8-9 or higher; the use of a strongly ammoniacal solution permits the separation of lead from silver, cadmium, and zinc. Palladium (II) is precipitated quantitatively as yellow Pd(C₇H₅O₂N)₂ from acid solution, and can thus be separated from platinum. Nickel may also be satisfactorily determined as the green complex Ni(C₇H₅O₂N)₂.

Salicylaldoxime is a white, crystalline solid, m.p. 57°C, which is sparingly soluble in water. The reagent is prepared by dissolving 1-0 g. of salicylaldoxime in 5 ml. of 95 per cent alcohol, and pouring
the solution slowly into 95 ml. of water at a temperature not exceeding 80° C.; the mixture is shaken until clear and filtered, if necessary. Another procedure, which by-passes the use of the expensive salicylaldoxime, is to add 2·22 g. of pure salicylaldehyde dissolved in 8 ml. of rectified spirit to 1·27 g. of A.R. hydroxylamine hydrochloride dissolved in 2 ml. of water: the resulting solution is diluted with 16 ml. of rectified spirit and poured slowly and with stirring into 225 ml. of water at 80° C.; when cold, the solution is filtered if necessary and stored in an amber bottle. The reagent decomposes in solution, and should not be kept for more than about three days.

$\checkmark$ F. $\alpha$-Nitroso-$\beta$-naphthol (IX). This organic reagent precipitates quantitatively cobalt, iron (III), palladium, and zirconium from slightly acid solutions; it precipitates partially tin, silver, bismuth, chromium (III), titanium, tungsten (VI), uranium (VI), and vanadium (V). The following elements are not precipitated: lead, cadmium, mercury, arsenic, antimony, beryllium, aluminium, nickel, manganese, zinc, calcium, and magnesium. The principal use of $\alpha$-nitroso-$\beta$-naphthol is in the separation of cobalt from large amounts of nickel after any ferric iron present has been removed. The red-brown, bulky precipitate obtained in dilute hydrochloric acid solution is reported to have the composition $\text{Co(C}_6\text{H}_5\text{O}_2\text{N}_2)_3$; but it is doubtful whether the complex is pure; careful ignition in the presence of oxalic acid gives a cobalt oxide to which the formula $\text{Co}_3\text{O}_4$ has been assigned, but this also is not perfectly pure, and should not be used except when dealing with minute amounts of cobalt. For larger amounts the cobalt oxide may (a) be reduced in hydrogen in a Rosé crucible and weighed as the metal, or (b) be treated with a few drops of concentrated nitric acid to convert it into the nitrate, the excess of nitric acid is expelled by evaporating cautiously, and then converted into the sulphate by at least two evaporations with concentrated sulphuric acid, followed by a few drops of water, and weighed as $\text{CoSO}_4$ after heating for a short time at 450–500° C. (very dull red heat); the cobalt sulphate solution may also be electrolysed and the resulting metal weighed.

$\alpha$-Nitroso-$\beta$-naphthol is a brown powder, m. p. 109° C.; it is insoluble in water. The reagent is prepared by dissolving 4 g. of $\alpha$-nitroso-$\beta$-naphthol in 100 ml. of glacial acetic acid and then adding 100 ml. of hot distilled water. The cold, filtered solution should be used immediately.

6. Phenyldihydantoic acid (X). This organic reagent will precipitate many metals of Group II (lead, bismuth, cadmium, copper, mercury, and antimony) as well as cobalt; nickel and iron are partially precipitated. Its chief application is to the determination of cobalt, which is precipitated in slightly ammoniacal solution: separation from arsenic, aluminium, chromium, manganese, zinc, titanium, tungsten, molybdenum, uranium, calcium, and magnesium can be effected under proper conditions. Nickel and iron, if present, will be co-precipitated; the co-precipitation may be diminished by the addition of citric acid.
The cobalt complex, which is of indefinite composition, may be cautiously ignited to the oxide (largely \( \text{Co}_3\text{O}_4 \)), and the cobalt content of the latter determined as under F.

Phenyldithiohydantoic acid is a solid, m. p. 158° C. The reagent is employed in the form of a 3 per cent aqueous or alcoholic solution.

**H. Nitron (XI).** The strong organic base 4 : 5-dihydro-1 : 4-diphenyl-3 : 5-phenylimino-1 : 2 : 4-triazole, which is named nitron, yields a sparingly soluble crystalline nitrate \( \text{C}_6\text{H}_5\text{N} = \text{N} \cdot \text{HNO}_3 \) in solutions acidified with acetic or sulphuric acid. Perchlorate, per-rhenate, and tungstate also form insoluble salts, and can be determined in a similar manner. Numerous other anions, including bromide, iodide, chlorate, thiocyanate, nitrite, and chromate, interfere, but may easily be removed by preliminary treatment. The results in the presence of chloride are generally high, possibly because of co-precipitation.

Nitron is a yellow, crystalline solid, m. p. 189° C., which is insoluble in water. The reagent consists of a 10 per cent solution in 5 per cent acetic acid; it should be filtered, if necessary, and the clear solution protected from light.

**I. Tannin.** Common tannin or tannic acid is essentially a colloidal suspension of negatively charged particles capable of flocculating the positively charged particles of certain inorganic compounds, such as the sols of metallic hydroxides. The separation of various elements depends to a large extent upon the proper adjustment of the pH of the solution.

This reagent in the form of a freshly prepared 3 or 10 per cent aqueous solution is useful for the separation of some of the so-called rarer elements. It may be employed inter alia for the quantitative determination of titanium and tungstates, for the separation of aluminium, chromium, iron, etc., from beryllium, and of niobium from tantalum. In most cases the flocculent precipitate of the tannin complex of the element is ultimately ignited and weighed as the oxide.

**J. The arsonic acids, \( R\text{-AsO(OH)}_2 \).** Alkyl and arylarsonic acids are of particular value for the precipitation of the quadrivalent metals (tin, thorium, titanium, and zirconium) of Group IV of the periodic system. Phenyl- \( (R = \text{C}_6\text{H}_5) \), \( n\)-propyl- \( (R = \text{C}_3\text{H}_7) \), and \( p\)-hydroxyphenyl- \( (R = \text{C}_6\text{H}_4\text{O}) \) arsonic acids are available commercially; the last-named is the least expensive (from Eastman Kodak).

Phenylarsonic acid, employed as a 10 per cent aqueous solution, will precipitate tin from fairly concentrated acid solutions, and separates it from all the common elements except titanium and zirconium. Thorium is precipitated quantitatively from acetic acid–ammonium acetate solution; rare earths and aluminium do not interfere, but titanium, zirconium, hafnium, and other quadrivalent ions are precipitated. The reagent provides a good separation of thorium from the rare-earth elements. The thorium phenylarsonate is dissolved in dilute hydrochloric acid, precipitated as the oxalate, ignited, and weighed as \( \text{ThO}_2 \).

\( n\)-Propylarsonic acid, employed as a 5 per cent aqueous solution, precipitates zirconium but not titanium in strongly acid solution. None of the common alloying elements, with the possible exception of
tin, which can be removed by ignition with ammonium iodide, interfere. The precipitate may be ignited to the oxide; heating is carried out first with a Bunsen and then with a Meker or Fisher burner.

- $p$-Hydroxyphenylarsonic acid, employed as a 4 per cent aqueous solution, gives precipitates with titanium and with zirconium in acid solution, and permits the separation of these elements from iron and all the common elements except tin and cerium (IV). Hydrogen peroxide prevents the precipitation of titanium, but does not affect the quantitative separation of zirconium.

K. Pyridine. Pyridine forms insoluble complexes with the thiocyanates of cadmium, copper, nickel, cobalt, zinc, and manganese; these have the general formula $\text{Me(CN)_3(C5H5N)n}$ ($n = 4$ for Co, Ni, and Mn; $n = 2$ for Cu, Cd, and Zn) (G. Spacu and co-workers, 1927-). In practice, alkali thiocyanate and a few ml. of pure pyridine are added to the neutral or very faintly acid solution of the metal ions. The complexes are readily filtered. They are washed first with water, then with dilute alcohol (both containing a little alkali thiocyanate and pyridine), followed successively by absolute alcohol and absolute ether, each containing a little pyridine. The precipitates are weighed after drying in a vacuum desiccator for 5-30 minutes at the laboratory temperature. The method is rapid, but, as is evident, many ions interfere. The results for manganese are not satisfactory because of the slight solubility of the complex in the wash solutions. The method is applicable in the presence of alkali and alkaline-earth metals and of magnesium; considerable quantities of ammonium salts must be absent.

L. Anthranilic acid (XII). The sodium salt of anthranilic acid precipitates in neutral or weakly acid solution zinc, cadmium, cobalt, nickel, copper, lead, silver, and mercury. Several of these salts, including the anthranilates of cadmium, zinc, cobalt, and copper, are suitable for the quantitative precipitation and gravimetric determination of these elements; the salts have the general formula $\text{M(C10H6N02)_2}$, and may be dried at 105-110°C. The precipitations must be carried out at a controlled pH range; in too strongly acidic solutions the precipitates will not form, while in too strongly basic solutions the organo-metallic complexes undergo decomposition. At present, sodium anthranilate is limited in use to the precipitation of a single substance from a relatively pure solution in which small amounts of ammonium, alkaline earths, and alkali-metal salts may be present. The reagent consists of a 3 per cent aqueous solution of pure sodium anthranilate.

M. Quinaldinic acid (XIII). This organic reagent gives insoluble complexes with copper, cadmium, zinc, manganese, silver, cobalt, nickel, lead, mercury, iron (II), palladium (II), and platinum (II), and insoluble basic salts with ferric iron, aluminium, chromium, beryllium, and titanium. The formation of insoluble quinaldinates is influenced by the pH of the solution. Thus copper quinaldinate $\text{Cu(C10H6N02)_2H2O}$ (after drying at 110-115°C) may be precipitated from relatively acidic
solutions, whilst under the same conditions the more soluble cadmium and zinc quinaldinates remain in solution. Complexing reagents may also assist in rendering the reagent more selective. The quinaldinates of copper, cadmium, and zinc are well-defined crystalline salts, which are readily filtered, washed, and dried.

The reagent consists of a 2 per cent aqueous solution of the acid or its sodium salt.

**Note on the recovery of quinaldic acid.** The reagent is expensive, but may be recovered after use. The precipitate and filtrate are best treated separately. The precipitate from a determination is acidified with dilute sulphuric acid and precipitated as copper quinaldinate with copper sulphate solution; the precipitate is filtered, washed, suspended in water, decomposed with hydrogen sulphide, filtered from cupric sulphide, the filtrate evaporated to dryness, and the residue recrystallised from glacial acetic acid. The pure acid has m.p. 156–156° C. The copper and cadmium complexes are decomposed with hydrogen sulphide and treated as above. Zinc quinaldinate is best dissolved in dilute hydrochloric acid or dilute sulphuric acid, the solution diluted until a precipitate just appears, and then precipitated with copper sulphate solution, etc.

**N. Pyrogallol (XIV).** This compound yields insoluble complex salts with bismuth and with antimony, and may be employed for the quantitative determination of these elements either alone or in the presence of arsenic, lead, cadmium, or zinc.

Pyrogallol is a white solid, m.p. 133–134° C., and is freely soluble in water. The reagent consists of a 3 per cent solution in air-free water; alternatively, the A.R. solid pyrogallol may be added to the solution for analysis.

**O. Ethylenediamine** (NH\(_2\)·CH\(_2\)·CH\(_2\)·NH\(_2\)). Ethylenediamine yields a complex cation with cupric ions:

\[
\text{Cu}^{++} + 2\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2 = [\text{Cu}(\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2)_2]^{++} = [\text{Cu en}_2]^{++}
\]

This reacts with the complex ions [HgI\(_4\)]\(^–\) or [CdI\(_4\)]\(^–\) to yield the insoluble complex salts [Cu en\(_2\)][HgI\(_4\)] and [Cu en\(_2\)][CdI\(_4\)] respectively:

\[
\text{HgCl}_2 + 4\text{KI} = K_2[\text{HgI}_4] + 2\text{KCl}
\]
\[
K_2[\text{HgI}_4] + [\text{Cu en}_2]\text{(NO}_3\text{)}_2 = [\text{Cu en}_2][\text{HgI}_4] + 2\text{KNO}_3
\]

The complex salts are insoluble in water, 95 per cent alcohol, and ether, and hence may be employed in the rapid determination of mercury, cadmium, and copper respectively (G. Spacu and co-workers, 1929). The mercury complex is stable in air and in a vacuum, and its precipitation is unaffected by the presence of ammonium salts; a valuable rapid method is thus available for the determination of mercury. The cadmium complex has similar properties, but is slightly soluble in the presence of ammonium salts or in strongly ammoniacal solution; the experimental details for the determination of cadmium are similar to those given for mercury (Section IV, 160) except that precipitation is effected in neutral solution with reagent (a) (see below).
The process also permits of a quantitative separation of copper and mercury. The acid solution of both metals is treated with ammonia solution until nearly neutral and is then rendered alkaline with ethylenediamine. The solution is heated to boiling, treated with excess of potassium iodide and copper ethylenediamine nitrate solution and allowed to cool; the mercury complex is filtered off and weighed (Section IV, 160). The copper is determined in another portion of the solution as in Section IV, 19F.

The reagent may be prepared by either of the following methods:

(a) Heat an aqueous solution containing 1 part of cupric nitrate and 2 parts of ethylenediamine on a water-bath until a crust forms on the surface of the violet-blue solution. Allow to cool, filter off the separated crystals of $\text{Cu en}_2([\text{NO}_3]_2\cdot 2\text{H}_2\text{O}$ at the pump, and wash them several times with alcohol, followed by ether. A concentrated solution of this salt is used for precipitations.

(b) Treat a solution of cupric sulphate with an aqueous solution of ethylenediamine (five to six times the theoretical quantity) until the dark blue-violet coloration, due to the $[\text{Cu en}_2]^{++}$ ion, appears and does not increase in intensity upon further addition of ethylenediamine. The presence of excess of the latter in the reagent has no harmful influence. Here the reagent consists of a solution of $[\text{Cu en}_2]\text{SO}_4$, and is as satisfactory as (a) for determinations of mercury.

P. 8-Hydroxyquinaldine (XV). The reactions of 8-hydroxyquinaldine are, in general, similar to 8-hydroxyquinoline (6), but unlike the latter it does not produce an insoluble complex with aluminium. In acetic acid-acetate solution precipitates are formed with bismuth, cadmium, copper, ferrous and ferric iron, chromium, manganese, nickel, silver, zinc, titanium ($\text{TiO}^{++}$), molybdate, tungstate, and vanadate. The same ions are precipitated in ammoniacal solution with the exception of molybdate, tungstate, and vanadate, but with the addition of lead, calcium, strontium, and magnesium; aluminium is not precipitated, but tartrate must be added to prevent the separation of aluminium hydroxide.

8-Hydroxyquinaldine (2-methyl-oxine) is a pale yellow, crystalline solid, m. p. 72° C.; it is insoluble in water, but readily soluble in hot alcohol, benzene, and ether. The reagent is prepared by dissolving 5 g. of 8-hydroxyquinaldine in 12 g. of glacial acetic acid and diluting to 100 ml. with water: the solution is stable for about a week.

Preparation. In view of the present high cost of the reagent, experimental details for its preparation are given. Dissolve 55 g. of o-aminophenol and 25 g. of o-nitrophenol in 100 g. of concentrated hydrochloric acid contained in a three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. Add 40 g. of re-distilled crotonaldehyde, with stirring, over a period of 45 minutes. Heat the mixture, with stirring, on the steam-bath for 6 hours and then allow to stand overnight. Remove the excess of o-nitrophenol (about 14 g.) by steam distillation from the acid solution. Nearly neutralise the residue with 6N-sodium hydroxide solution, saturated with sodium carbonate and steam distil. The yield of crude 8-hydroxyquinaldine (2-methyl-oxyline) is about 30 g. Purify the crude product by distillation under reduced pressure (water-pump), and re-crystallise twice from 60 per cent alcohol (6 ml. per gram). The recrystallised product has m. p. 72° C.
Evolution or volatilisation methods depend essentially upon the removal of volatile constituents. This may be effected in several ways: (i) by simple ignition in air or in a current of an indifferent gas; (ii) by treatment with some chemical reagent whereby the desired constituent is rendered volatile; and (iii) by treatment with a chemical reagent whereby the desired constituent is rendered non-volatile. The volatilised substance may be absorbed in a weighed quantity of a suitable medium when the estimation is a direct one, or the weight of the residue remaining after the volatilisation of a component is determined, and the proportion of the constituent calculated from the loss in weight; the latter is the indirect method. Examples of each of these procedures are given in the following paragraphs; full experimental details will be found in Chapter IV.

The determination of superficially bound moisture or of water of crystallisation in hydrated compounds may be carried out simply by heating the substance to a suitable temperature and weighing the residue (see Section VI, 5 for a method involving the use of the Karl Fischer reagent). It is assumed, of course, that the substance does not decompose upon heating. The water may also be absorbed in a weighed quantity of an appropriate drying agent, such as anhydrous calcium chloride or magnesium perchlorate.

The determination of carbon dioxide in carbonate-containing materials may be effected by treating the sample with excess of acid and absorbing the carbon dioxide in alkaline absorbent, such as soda lime, soda lime-asbestos, or sodium hydroxide-asbestos ("ascarite"). The gas is completely expelled by heating the solution and by passing a current of purified air through the apparatus; it is, of course, led through a drying agent to remove water vapour before passing to the carbon-dioxide-absorption apparatus. The gain in weight of the latter is due to carbon dioxide.

In the determination of carbon in steels and alloys, the substance is burnt in pure oxygen in the presence of catalysts and the carbon dioxide absorbed as in the previous example. Precautions are taken to remove other volatile constituents such as sulphur dioxide. This method is employed in the determination of carbon and hydrogen in organic compounds; the sample is burnt in a controlled stream of oxygen, and the water and carbon dioxide are absorbed separately in an appropriate absorbent, e.g., in calcium chloride saturated with carbon dioxide and in soda lime (or "sofnolite"—see Section IV, 76).

A similar determination is the estimation of ammonia. By heating an ammonium compound with excess of caustic alkali, ammonia is quantitatively evolved and is absorbed in a measured excess of a standard solution of an acid. The excess of the latter is then estimated by titration with standard alkali.

\[ (\text{NH}_4)_2\text{SO}_4 + 2\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{NH}_3 \]

This method may be adapted to the determination of nitrogen in many, but not all, complex organic compounds and to substances containing nitrogen in the organic form. The latter are heated with excess of concentrated sulphuric acid, preferably in the presence of a catalyst such as selenium oxychloride or copper sulphate, whereby the organic
nitrogen is converted into ammonium bisulphate. Some potassium sulphate is usually added to raise the boiling point of the acid and thus accelerate the conversion. The acid is then neutralised, and the ammonia liberated with alkali as above. This is the Kjeldahl method for the determination of nitrogen.

Some elements, such as sodium and potassium, may be determined in solution or when combined by evaporating to dryness with sulphuric acid; the residual sulphate is then weighed:

\[ 2\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HNO}_3 \]

Interfering metals must, of course, be removed first.

An example of a related kind is the determination of pure silica in an impure ignited silica residue. The latter is treated in a platinum crucible with a mixture of sulphuric and hydrofluoric acids; the silica is converted into the volatile silicon tetrafluoride:

\[ \text{SiO}_2 + 4\text{HF} \Rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \]

The residue consists of the impurities, and the loss in weight of the crucible gives the amount of pure silica present.

**ELECTRO-ANALYTICAL METHODS**

I. 64. Theory of electro-analysis.—In electro-analysis the element to be determined is deposited electrolytically upon a suitable electrode. Filtration is thus avoided, and co-precipitation, if the experimental conditions are carefully controlled, is very rare. The method, when applicable, has many advantages, and we shall therefore study the theory of the process in order to understand how and when it may be applied.

Electro-deposition is controlled by Ohm's law and by Faraday's two laws of electrolysis (1833-34). The latter state:

(1) The amounts of substances liberated at the electrodes are proportional to the quantity of electricity which passes through the solution.

(2) The amounts of different substances which are deposited, or liberated, by the same quantity of electricity are proportional to their chemical equivalents.

It follows from the second law that when a given current is passed in series through solutions containing, say, copper sulphate and silver nitrate respectively, then the weights of copper and silver deposited will be in the ratio of their equivalents, viz., \(107.88 : 63.57/2\).

Ohm's law expresses the relation between the three fundamental quantities, current, electromotive force, and resistance.

The current \(C\) is directly proportional to the electromotive force \(E\) and inversely proportional to the resistance \(R\), i.e.,

\[ C = E/R \]

**Electrical units.** The unit of current is called the ampere, and is defined as that current which, flowing for one second, will cause the deposition of 1.11800 mg. of silver, or 0.3294 mg. of copper, from solutions of their respective salts.

The unit of electrical resistance is the ohm. The International ohm is the resistance at 0° C. of a column of mercury, of uniform cross-section, 106.3 cm. long, and weighing 14.8521 g.
The unit of electromotive force (e.m.f.) is termed the volt, and is the difference of electrical potential required to maintain a current of 1 amp. through a system having a resistance of 1 ohm.

The unit quantity of electricity is the coulomb, and is defined as the quantity of electricity passing when 1 amp. flows for 1 second. Each coulomb will deposit 1.11800 mg. of silver, or 0.3294 mg. of copper.

The weight of an element liberated by the passage of 1 coulomb of electricity (or 1 amp. for 1 second) is called the electrochemical equivalent of the element. The equivalent weight of silver is 107.88, hence 107.88/0.0011180, i.e., 96,494 coulombs will be required to liberate 1 g.-equivalent of silver. The value generally employed is 96,500 coulombs, and this is termed a faraday (F). The second law of electrolysis may be stated in the form that 1 faraday of electricity will liberate 1 g.-equivalent of any substance at each electrode.

I, 65. Decomposition potential.—If a small voltage of, say, 0.5 volt is applied to two smooth platinum electrodes immersed in a solution of M-sulphuric acid, then an ammeter placed in the circuit will at first show that an appreciable current is flowing. Its strength, as shown by the ammeter, decreases rapidly, and after a short time becomes virtually equal to zero. If the applied voltage is gradually increased, there is a slight increase in the current until, when the applied voltage reaches a certain value, the current suddenly increases rapidly with increase in the e.m.f. It will be observed, in general, that at the point at which there is a sudden increase in current, bubbles of gas commence to be freely evolved at the electrodes. The experiment may be carried out by means of the apparatus shown diagrammatically in Fig. I, 65, 1.

A storage battery C is connected across a uniform resistance wire AB, along which a contact maker D can be moved; the fall of potential between A and D can thus be varied gradually. Two smooth platinum electrodes are immersed in M-sulphuric acid in the cell E. V is a suitable voltmeter placed between the two electrodes across the cell; M is a milliammeter and F is a switch.

When the sliding contact is near to A only a small potential is applied to the electrodes of the cell; the fall of potential across the cell and the current flowing through it are read off on the instruments V and A respectively. The applied voltage is slowly increased by moving D towards B, and the readings in the voltmeter and ammeter noted after allowing a short time for the values to become steady. Upon plotting the current against the applied voltage, a curve similar to that shown in Fig. I, 65, 2 is obtained; the point D at which the current suddenly
increases is clearly shown, and in the instance under consideration is about 1.7 volts. The voltage at the point $D$ is termed the decomposition potential, and it is at this point that the evolution of both hydrogen and oxygen in the form of bubbles is first observed. We may define the decomposition potential of an electrolyte as the minimum external voltage that must be applied in order to bring about continuous electrolysis.*

If the current is broken after the e.m.f. has been applied, it will be observed that the reading on the voltmeter $V$ is at first fairly steady, and then decreases, more or less rapidly, to zero. The cell $E$ is clearly behaving as a source of current, and is said to exert a back or counter or polarisation e.m.f., since the latter acts in a direction opposite to that of the applied e.m.f. This back e.m.f. arises from the accumulation of oxygen and hydrogen at the anode and cathode respectively; two gas electrodes are consequently formed, and the potential difference between them opposes the applied e.m.f. When the primary current from the battery is shut off, the cell produces a moderately steady current until the gases at the electrodes are either used up or have diffused away; the voltage then falls to zero. This back e.m.f. is present even when the current from the battery passes through the cell and accounts for the shape of the curve in Fig. 1, 65, 2. It is evident that the minimum value of the counter e.m.f. may be computed, for it is equal to the algebraic difference of the electrode potentials which exist at the anode and cathode respectively. This calculation will be referred to again in the succeeding paragraphs.

Some results of decomposition potential measurements, made by Le Blanc in 1891-93, are collected in Table XXII.

**Table XXII.—Decomposition Voltages of $N$-Solutions Between Smooth Platinum Electrodes**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Decomp. Voltage</th>
<th>Substance</th>
<th>Decomp. Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO$_4$</td>
<td>2.55</td>
<td>NiCl$_2$</td>
<td>1.85</td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>2.09</td>
<td>ZnBr$_2$</td>
<td>1.80</td>
</tr>
<tr>
<td>CdSO$_4$</td>
<td>2.03</td>
<td>CoCl$_2$</td>
<td>1.78</td>
</tr>
<tr>
<td>Cd(NO$_3$)$_2$</td>
<td>1.98</td>
<td>Pb(NO$_3$)$_2$</td>
<td>1.52</td>
</tr>
<tr>
<td>CoSO$_4$</td>
<td>1.92</td>
<td>CuSO$_4$</td>
<td>1.49</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>1.88</td>
<td>AgNO$_3$</td>
<td>0.70</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>1.69</td>
<td>HBr</td>
<td>0.94</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>1.67</td>
<td>HI</td>
<td>0.52</td>
</tr>
<tr>
<td>H$_2$PO$_4$</td>
<td>1.70</td>
<td>NaOH</td>
<td>1.09</td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>1.65</td>
<td>KOH</td>
<td>1.67</td>
</tr>
<tr>
<td>HCl</td>
<td>1.31</td>
<td>NH$_4$OH</td>
<td>1.74</td>
</tr>
</tbody>
</table>

It will be observed that whereas the decomposition potentials of salt solutions vary considerably, those for the acids and alkalis, with the exception of the halogen acids, are all approximately 1.7 volts. It was therefore concluded that the same electrolytic process occurs with these acids and bases; this can only be the discharge of hydrogen and

* Strictly speaking, the voltage across the cell, measured by the voltmeter $V$, is greater than the decomposition potential by the quantity $cr$, where $c$ is the current flowing in amperes and $r$ is the resistance in ohms. However, since $c$ is very small and $r$ is not very large, the quantity $cr$ may be neglected, and the voltage measured on $V$ taken as the decomposition potential.
hydroxyl ions at the cathode and anode respectively leading to the liberation of hydrogen and oxygen.

\[ 2H^+ + 2e \rightleftharpoons H_2 \]
\[ 2OH^- \rightarrow 2e + 2OH \rightarrow H_2O + \frac{1}{2}O_2 \]

With the halogen acids in \( N \) solution, the halogen and not oxygen is liberated at the anode, since the discharge of the halogen can occur more readily than the hydroxyl ions.

**1, 66. Electrode reactions.**—In electro-analysis we are largely concerned with the electrolysis of salt solutions, and it is therefore proposed to study in some detail the reactions which take place at the electrodes. Let us consider the electrolysis of a molar solution of zinc bromide between smooth platinum electrodes. The application of a voltage will result in the deposition of zinc on the cathode (thus producing a zinc electrode) and bromine at the anode (thus producing a bromine electrode). The reaction at the cathode is:

\[ Zn^{++} + 2e \rightleftharpoons Zn \]

i.e., a reduction (Section I, 23), and that at the anode is:

\[ 2Br^- \rightleftharpoons Br_2 + 2e \]

i.e., an oxidation. Thus reduction occurs at the cathode and oxidation at the anode. We may calculate the potential at the cathode at 25° C. from the formula (Section I, 42; compare I, 47).

\[ E_{\text{cathode}} = E^{\circ}_{zn} + 0.0591 \log [Zn^{++}] = E^{\circ}_{zn} \]

since \([Zn^{++}] = 1\). At the anode:

\[ E_{\text{anode}} = E^{\circ}_{br_2} - \frac{0.0591}{1} \log [Br^-] = E^{\circ}_{br_2} - \frac{0.0591}{1} \log 2 \]

since \([Br^-] = 2\). The e.m.f. of the resultant cell will therefore be:

\[ E^{\circ}_{zn} - E^{\circ}_{br_2} - \frac{0.0591}{1} \log 2 = 0.76 - (-1.07) - 0.02 = 1.81 \text{ volts} \]

This value is in agreement with the observed decomposition potential (see Table XXII).

For a similar electrolysis of normal zinc sulphate solution, the reaction at the anode is:

\[ 2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e \]

for the hydroxyl ion is more easily discharged than the sulphate ion. An oxygen electrode is thus produced at the anode. The potential of a reversible oxygen electrode is a function of the \( pH \) of the solution, and has been shown to be given by the expression:

\[ E = E^{\circ}_{o_2} + 0.0591 \log [H^+] \]

\( E^{\circ}_{o_2} \) is 1.23 volts, and the oxygen potential of a solution normal with respect to hydrogen ions is accordingly 1.23 volts.

In general, it may be stated that the theoretical back or polarisation e.m.f. \( E_b \) is given by:

\[ E_b = E_{\text{cathode}} - E_{\text{anode}} \]
where $E_{\text{cathode}}$ and $E_{\text{anode}}$ are calculated as already described (Section I, 43).

I, 67. Overvoltage.—It has been found by experiment that the decomposition voltage of an electrolyte varies with the nature of the electrodes employed for the electrolysis and is, in many instances, higher than that computed from the difference of the reversible electrode potentials. The excess voltage over the calculated back e.m.f. is termed the overvoltage. The overvoltage may occur at the anode as well as at the cathode. The decomposition voltage $E_D$ is therefore:

$$E_D = E_{\text{cathode}} + E_{\text{o.c.}} - (E_{\text{anode}} + E_{\text{o.a.}})$$

where $E_{\text{o.c.}}$ and $E_{\text{o.a.}}$ are the overvoltages at the cathode and anode respectively.

The overvoltage at the anode or cathode is a function of the following variables:

1. The nature and the physical state of the metal employed for the electrodes.
2. The physical state of the substance deposited. If it is a metal, the overvoltage is usually small; if it is a gas, such as oxygen or hydrogen, the overvoltage is relatively great.
3. The current density employed. For current densities up to 0·01 amp./sq. cm., the increase in overvoltage is very rapid; above this figure the increase in overvoltage continues, but less rapidly.
4. The change in concentration, or the concentration gradient.

* The current density, C.D., is defined as the current per unit area of electrode surface. It is generally expressed in amperes per square centimetre ND, or per square decimetre (100 sq. cm.), ND₀₀.
existing in the immediate vicinity of the electrodes; as this increases, the overvoltage rises. The concentration gradient depends upon the current density, the temperature, and the rate of stirring of the solution.

As a rule, metals exhibit small overvoltage effects. Oxygen shows an overvoltage of about 0.45 volt at the anode in acid solution, and is of the order of 1 volt in alkaline solution on a smooth platinum surface with current densities of 0.02-0.03 amp. sq. cm. The hydrogen overvoltage is of great importance in electrolytic determinations and separations. The values in m-sulphuric acid are shown diagrammatically in Fig. 1, 67, 1. In alkaline solutions the hydrogen overvoltage is slightly higher (0.05-0.3 volt) than in acid solutions.

I, 68. Completeness of deposition.—Let us consider the variations in e.m.f. at the cathode during the deposition of a metal in an electrolytic determination. Let the ionic concentration at the commencement of the estimation be \( c_i \). For a bivalent metal, e.g., copper, the cathode potential at 25° C. will be:

\[
E^o_{\text{Cu}} + \frac{0.0591}{2} \log c_i = E^o_{\text{Cu}} + 0.0296 \log c_i \text{ volts}
\]

If the ionic concentration is reduced to one ten-thousandth of its original value (i.e., to secure an accuracy of 0.01 per cent in the determination), the new cathode potential will be:

\[
E^o_{\text{Cu}} + 0.0296 \log c_i 	imes 10^{-4}
\]

\[
= E^o_{\text{Cu}} + 0.0296 \log c_i + 0.0296 \log 10^{-4}
\]

\[
= (E^o_{\text{Cu}} + 0.0296 \log c_i) - 4 \times 0.0296
\]

\[
= \text{Potential at commencement of deposition} - 0.118 \text{ volt}
\]

This is independent of the value of \( c_i \), and hence whenever the ionic concentration is reduced to one ten-thousandth of its initial value (this may be regarded as the ultimate limit of the electro-analytical estimation, although for most purposes an accuracy of 0.1 per cent is regarded as sufficient), the potential is altered by 4 \( \times \) 0.0591/2 = 0.118 volt for a bivalent ion. For a univalent ion, the change is 4 \( \times \) 0.0591/1 = 0.236 volt, and for a tervalent ion it is 4 \( \times \) 0.0591/3 = 0.079 volt. Since the back e.m.f. is produced by a cathode metal acting as the negative pole of a cell, the positive pole being, say, oxygen, it follows that the back e.m.f. will become greater as the metal becomes more negative during the course of the analysis. Otherwise expressed, the decomposition potential increases as the deposition of the metal proceeds. For quantitative deposition the applied e.m.f. must equal or exceed the decomposition voltage when the concentration of the given cation is negligibly small (say 10^{-4} of the initial value).

It is important to know the conditions for the deposition of the metal in preference to hydrogen in an electrolysis. The condition for the deposition of the metal is evidently that the potential difference between the electrolyte and the cathode, \( E_{\text{solution, metal}} \), must be less than the reversible deposition potential of hydrogen plus the overvoltage of hydrogen (\( \alpha_H^+ \)) for the metal under consideration. The relationship may be expressed in several ways:

\[
E_{\text{solution, metal}} \leq (E_{\text{H}^+, H} + \alpha_H),
\]

\[
\leq (-E_{\text{H}^+, H} + \alpha_H),
\]

\[
\leq (0.059 pH + \alpha_H) \quad \text{(at 25° C.)}
\]
If the cathode potential, $E_{\text{metal, ion}}$, is substituted for $E_{\text{solution, metal}}$ the expression becomes:

$$E_{\text{metal, ion}} < (0.059 \, \text{pH} + \sigma_{\text{H}})$$

**1, 69. Electrolytic separation of metals.**—It will be clear from what has been stated in the preceding Section that the initial deposition potentials of two metals must differ by at least 0.25 volt for a virtually quantitative separation to be theoretically possible. This minimum value would require a very precise control of the potential drop at the cathode; for most practical purposes, the difference in potential should be at least 0.4 volt. (The procedure for controlled cathode potential is discussed in Section I, 71.) From an inspection of Table XXII it is apparent that certain metals can be separated electrolytically with great ease, for example, copper from zinc, nickel, cobalt or lead, silver from copper, etc. When, however, the standard potentials of the two metals differ only slightly, the electro-separation is more difficult. The obvious method is to alter the electrode potential of one of the metals in some way. This is most simply achieved by decreasing the ionic concentration of the ion being discharged by incorporating it in a complex ion of small instability constant (Section I, 12). The decomposition potential of the metal forming a complex ion is thus raised. Furthermore, the overvoltage at the small ionic concentration is also usually increased. A possible consequence of changing the electrode potential in this way is that a metal which in simple ionic solution is liberated at a lower voltage than another metal, may exhibit the reverse behaviour in a complex-forming medium.

Some results, largely due to Foerster (1906), for the deposition potentials ($= - E_{\text{cathode}}$) of some metals in simple and alkali cyanide solutions are given in Table XXIII.

**Table XXIII.**—Deposition Potentials $E_D$ of Some Metals in Simple and in Alkali Cyanide Solutions

<table>
<thead>
<tr>
<th>Metal</th>
<th>$E_D$ for 0.1M solutions of $M^{++}$ ions (volt).</th>
<th>Concentration of Excess of KCN per 0.1 Mol. of Simple Metallic Cyanide.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.2M.</td>
</tr>
<tr>
<td>Zn</td>
<td>+0.79</td>
<td>+1.03</td>
</tr>
<tr>
<td>Cd</td>
<td>+0.44</td>
<td>+0.71</td>
</tr>
<tr>
<td>Cu</td>
<td>-0.31</td>
<td>+0.61</td>
</tr>
</tbody>
</table>

An interesting application of these results is to the direct quantitative separation of copper and cadmium. The copper is first precipitated in acid solution; the solution is then neutralised with pure aqueous sodium hydroxide, potassium cyanide is added until the initial precipitate just re-dissolves, and the cadmium is deposited electrolytically. Another application is to the separation of copper and bismuth: these two metals cannot be separated electrolytically from solutions of their simple salts. If cyanide is added, the copper ions form a complex cuprocyanide, and the deposition potential is much more negative than before; the bismuth-ion concentration and the electrode potential are hardly affected and a separation from copper becomes
possible, the bismuth depositing first. The separation is improved if tartrate is also added.

I, 70. Character of the deposit.—The ideal deposit for analytical purposes should be coherent, dense, and smooth; in this form it is readily washed and the solution rinsed off without loss. Flaky, spongy, powdery, or granular deposits adhere only loosely to the electrode, and for this and other reasons should be avoided.

As a rule, more satisfactory deposits are obtained when the metal is deposited from a solution in which it is present as complex ions rather than as simple ions. Thus silver is obtained in a more adherent form from an argentocyanide solution than from silver nitrate solution. Nickel when deposited from solutions containing the complex ion [Ni(NH₃)₆]⁺⁺ is in a very satisfactory state for drying and weighing. Mechanical stirring often improves the character of the deposit, since large changes of concentration at the electrode are reduced, i.e., concentration polarisation is brought to a minimum.

Increased current density up to a certain critical value leads to a diminution of grain size of the deposit. Beyond this value, which depends inter alia upon the nature of the electrolyte, the rate of stirring, and the temperature, the deposits tend to become unsatisfactory. At sufficiently high values of the current density, evolution of hydrogen may occur owing to the depletion of metal ions near the cathode. If an appreciable evolution of hydrogen occurs, the deposit will usually become broken up and irregular; spongy and non-coherent deposits are generally obtained under such conditions. For this reason the addition of nitric acid or ammonium nitrate is often recommended in the determination of certain metals, such as copper; bubble formation is thus prevented. The nitrate ion reacts with the hydrogen as it is formed at the cathode:

\[
\begin{align*}
\text{NO}_3^- + 10\text{H}^+ + 8\varepsilon &= \text{NH}_4^+ + 3\text{H}_2\text{O} \\
\text{HNO}_3 + 4\text{H}_2 &= \text{NH}_3 + 3\text{H}_2\text{O}
\end{align*}
\]

For analytical purposes the current densities usually range between 0·1 and 0·5 amp. per sq. decimetre for electrolysis made in still electrolytes; somewhat higher values are, however, occasionally employed. Raising the temperature, say, to between 60° and 90° C. often improves the physical properties of the deposit. This is due to several factors, which include the decrease in resistance of the solution, increased rate of diffusion, and changed ionisation and overvoltage effects.

In practice, two methods of electrolysis are utilised. In the first method stationary electrodes are used and the solution is not stirred; small current densities must of necessity be applied in order to secure a coherent deposit, and the procedure is a slow one (slow electrolysis). In the second method, which is largely superseding the first, the solution is rapidly stirred (rapid electrolysis). Various devices are employed for stirring. An independent mechanical stirrer may be used, but it is more usual to have a rotating anode, which may consist, after Sand, of a platinum-wire-gauze cylinder surrounded by a similar (but stationary) cylinder, which constitutes the cathode, the intervening space being small (3–5 mm.). A very much higher current density may then be applied (\(\text{ND}_{100}\), i.e., a current density per 100 sq. cm., of 5–10 amps.) without seriously affecting the purity or the physical character of the
The stirring results in a liberal supply of metal ions always being present near the cathode, and consequently the current is principally used in the deposition of the metal or other plate. A considerable saving of time is thus effected, and this accounts for the popularity of the method. It must be emphasised that when the electrolysis is complete, the current must not be switched off as long as the electrodes are in the solution. If the current were broken, the counter e.m.f. would come into play, and this would cause part of the metallic deposit to pass back into solution.

I, 71. Electrolytic separation of metals with controlled cathode potential.—The decomposition voltage (or deposition potential) $E_D$ of an aqueous solution of an electrolyte is given by the expression (compare Section I, 67):

$$E_D = E_{\text{cathode}} + E_{\text{o.c.}} - (E_{\text{anode}} + E_{\text{o.a.}}) + cr$$

where $E_{\text{cathode}}$ is the reversible, single electrode potential between the cathode and the solution, $E_{\text{o.c.}}$ is the overvoltage at the cathode, $E_{\text{anode}}$ and $E_{\text{o.a.}}$ are the corresponding terms at the anode, $c$ is the current flowing in amperes, and $r$ is the resistance in ohms; $cr$ is the potential drop between the cathode and anode. In the common method of electro-analysis, a voltage slightly greater than $E_D$ is applied and the electrolysis is allowed to proceed without further attention, except perhaps to occasionally increase the applied voltage to maintain the current at approximately the same value. This process, termed constant current electrolysis, when applied to the separation of metals is limited to the separation of those metals below hydrogen in the electromotive series from those above hydrogen. Following the deposition of the first metal (the one lower in the series) hydrogen is evolved at the cathode, and as long as the solution remains acid the second metal is not deposited. This is exemplified by the separation of copper from nickel, and zinc from a sulphuric acid solution. If the second metal lies only slightly above the other in the electromotive series, separation is no longer possible unless the decomposition potentials can be displaced either through the formation of an appropriate complex ion or by other means (compare Section I, 69). The separation of such a mixture may be effected by the application of the controlled-cathode potential electrolysis (Sand, 1907; Lindsey and Sand, 1934–35, etc.). An auxiliary standard electrode (which may be a saturated calomel electrode) is inserted in the solution, and thus the voltage between the cathode and the reference half-cell may be measured. It is thus possible to isolate the effect at the cathode and to limit the potential at this electrode during the electrolysis to a definite value by decreasing the voltage applied to the cathode and anode. We have already seen (Section I, 68) that every ten-fold decrease in metal-ion concentration shifts the cathode potential $0.0591/n$ volt more negative at $25^\circ$ C. ($n$ is the valency of the ion). For an accuracy of 0.1 per cent, the concentration of the ion is reduced to $10^{-2}$ of the original value, consequently the potential will decrease by $3 \times 0.0591/n$ volt, i.e., 0.177 volt for a univalent ion, 0.088 volt for a divalent ion, etc. Thus by controlling the cathode potential with the aid of an auxiliary electrode, the separation of one metal from another lying somewhat higher in the electromotive series becomes possible. The manual control of the potential may become tedious except for occasional determinations, but the time may
be materially reduced by the use of high current densities; methods for
the automatic control of cathode potential have been developed and one
apparatus is described in Section IV, 88.

A simple circuit and apparatus for controlled cathode potential
electro-analysis is shown in Fig. I, 71, 1; this will serve to illustrate
the principles of the technique involved. The various components of
the apparatus are: a source of current, which may be a large
storage battery; a saturated calomel electrode; a voltmeter $P$ to
indicate the potential applied to the cell for the electrolysis; a
vacuum voltmeter or a potentiometer $V$; an adjustable resistance
$R$ capable of carrying current up to $10-15$ amps.; a platinum-gauze
cathode $C$; and a platinum-gauze anode $A$ which can be rotated with
the aid of a chuck and pulley. The
potential between the saturated
calomel electrode and the cathode
must be measured with an instrument which draws little or negligible
current from the reference cell: a
valve voltmeter is satisfactory. The total potential measured $E$ is equal
to the difference between the potentials of the calomel electrode and
the cathode:

$$E = E_{\text{cat., sat.}} - (E_{\text{cathode}} + E_{\text{o.c.}})$$

Since $E_{\text{cat., sat.}}$ is known, the electrode potential of the cathode can
be easily referred to the hydrogen scale. In order to prevent the
 cathode potential from exceeding a fixed value, it is simply necessary
to decrease the potential applied to the cathode and anode by increasing
the value of the resistance $R$. Thus in Fig. I, 71, 2, are plotted the
cathode-calomel potential $E$ and the electrolyzing current $C$ against
time for the deposition of copper from a solution containing about $0.4$ g.
of copper, about $0.2$ g. of tin, and $15$ per cent sulphuric acid. The
cathode potential became more negative rapidly at the commencement
of the electrolysis as the platinum-gauze electrode was covered with
copper and as the copper was deposited. When the potential had
fallen to $-0.35$ volt towards the saturated calomel electrode the applied
voltage had decreased, causing a decrease in the current. The applied
potential (to the anode and cathode) was reduced by increasing the
resistance $R$ so that at no time was the cathode more than $0.35$ volt
negative to the calomel electrode. Ultimately all the copper separates,
but the current never falls to zero owing to the minor cyclic side re-
actions of the stannous and stannic ions. It must be emphasised that
rapid stirring or rotation of the anode is essential; concentration
polarisation effects are thereby reduced and higher current densities
(with consequent decrease in the time required for the electro-analysis)
may be employed.
It may be noted that in evaluating the limiting cathode potential to effect the separation of one metal from another, a simple computation of the equilibrium potential from the Nernst equation (compare Sections I, 66 and I, 68) is not sufficient. The equilibrium potential must be increased by the overvoltage (or polarisation potential). The latter depends upon the rate of stirring and on the current density as well as upon the nature of the metal surface; in consequence, the limiting potential must be established more or less empirically.

Anodic re-oxidation of the metal if it can exist in more than one valency state or any reaction between the plated metal and the anodic oxidation products must be reduced to a minimum for trustworthy results, and also to minimise the time required for the deposition. This may be achieved by such methods as (i) the use of a reducing agent which will be oxidised in preference to the intermediate valency state, i.e., a depolariser, (ii) increasing the initial cathode potential to a value sufficient to reduce instantly to the metallic state more than half of the intermediate valency state before the latter has been stirred away from the immediate vicinity of the cathode, (iii) isolation of the anode by means of a porous cup or a membrane, and (iv) reduction of the anode potential to a value which will not oxidise the ion in the intermediate valency state.

I, 72. Internal electrolysis.—The term internal electrolysis was applied by H. J. S. Sand (1930) to electro-analysis in which an attackable anode is used and there is an external wire connexion between the cathode and anode so that electrolysis proceeds spontaneously without the application of an external e.m.f. The arrangement is, in effect, a short-circuited voltaic cell. It is a special case of controlled-cathode potential electro-analysis. Internal electrolysis has also been described as electro-analysis by the spontaneous discharge of a galvanic cell in which a solution of the alloy, etc., to be analysed constitutes the catholyte. The main usefulness of the method of internal electrolysis lies in the fact that it provides a method for the separation of a nobler metal from a baser one. The anode consists of a metal, such as lead.
or zinc, which is to remain in solution; all nobler metals will thus deposit on the cathode, which may be of platinum. To prevent the deposition of the anode metal, the concentration of its ions should always be maintained slightly higher in the anode than in the cathode compartment, which are separated by a parchment or other suitable (e.g., treated alundum) membrane. The metal being deposited must be lower in the electromotive series than the metal from which it is being separated.

Since platinum anodes are not employed, separations may be made in chloride solutions in the absence of an anodic depolariser. Iron does not interfere with the plating of metals from chloride or sulphate solutions because the anodes are shielded. The procedure is rapid, and may therefore be applied in routine analysis. The method is, however, subject to certain limitations. In general, its application is limited to the determination of small quantities of metals. Its greatest usefulness is for the separation of impurities from the bulk of the base metal, for example, bismuth and copper from lead. Frequently the method serves only for a preliminary separation. The cell will not function unless there is free and uninterrupted dissolution of the anode; the value of the anode potential must be such as to cause rapid and complete deposition of the metal being determined. For further details, the reader is referred to references 10, 11, 12, and 13 in the Selected Bibliography (Section 1, 78).

Internal electrolysis has been applied to such problems as the determination of small quantities of:

(i) silver in galena and in pyrites;
(ii) mercury in brass;
(iii) copper in steel;
(iv) bismuth and copper in lead or in galena; and
(v) cadmium in zinc.

I, 78. SEPARATION BY MISCELLANEOUS PHYSICAL METHODS

A. Extraction of solid mixtures by solvents. This method is based upon the dissolution of the desired constituent in some liquid, usually an organic solvent, in which the solubility of any other substances present is so small as to be negligible. Thus in one method for the separation of the alkaline earths, the metals are converted into the anhydrous nitrates, and use is made of the fact that calcium nitrate is soluble whilst strontium and barium nitrates are insoluble in absolute alcohol. After extraction of the calcium nitrate with alcohol, say, in a Soxhlet apparatus, the residue is converted into the chlorides by repeated evaporation with hydrochloric acid. Strontium chloride may then be extracted with absolute alcohol, and barium chloride remains behind.

Other examples include the separation of lithium chloride from sodium and potassium chlorides by extraction with normal butyl alcohol, amyl alcohol, a mixture of ether and absolute ethyl alcohol, acetone, or dioxan (diethylene dioxide), and the separation of sodium and potassium perchlorates by extraction of the soluble sodium salt with a mixture of equal volumes of ethyl acetate and normal butyl alcohol. Strontium may be separated from calcium by making use of the fact
that calcium nitrate is soluble in anhydrous acetone whilst strontium nitrate is insoluble.

**B. Extraction of solutions by solvents. Partition or distribution method.** A mixture of two substances in a given solvent may often be separated virtually completely if a solvent can be found, which is immiscible with the first, and in which one of the substances is readily soluble and the other practically insoluble. Thus if a mixture of ferric and aluminium chlorides in 6N-hydrochloric acid be shaken with ethyl ether saturated with hydrogen chloride, the ferric chloride passes largely into the ether layer. By repeating the extraction with fresh portions of ether, the separation may be made practically complete. The results for a number of chlorides are collected in Table XXIV below.

<table>
<thead>
<tr>
<th>Element</th>
<th>Per cent Extracted at Each Extraction</th>
<th>Element</th>
<th>Per cent Extracted at Each Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb (SbCl₅)</td>
<td>6</td>
<td>Fe (FeCl₃)</td>
<td>99</td>
</tr>
<tr>
<td>Sb (SbCl₅)</td>
<td>81</td>
<td>Hg (HgCl₂)</td>
<td>0-2</td>
</tr>
<tr>
<td>As (AsCl₅)</td>
<td>68</td>
<td>Mo (MoCl₅)</td>
<td>80-90</td>
</tr>
<tr>
<td>Cu</td>
<td>0-05</td>
<td>Te (TeCl₄)</td>
<td>34</td>
</tr>
<tr>
<td>Ga</td>
<td>97</td>
<td>Ti (TiCl₄)</td>
<td>90-95</td>
</tr>
<tr>
<td>Ge</td>
<td>40-60</td>
<td>Sn (SnCl₄)</td>
<td>17</td>
</tr>
<tr>
<td>Au (AuCl₃)</td>
<td>95</td>
<td>Sn (SnCl₄)</td>
<td>15-30</td>
</tr>
<tr>
<td>Ir (IrCl₄)</td>
<td>5</td>
<td>Zn</td>
<td>0-2</td>
</tr>
</tbody>
</table>

Al, Bi, Be, Ca, Cd, Cr, Co, Fe, Pb, Mn, Ni, Os, Pd, rare earths, Rh, Ag, Th, Ti, W, U, and Zr are not extracted.

The ethyl ether extraction method may be employed to separate ferric iron from elements like aluminium, chromium, cobalt, nickel, vanadium, molybdenum, and titanium, which accompany it in many alloys. The procedure is to evaporate the hydrochloric acid solution of iron, etc., which should be free from alkali chlorides (these are insoluble in ether-hydrochloric acid) and from substances that decompose ether (chlorine, nitric acid, etc.), to take up the residue with hydrochloric acid (sp. gr. 1·1), and to transfer it with the aid of this acid to a separating-funnel. The cold acid solution is extracted three times by shaking with ethyl ether: between each extraction the ether layer is allowed to separate before the lower layer is drawn off for re-extraction. The iron is removed from the ethereal extract by shaking it with water and drawing off the lower aqueous layer. Heat is generated by the mixing of the ether and ferric chloride-hydrochloric acid solution so that cooling the mixture under the tap or in ice is essential. The liberation of heat is considerably reduced by the use of concentrated hydrochloric acid saturated with ether for dissolving the syrupy residue of ferric chloride, etc. (100 ml. of hydrochloric acid, sp. gr. 1·19, dissolve 150 ml. of ethyl ether; if the sp. gr. of the acid is 1·1, only 30 ml. of ether is dissolved).

Improved results are obtained with the less-volatile di-isopropyl ether. In particular, the extraction of ferric chloride from aqueous hydrochloric acid solutions is more efficient for a wider range of acid
concentration (8·5–8·5N; the optimum concentration is 7·75–8·0N and the efficiency is 99·9 per cent after three extractions) than for ethyl ether, and furthermore, the volume changes of the isopropyl ether and aqueous layers are smaller. Satisfactory separations of iron from copper, cobalt, nickel, manganese, zinc, aluminium, chromium, quadrivalent vanadium, titanium, and sulphur (as sulphuric acid) can be obtained. Large amounts of quinquevalent vanadium are extracted; phosphoric acid and hexavalent molybdenum pass into the ether layer with ferric iron.

Gold chloride may also be extracted in a similar manner using ethyl acetate as solvent. An interesting application is to the determination of molybdenum in steel; the brown coloration produced by the formation of molybdenum thiocyanate is extracted with cyclohexanol or with diethyl ether (see Section V, 19).

The theory of the process is as follows. If a solute is shaken with two immiscible solvents, and its molecular state is the same in both, then it has been found that at any given temperature:

\[
\frac{\text{Concentration of solute in solvent } A}{\text{Concentration of solute in solvent } B} = \frac{C_A}{C_B} = \text{a constant} = K
\]

where \(K\) is the distribution or partition coefficient. Thus \(K\) for iodine distributed between carbon disulphide \((A)\) and water \((B)\) is about 410 at 18° C. The problem in practice is to determine what is the most efficient method for removing a substance quantitatively from solution. It can be shown that if \(W\) ml. of, say, an aqueous solution containing \(x_o\) g. of a substance be extracted \(n\) times with \(L\) ml. portions of a given solvent, then the weight of the substance \(x_n\) remaining in the water is given by the expression:

\[
x_n = x_o \left(\frac{K W}{K W + L}\right)^n
\]

where \(K\) is the distribution coefficient between water and the given solvent (compare Section I, 60). It follows, therefore, that the best method of extraction with a given volume of extracting liquid is to employ several fractions of the liquid rather than to utilise the whole quantity in a single extraction.

Let us take a particular example. Let us suppose that we shake 50 ml. of water containing 0·1 g. of iodine with 25 ml. of carbon tetrachloride. The distribution coefficient of iodine between water and carbon tetrachloride at the ordinary laboratory temperature is 1/85, i.e., at equilibrium the iodine concentration in the aqueous layer is 1/85th of that in the carbon tetrachloride layer. We will compute the weight of iodine remaining in the aqueous layer after one extraction with 25 ml. and also after, say, three extractions with 8·33 ml. of the solvent by application of the above formula. The former can be simply computed as follows. If \(x_1\) g. of iodine remains in the 50 ml. of water, its concentration is \(x_1/50\) g. per ml.; the concentration in the carbon tetrachloride layer will be \((0·1 - x_1)/25\) g. per ml. Hence:

\[
\frac{x_1/50}{(0·1 - x_1)/25} = \frac{1}{85}, \text{or } x_1 = 0·00230 \text{ g.}
\]
The concentration in the aqueous layer after three extractions with 8·33 ml. of carbon tetrachloride is given by:

\[ x_3 = 0.1 \left( \frac{1/85 \times 50}{(50/85) + 8.33} \right)^3 = 0.0000145 \text{ g.} \]

The extraction may therefore be regarded as virtually complete.

If the distribution coefficient is favourable, a separating-funnel may be employed; if it is comparatively small, some continuous form of extraction apparatus is to be preferred.*

**I. 74. ERRORS IN QUANTITATIVE ANALYSIS**

When a quantity is measured with the greatest exactness that the instrument, method, and observer are capable of, it is found that the results of successive determinations differ among themselves to a greater or lesser extent. The average value is accepted as the most probable. This may not always be the true value. In some cases the difference may be small, in others it may be large; the reliability of the result depends upon the magnitude of this difference. It is therefore of interest to enquire briefly into the factors which affect and control the trustworthiness of chemical analysis.

The absolute error of a determination is the difference between the observed or measured value and the true or most probable value of the quantity measured. The absolute error is a measure of the accuracy of the measurement. The accuracy of a determination may therefore be defined as the concordance between it and the true or most probable value. The relative error is the absolute error divided by the true or most probable value; it is usually expressed in terms of percentage or in parts per thousand. The true or absolute value of a quantity cannot be established experimentally, so that the observed result must be compared with the most probable value. With pure substances the quantity will ultimately depend upon the atomic weights of the constituent elements. Determinations of the atomic weights have been made with the utmost care, and the accuracy obtained far exceeds that attained in ordinary quantitative analysis; the analyst must accordingly accept their reliability. With natural or industrial products, we must accept provisionally the results obtained by analysts of repute using carefully tested methods. If several analysts determine the same constituent in the same sample by different methods, the most probable value, which is usually the average, can be deduced from their results. In both cases the establishment of the most probable value involves the application of the theory of probability and the concept of precision.

The agreement between a series of results is measured by computing their mean deviation. This is evaluated by determining the arithmetical mean of the results, then calculating the deviation of each individual measurement from the mean, and finally dividing the sum of the deviations, regardless of sign, by the number of measurements. The relative mean deviation is the mean deviation divided by the mean. This may be expressed in terms of percentage or in parts per thousand. An example will make this clear.

* See, for example, the author's *Text Book of Practical Organic Chemistry*, Second Edition, 1951 (Longmans, Green).
Example. The percentages of a constituent $A$ in a compound $AB$ were found to be 48.32, 48.36, 48.23, 48.11, and 48.38 per cent. Calculate the mean deviation and the relative mean deviation.

**Results.**

<table>
<thead>
<tr>
<th>Results</th>
<th>Deviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.32</td>
<td>0.04</td>
</tr>
<tr>
<td>48.36</td>
<td>0.08</td>
</tr>
<tr>
<td>48.23</td>
<td>0.05</td>
</tr>
<tr>
<td>48.11</td>
<td>0.17</td>
</tr>
<tr>
<td>48.38</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Mean deviation = \( \sqrt{0.04 + 0.08 + 0.05 + 0.17 + 0.10} = 0.11 \) per cent

Relative mean deviation = \( \frac{0.11}{48.28} \times 100 = 0.23 \text{ per cent} \)

**Precision** may be defined as the concordance of a series of measurements of the same quantity. The mean deviation or the relative mean deviation is a measure of precision. In quantitative analysis, the precision of measurements rarely exceeds 1 to 2 parts per thousand.

Accuracy expresses the correctness of a measurement, and precision the reproducibility of a measurement. Precision always accompanies accuracy, but a high degree of precision does not imply accuracy. This may be illustrated by an example.

Example. A substance was known to contain 49.06 ± 0.02 per cent of a given constituent $A$. The results obtained by two observers using the same substance and the same general technique were:

Observer 1. 49.01; 49.21; 49.08. Mean = 49.10 per cent.

Relative mean error = \( \frac{49.01 - 49.06}{49.06} \times 100 = 0.10 \text{ per cent} \)

Relative mean deviation = \( \frac{1}{3} (0.09 + 0.11 + 0.02) \times 100/49.10 = 0.15 \text{ per cent} \)

Observer 2. 49.40; 49.44; 49.42. Mean = 49.42 per cent.

Relative mean error = \( \frac{49.42 - 49.06}{49.06} \times 100 = 0.73 \text{ per cent} \)

Relative mean deviation = \( \frac{1}{3} (0.02 + 0.02 + 0.00) \times 100/49.42 = 0.03 \text{ per cent} \)

The analyses of observer 1 were therefore accurate and precise; those of observer 2 were unusually precise, but less accurate than those of observer 1. Some small source of constant error appears to be present in the results of 2.

I. 75. **Classification of errors.**—The errors which affect an experimental result may be conveniently divided into those of the determinate and the indeterminate kind.

Determinate or constant errors. These are errors which can be avoided, or whose magnitude can be determined. The most important of these are:

1. Personal errors.—These are due to factors for which the individual analyst is responsible; they form part of the "personal equation" of an observer. Examples are: the inability of some persons to judge colour changes sharply in titrations, which may result in a
slight overstepping of the end point; the persistent use of an off-centre position in observing the swings of a balance pointer.

2. Instrumental and reagent errors.—These arise from the faulty construction of balances, the use of uncalibrated or improperly calibrated weights, volumetric apparatus, and other instruments; the attack of reagents upon glass-ware, porcelain, etc., resulting in the introduction of foreign materials; volatilisation of platinum at very high temperatures; and the utilisation of reagents containing impurities.

3. Errors of method.—These originate from such factors as incorrect sampling, incompleteness of a reaction, appreciable solubility of a precipitate, adsorption errors, co-precipitation and post-precipitation, and a difference between the end point and the stoichiometric point of a reaction.

Indeterminate or accidental errors. These errors manifest themselves by the slight variations that occur in successive measurements made by the same observer with the greatest care under as nearly identical conditions as possible. They are due to causes over which the analyst has no control, and which, in general, are so intangible that they are incapable of analysis. If a sufficiently large number of observations is taken, it can be shown that these errors follow the law of chance, the equation for which is:

\[ y = \frac{h}{\sqrt{\pi}} e^{-x^2} \]

where \( y \) is the frequency of occurrence of an error of the magnitude \( x \), and \( h \) is a constant, the value of which depends upon the character of the measurements and which affords a measure of their precision; \( \pi \) and \( e \) have their usual significance. The curve represented by this equation is called the probability curve or the error curve; it is shown in Fig. I, 75, 1. An inspection of this curve shows: (a) small errors occur more frequently than large ones; (b) large errors occur relatively infrequently; (c) positive and negative errors of the same numerical magnitude are equally likely to occur. It is evident from (c) that the best value to select for a series of observations is the arithmetical mean.

Another quantity that should be mentioned here is the probable error (or probable deviation). By the term probable error is meant, not the error most likely to occur, but a quantity of such magnitude that, in a given series of observations, it will be equally probable that there will be the same number of errors less than it as there are greater than it, the errors being arranged in order of their magnitude without regard to sign. It can be shown that the magnitude of the probable error of a single observation is given by the formula:

\[
\text{Probable error of a single observation} = 0.6745 \sqrt{\frac{d_1^2 + d_2^2 + \cdots + d_n^2}{n - 1}}
\]
where \( d_1, d_2, \text{ etc.}, \) refer to the deviations from the mean, and \( n \) is the number of determinations. The probable error of the arithmetical mean of a whole series of determinations is given by:

\[
\text{Probable error of the arithmetical mean} = 0.6745 \sqrt{\frac{d_1^2 + d_2^2 + \ldots + d_n^2}{n(n-1)}}
\]

In both calculations \( \frac{1}{\sqrt{n}} \) is usually substituted for \( 0.6745 \).

The problem sometimes arises of evaluating a series of results obtained by two or more analysts who have followed the same method to the best of their ability, or even different methods, provided all obvious errors inherent in the method have been eliminated. It is desirable for this purpose to employ a more reasonable or conservative estimate of the uncertainty in each analyst's results than that furnished by the probable error or deviation. If the individual results are available, the probable error of each analyst's mean results should be computed and then some reasonable multiple of it taken as an expression of the uncertainty in the result. No fixed multiple of the probable error is universally employed, but 3 and 5 are frequently used. For purpose of illustration we shall employ the factor 3 to denote the reasonable uncertainty in the arithmetical mean. This is then added to, or subtracted from, the arithmetical mean to obtain the reasonable limits represented by the result. Sets of results so treated are regarded as consistent if they show at least one common value within their reasonable limits. An example will make this clear. The table below contains the results obtained by two analysts for the percentage of a constituent A in a certain ore: the various quantities referred to in the preceding discussion have also been calculated.

<table>
<thead>
<tr>
<th>Analyst</th>
<th>Percentage of A Found</th>
<th>Arithmetical Mean</th>
<th>Probable Error of a Single Determination</th>
<th>Probable Error of the Arithmetical Mean</th>
<th>Reasonable Limit of the Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>68.25</td>
<td>68.30</td>
<td>0.04</td>
<td>0.032</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>68.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>68.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>68.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>68.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>68.20 68.21 68.22</td>
<td>68.24</td>
<td>0.027</td>
<td>0.007</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>68.27 68.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>68.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The first analyst's results lead to a value of 68.30 ± 0.048 (i.e., to limits of 68.252 and 68.348), and the second analyst's to 68.24 ± 0.02 (i.e., to limits of 68.22 and 68.26). The two results are consistent.
because they overlap within a small but definite portion of the limit range. The results would be reported:

1. $68.30 \pm 0.05$; 2. $68.24 \pm 0.02$.

I, 76. Minimisation of errors.—Determinate errors can often be materially reduced by one of the following methods:

(i) Calibration of apparatus and application of corrections. All instruments (weights, flasks, burettes, pipettes, etc.) should be calibrated, and the appropriate corrections applied to the original measurements. In some cases where an error cannot be eliminated, it is possible to apply a correction for the effect that it produces; thus an impurity in a weighed precipitate may be determined and its weight deducted.

(ii) Running a blank determination. This consists in carrying out a separate determination, the sample being omitted, under exactly the same experimental conditions as are employed in the actual analysis of the sample. The object is to find out the effect of the impurities introduced through the reagents and vessels, or to determine the excess of standard solution necessary to establish the end point under the conditions met with in the titration of the unknown sample. A large blank correction is undesirable, because the exact value then becomes uncertain.

(iii) Running a control determination. This consists in carrying out a determination under as nearly as possible identical experimental conditions upon a quantity of a standard substance which contains the same weight of the constituent as is contained in the unknown sample. The weight of the constituent in the unknown can then be calculated from the relation:

\[
\frac{\text{Result found for standard}}{\text{Result found for unknown}} = \frac{\text{Weight of constituent in standard}}{x}
\]

where $x$ is the weight of the constituent in the unknown.

In this connexion it must be pointed out that standard samples which have been analysed by a number of skilled analysts are commercially available. These include certain primary standards (sodium oxalate, potassium hydrogen phthalate, arsenious oxide, and benzoic acid) and ores, ceramic materials, irons, steels, steel-making alloys, and non-ferrous alloys. All of these are obtainable from the U.S. Bureau of Standards, Department of Commerce, Washington, D.C. Many of these are also available as the so-called "British Chemical Standards" and are supplied by the Bureau of Analysed Samples, Ltd., 234, Marton Road, Middlesbrough, England; these are, however, inferior to the samples of the U.S. Bureau of Standards, but are satisfactory for most practical purposes. A commendable enterprise is that of the firm of Ridsdale and Co., of 234, Marton Road, Middlesbrough, England, who supply what they term "Analyzed Samples for Students." These are analysed samples of irons, steels, non-ferrous alloys, and minerals, and are comparatively inexpensive. The results of analyses do not attain the high accuracy of the "British Chemical Standards," but are sufficient for use by students in the course of their training in the methods of analysis. The analyses do not appear on the bottle, but are given

* See references 14, 15, 16, 17, and 18 in Selected Bibliography Section I, 78, for a more detailed study.
on a separate sheet, which can be retained by the teacher. They are recommended for use in many of the analyses described in this book.

The National Physical Laboratory, of Teddington, Middlesex, England, in association with the Iron and Steel Institute, issue a limited number of "British-Standardised Steel Samples"; these comprise standard samples of steels for sulphur, phosphorus, carbon, and manganese respectively and a cast iron (for Si, P, Mn, and S). It is to be hoped that the range will be considerably extended in the future.

The standard samples are useful in revealing constant errors, for standardisation, and for comparatively rapid testing of the accuracy of a new method of analysis. A detailed list is given in the Appendix (Section A, 8).

(iv) Use of independent methods of analysis. In some instances the accuracy of a result may be established by carrying out the analysis in an entirely different manner. Thus iron may first be determined gravimetrically by precipitation as ferric hydroxide after removing the interfering element, followed by ignition of the precipitate to ferric oxide. It may then be determined volumetrically by reduction to the ferrous state, and titration with a standard solution of an oxidising agent, such as potassium dichromate or ceric sulphate. Another example that may be mentioned is the estimation of the strength of a hydrochloric acid solution both by titration with a standard solution of a strong base and by precipitation and weighing as silver chloride. If the results obtained by the two radically different methods are concordant, it is highly probable that the values are correct within small limits of error.

(v) Running of parallel determinations. These serve as a check on the result of a single determination and indicate only the precision of the analysis. The values obtained for constituents which are present in not too small an amount should not vary among themselves by more than three parts per thousand. If larger variations are shown, the determinations must be repeated until satisfactory concordance is obtained. Duplicate, and at most triplicate, determination should suffice. It must be emphasised that good agreement between duplicate and triplicate estimations does not justify the conclusion that the result is correct; a constant error may be present. The agreement merely shows that the accidental errors, or variations of the determinate errors, are the same, or nearly the same, in the parallel determinations.

I, 77. Significant figures and computations.—The term digit denotes any one of the ten numerals, including the zero. A significant figure is a digit which denotes the amount of the quantity in the place in which it stands. The digit zero is a significant figure except when it is the first figure in a number. Thus in the quantities 1·2680 g. and 1·0062 g. the zero is significant, but in the quantity 0·0025 kg. the zeros are not significant figures; they serve only to locate the decimal point and can be omitted by proper choice of units, e.g., 2·5 g. The first two numbers contain five significant figures, but 0·0025 contains only two significant figures.

Observed quantities should be noted with one uncertain figure retained. Thus in most analyses weights are determined to the nearest tenth of a milligram, e.g., 2·1546 g. This means that the weight is less than 2·1547 g. and more than 2·1545 g. A weight of 2·150 g. would signify that it has been determined to the nearest milligram, and that the
Quantitative Inorganic Analysis

weight is nearer to 2.150 g. than is either 2.151 g. or 2.149 g. The digits of a number which are needed to express the precision of the measurement from which the number was derived are known as significant figures.

There are a number of rules for computations with which the student should be familiar.

1. Retain as many significant figures in a result or in any data as will give only one uncertain figure. Thus a volume which is known to be between 20.5 ml. and 20.7 ml. should be written as 20.6 ml., but not as 20.60 ml., since the latter would indicate that the value lies between 20.59 ml. and 20.61 ml. Also, if a weight, to the nearest 0.1 mg., is 5.2600 g., it should not be written as 5.260 g. or 5.26 g., since in the latter case an accuracy of a centigram is indicated and in the former a milligram.

2. In rounding off quantities to the correct number of significant figures, add one to the last figure retained if the following figure (which has been rejected) is 5 or over. Thus the average of 0.2628, 0.2623, and 0.2626 is 0.2626 (0.2625 7 ),

3. In addition or subtraction, there should be in each number only as many significant figures as there are in the least accurately known number. Thus the addition

\[ 168.11 \pm 7.045 \pm 0.6832 \]

should be written

\[ 168.11 \pm 7.05 \pm 0.68 = 175.84 \]

The sum or difference of two or more quantities cannot be more precise than the quantity having the largest uncertainty.

4. In multiplication or division, retain in each factor one more significant figure than is contained in the factor having the largest uncertainty. The percentage precision of a product or quotient cannot be greater than the percentage precision of the least precise factor entering into the calculation. Thus the multiplication

\[ 1.26 \times 1.236 \times 0.6834 \times 248652 \]

should be obtained by using the values

\[ 1.26 \times 1.236 \times 0.683 \times 2487 \]

and the result expressed to three significant figures.

Where a large number of multiplications and divisions are to be made, the use of logarithms is recommended. Four-figure logarithm tables (Section A, 17) are sufficiently precise if interpolation is used; five-figure tables (Section A, 18) are preferable as interpolation is avoided. A 10-in. slide rule is accurate to about 0.25% per cent, and is useful in checking calculations. The Otis King's calculator * has an accuracy of about four times that of the 10-in. slide rule, and the rotary scales are 66 in. long; it is of convenient size for the pocket, and is very useful in the analytical laboratory.

SELECTED BIBLIOGRAPHY ON THE THEORY OF GRAMMETRIC ANALYSIS, ORGANIC REAGENTS, ELECTROANALYSIS AND RELATED SUBJECTS

CHAPTER II

EXPERIMENTAL TECHNIQUE OF QUANTITATIVE INORGANIC ANALYSIS

II, 1. BALANCE, WEIGHTS, AND WEIGHING

The analytical balance. One of the most important tools of the analytical chemist is the balance. It is therefore essential that the student should possess a proper understanding of its construction, use, and care. Balances differ in details of construction and in sensitivity. For most analytical purposes a balance with a maximum load of 100-200 g. and a sensitivity of 0.1 mg. is all that is usually required. The underlying principles of the theory and construction of the analytical balance will be discussed in the following paragraphs.

Essentially the balance may be regarded as a rigid beam or lever $BC$ having a central fulcrum and two arms of equal length; the two ends of the beam carry prism edges upon which the balance pans are supported by means of a suitable suspension (Fig. II, 1, 1). Let us suppose a body having the mass $M_1$ is placed on the left-hand pan of the balance; the pointer $P$ will be deflected to the right. To restore the pointer to its original position, bodies of known mass, termed "weights," are added to the right-hand pan. When equilibrium is restored, the principle of the lever requires that the following relation holds:

$$F_1 \times d_1 = F_2 \times d_2$$

where $F_1$ and $F_2$ are the forces acting upon the left-hand and right-hand prism edges respectively, and $d_1$ and $d_2$ are the respective distances of these from the central prism edge. Since the balance has equal arms, $d_1 = d_2$ and $F_1 = F_2$. Now the origin of the forces $F_1$ and $F_2$ lies in the attraction of gravity on the bodies in the left-hand and right-hand pans respectively, or, otherwise expressed,

$$F_1 = M_1g \text{ and } F_2 = M_2g$$

where $M_1$ and $M_2$ are the masses (or quantities of matter) in the left-hand and right-hand pans respectively, and $g$ is the acceleration due to gravity. Strictly speaking, $F_1$ and $F_2$ are the true weights in the two pans. But:

$$\frac{F_1}{F_2} = \frac{M_1g}{M_2g} = \frac{M_1}{M_2}$$

i.e., the ratio of the forces with which the bodies in the two pans are attracted by gravity is equal to the ratio of the two masses. In quantitative analysis we are interested only in the amount of matter in the body, i.e., in its mass: this is independent of $g$. At any given place, the weights are proportional to the masses. It has become
customary to employ the term "weight" synonymously with the mass, and it is in this sense that "weight" is employed in quantitative analysis. The analytical balance, strictly speaking, determines mass and not weight.

II. 2. Description of a typical analytical balance.—The essential features of a typical analytical balance are shown diagrammatically in Fig. II, 2, 1. The beam, which is constructed as rigidly and as light in weight as possible, is mounted at its centre upon a prism-form knife edge of agate or synthetic sapphire (corundum), which rests upon an agate or pure corundum plate (when the balance is in use) attached to the central beam support. The two terminal agate or pure corundum knife edges, fixed at equal distances from the central knife edge, each support a suspension (stirrup) from which the pans are hung, contact being made upon agate or pure corundum planes fixed to the stirrups. A long pointer is attached to the centre of the beam: this moves over a scale at the foot of the pillar and serves to indicate the deflection of the beam from the horizontal position when the balance is in operation. The balance is levelled with the aid of levelling-screws and a plumb line suspended from the column; in some balances a pair of spirit levels are provided. In the figure the whole of the beam is divided into 100 equal parts so that weight adjustments smaller than 10 mg. can be made readily by moving a small piece of platinum or gold wire (the rider) along the beam by means of the rider hook and rider carriage. For the beam graduated as shown in the figure a 5-mg. rider is employed; in many balances only the right half of the beam is graduated, a 10-
mg. rider is then necessary. A small weight is attached to the pointer; this serves to move the centre of gravity and thereby alter the sensitivity of the balance. The adjusting screws at the ends of the beam are employed for the purpose of adjusting the equilibrium position of the pointer so that it rests at the centre of the scale, thereby ensuring that the beam is horizontal when unloaded. In the better type of balances, the sensitivity and equilibrium position of the pointer are adjusted by means of a screw-nut device attached to the centre of the beam behind the rider bar and is shown diagrammatically in Fig. II, 2, 2; the screws at the end of the beam and on the pointer are then, of course, omitted.

In order to protect the knife edges from undue wear and from injury during the transfer of weights and objects, the balance is provided with a device whereby the moving parts can be raised so that the knife edges and planes are very slightly separated. This is operated by means of a large screw attached to the base of the balance, placed either centrally in the front of the base as shown in the figure, or, in some cases, in the centre of the left-hand side of the base. In many balances the beam arrest is combined with the pan arrest; in others, the pan-arrest mechanism is separately controlled by a push button (not shown in the figure).

II, 3. The requirements of a good balance.—These are:
(a) The balance must be accurate and give the same result in successive weighings.
   This requisite is obtained if the arms are of equal length, if the beam is rigid and does not bend appreciably under load, and if all the three knife edges lie in the same plane and are parallel to one another.
(b) The balance must be stable, that is, the beam must return to the horizontal position after swinging.
   This is attained by a proper adjustment of the centre of gravity.
(c) The balance must be sensitive, that is, 0.1 mg. should be readily detectable with average loads.

We may define the sensitivity of a balance as the angular deflection \( \alpha \) of the beam when a known small weight is added. It can be shown that the angle \( \alpha \) is determined by the excess of weight \( w \) producing the deflection \( \alpha \), the length of the balance arm \( d \), the weight of the beam \( W \), and the distance between the centre of gravity and the point of support of the beam \( h \). Expressed mathematically:

\[
\tan \alpha = \frac{wd}{Wh}
\]

Since \( \alpha \) is small, we may put \( \tan \alpha = \alpha \). The angular deflection of the beam is equal to the angular deflection of the pointer, and the latter is directly proportional to the number of divisions between the two points of rest on the scale at the foot of the beam. This leads directly to the usual definition of sensitivity, viz., the sensitivity \( * \) of a balance is the number of scale divisions that the rest point (or equilibrium point) is displaced by an excess of weight of 1 mg.

\*

† Also termed sensibility and sensitiveness.
It follows from the above expression that: (i) the longer the balance arms, the greater is the sensitivity; (ii) the lighter the beam, the greater is the sensitivity; and (iii) the smaller the distance between the point of suspension of the beam and the centre of gravity, the greater is the sensitivity. These conditions for maximum sensitivity are unfortunately conflicting with one another. Thus long arms are incompatible with minimum weight. The length of the arm is also limited by the fact that the time of swing of the pointer, which must not be excessive, increases with its length. It is also important that the balance beam be rigid in order that the centre of gravity, and therefore the sensitivity, should not change appreciably with the load. The centre of gravity must always be below the central knife edge, otherwise the balance will be in neutral or unstable equilibrium. The sensitiveness may be changed by moving the small weight attached to the pointer or, in some balances, by rotation of the nut on the screw attached to the central portion of the beam, which affect the position of the centre of gravity. In general, a balance adjusted to give a deflection of three to four scale divisions per milligram is quite satisfactory for macro-quantitative work.

(d) The period of oscillation should be short. This is necessary in order that weighings can be made rapidly. For this reason “short-arm” balances, which have a period of swing of 5–10 seconds, are almost universally employed in analytical practice. The so-called “long-arm” balances, although more sensitive, have a long time of swing (about 15 seconds) which renders weighing a tedious process.

Sensitivity and maximum load of a balance. In an ideal balance, free from friction and with a perfectly rigid beam, the sensitivity would be independent of the load. Most balances, however, exhibit a decreasing sensitivity with increasing load, and this change of sensitivity provides a good criterion as to the maximum safe load that a balance can carry. The criterion is: no greater load should ever be placed upon the balance pans than the load at which the sensitivity becomes 40 per cent of its maximum value (see Section II, 6 (a) and Fig. II, 6, 1).

II, 4. Weights, reference masses.—The determination of the mass of an object with an equal-arm balance necessitates the use of a series of reference masses termed weights. For scientific work, the international metric system of weights and measures is employed. The fundamental standard of mass is the international prototype kilogram, which is a mass of platinum-iridium alloy made in 1887 and deposited in the International Bureau of Weights and Measures near Paris. It represents as closely as possible the mass of 1000 g. of water at the temperature of its maximum density (4°C.). Authentic copies of the standard are kept by the appropriate responsible authorities* in the various countries of the world; these copies are employed for the comparison of secondary standards, which are used in the calibration of weights for scientific work. The unit of mass that is almost universally employed in laboratory work, however, is the gram, which may be defined as the one-thousandth part of the mass of the international prototype kilogram.

* The National Physical Laboratory (N.P.L.) in Great Britain, the Bureau of Standards in U.S.A., etc.
Multiples and sub-multiples of units in the metric system are indicated by the following prefixes:

- kilo = a thousand times; milli = a thousandth part, or 0.001;
- hecto = a hundred times; centi = a hundredth part, or 0.01;
- deca = ten times; deci = a tenth part, or 0.1.

The following weights are frequently encountered: kilogram (kg.), decigram (dg.), centigram (cg.), and milligram (mg).

An ordinary set of analytical weights contains the following: grams: 100, 50, 20, 10, 5, 2, 1, 1 (or 5, 2, 2, 1); milligrams: 500, 200, 100, 50, 20, 10, 5, 2, 2, 1. Weights smaller than 10 mg. are not actually used in weighing, and are therefore not really essential. In addition to the weights, a set includes two "riders," which are small weights of 5 or 10 mg. denomination, made of platinum, gold, or aluminium wire, for use on the beam of the balance. The weights from 1 g. upwards are generally constructed of polished brass; these are often plated with gold or platinum to avoid corrosion. Recently weights of stainless steel have been introduced. The fractional weights, from 0.5 g. downwards, are made of platinum, gold, aluminium, or tantalum; they are usually square in shape and have one corner turned up to facilitate handling. The nominal mass is stamped on each weight, the numbers indicating grams, fractions of a gram, or milligrams. Duplicate and triplicate weights are stamped with one or two asterisks. For handling the weights, a pair of forceps, frequently tipped with ivory or some similar material, is provided: on no account should weights be touched with the fingers.

All weights should be calibrated (Section II, 8). The values may change with time, and it is advisable to recalibrate the weights at least once a year.

II, 5. Care and use of the balance.—1. The balance should be placed upon a firm foundation which is as free from mechanical vibration as possible. The ideal foundation is a concrete or stone slab resting upon brick piers, which are either sunk into the ground or, if this is not practicable, into the stone or concrete flooring beneath the floorboards of the laboratory. If this is not possible, the balance should be placed upon a stout table or shelf and protected, when necessary, by shock-absorbing media, such as cork mats or sheet rubber under the table: anti-vibration tables, designed for balances, are available from most laboratory suppliers. It is best to keep the balance in a room separate from the laboratory in order to protect it from fumes. Its position should be such that the two arms are at the same temperature. Hence the balance should not be placed with one side near a window or radiator, or in direct sunlight, or in a position where it is likely to come into contact with draughts.

The balance should be level. This adjustment may be made with the aid of the levelling-screws.

2. When not in use, the balance beam and the pan supports should be raised so as to protect the agate prisms and planes. The doors of the balance should be kept closed as much as possible.

3. To release the balance, the beam and pans should be lowered very carefully and set swinging by fanning one pan gently with the hand, or by carefully turning the arresting screw. The beam should never be
set swinging by touching the pan with the forceps or with some other object, or by suddenly lowering it upon its prism edges.

4. Objects to be weighed must be allowed to attain the temperature of the balance before weighing is attempted, otherwise the air currents produced inside the balance case may introduce serious errors. If the object has been heated, sufficient time must be allowed for cooling. The time required to attain the balance-room temperature varies with the size, etc., of the object, but as a rule 30-40 minutes is sufficient.

5. Weights and the object to be weighed should always be placed in the centre of the pans.

6. During a weighing or upon any occasion when objects are being added to or removed from the pans, both the beam arrests and the pan supports must be raised so as to protect the prism-edges from injury. Always close the balance case when using the rider.

7. No chemicals or objects which might injure the balance pans should ever be placed directly upon them. Substances must be weighed upon suitable containers, such as watch glasses, small beakers, weighing-bottles, or crucibles. Liquids and volatile or hygroscopic solids must be weighed in a tightly closed vessel, such as a stoppered weighing-bottle.

8. The balance must not be overloaded (see Section II, 3 (d)).

9. Weights should be handled only with the forceps provided with the box.

10. Nothing must be left on the pans when the weighing has been completed. If any substance is spilled accidentally upon the pans or upon the floor of the balance-case, it must be removed at once. The pans should be lightly brushed periodically with a camel-hair brush to remove dust which may have collected.

11. If the balance requires adjustment, the teacher should be notified immediately.

II. METHODS OF WEIGHING

There are three methods of weighing, viz.,

(a) Direct weighing.
(b) Gauss's methods of double weighing.
(c) Borda's method of substitution.

Of these, method (a), in one of its various modifications, is most widely employed in quantitative analysis. It will therefore be discussed in some detail.

(a) Direct weighing. The object is placed on the left-hand balance-pan, and weights are added to the other pan until the beam returns to its original equilibrium position. The modifications of this method differ only in the procedure for determining the equilibrium position of the beam.

(i) Weighing by point of rest and sensitivity. The first step in any method of weighing is the determination of the equilibrium position of the beam when the pans are unloaded. The position of the beam is, of course, indicated by the position of the pointer on the scale. We shall call the equilibrium position the zero point when the pans are empty, and the point of rest when the pans are loaded.

Determination of the zero point. See that the balance is level; if
necessary, turn the levelling-screws at the base until the balance is suitably adjusted (spirit level or plumb-line). Note also whether the prism edges are in proper position with respect to their bearings, and also whether the pans are free from dust (the latter can be removed, if necessary, by means of a camel-hair brush). The rider should be placed on the zero graduation if the whole of the beam is graduated; if only the right half of the beam is graduated, the rider should be removed from the beam. The beam and pan arrests are lowered very carefully, and the beam set swinging either by fanning one pan gently with the hand or, more usually, by careful manipulation of the arresting control. The doors of the balance are then closed.

The pointer scale may be regarded as being graduated as shown in Fig. II, 2, 1, i.e., numbered from zero to twenty. It is convenient to have the pointer swinging about five to six divisions on either side of the centre mark (10) of the scale. The beam is allowed to make two or three swings, and then readings are taken to the nearest tenth of a division of the extreme positions of the pointer. An odd number of swings, usually three, is taken on the left-hand side and an even number, usually two, on the right-hand side. The eye of the observer should remain in the same position to avoid errors due to parallax. The two sets of observations are averaged separately, and the mean of their average taken. This mean value is the zero point.* The procedure is best made clear with the aid of an example. Five successive readings of the pointer might be:

\[
\begin{array}{ll}
\text{Left} & \text{Right} \\
(i) & 5.3 \\
(ii) & 5.7 \\
(iii) & 6.0 \\
\text{Average} & 5.7 \\
\end{array}
\]

\[
\begin{array}{ll}
\text{Average} & 15.1 \\
\text{Mean} = (5.7 + 15.1)/2 = 10.4 = \text{zero point.}
\end{array}
\]

After some practice, the zero point may be calculated from three successive readings of the extreme positions instead of five. If the zero point lies outside the positions 9 and 11, i.e., more than one division from the centre line of the scale, the student should ask the teacher to make an adjustment on the nuts attached to the ends of the beam or, for some balances, on the nuts upon a small lever attached to the centre of the beam.

The next step is the determination of the sensitivity of the balance. The sensitivity of a balance depends \textit{inter alia} upon the distance between the centre of gravity and the point of suspension of the beam (Section II, 3). Since most beams are not perfectly rigid, the distance, and consequently the sensitivity, will change with the load. Whether the sensitivity increases or decreases with increase of load depends upon the relative positions of the beam prism-edge and the pan prism-edges. The \textit{sensitivity} has already been arbitrarily defined as the number of scale

* For a mathematical justification of this procedure, see H. A. Fales and F. Kenny, \textit{Inorganic Quantitative Analysis}, 1939, pp. 85, 676. It must be realised that the beam swings about the prism edge like a compound pendulum and that the oscillations are damped, or shortened, by the friction in the bearings and by air resistance; consequently each swing will be slightly less in amplitude than the preceding one.
technique of quantitative analysis

Divisions that the point of rest is displaced by an excess of weight of 1 mg.*

The pans and beam are arrested, and the rider is placed exactly on the 1-mg. graduation of the beam. The beam is then set swinging and the rest point determined exactly as described above. Thus, if the zero point is 10-4 and the rest point with a load of 1 mg. is 6-3, then the sensitivity at this load is 1 mg. = 4-1 scale divisions, and the displacement of one division corresponds to 0.0010/4.1 = 0.0002 g. The sensitivity for a load of 10 g. is obtained by placing 10 g. in each pan and determining the rest point; the rider is displaced 1 mg. and the rest point again determined. The difference gives the sensitivity. Similar estimations are made for loads on each pan of 30, 40, 50, and 100 g. The results may then be plotted as shown in Fig. II, 6, 1. The sensitivity at any load can then be found by reference to the curve. Alternatively, a table may be constructed showing the sensitivity at various loads, and also the number of mg. corresponding to one scale division. Either the graph or the table should be placed in a conspicuous position in the balance-case.

Weighting by the method of swings. Having determined the zero point and the sensitivity at various loads, the actual weighing operation may be performed. The object is placed on the left-hand pan, and weights are added to the right-hand pan in systematic order. The beam and pans should be raised before an object or a weight is placed on the pans. A weight estimated to be slightly heavier than the object is removed from the box with the forceps and placed in the centre of the right-hand pan. The beam is lowered just enough to see which way the pointer moves; the beam is then raised. If the weight is too heavy, it is removed and the next smaller weight substituted for it. If the latter is too light, it is allowed to remain on the pan and the next lower weight added. This process is repeated in a systematic order until the gram weight is reached. The fractional weights are similarly added in order of decreasing denomination down to and including the 10-mg. weight. Here, particularly in the concluding stages, it will be necessary to lower the beam and pans completely in order to detect the inequality.

The final adjustment is made with the rider with the balance-case closed. For very accurate weighing, the rider is adjusted to the nearest mg., and the tenths (or hundredths) of a milligram are then calculated from the difference between the zero point and the rest point, the sensitivity being known for the load on the pans. An example will

* An alternative definition which is sometimes employed is the following: the sensitivity is the weight necessary to shift the equilibrium position of the pointer by one scale division.
make the method of calculation clear. A certain object is found to weigh between 12.673 and 12.674 g. The rider is then placed exactly on division 3 (mg.), and the rest point determined by the method of swings. Suppose this is 12.4. The zero point is, say, 10.4. The sensitivity of the balance, estimated from the sensitivity-load graph, is 3.8 divisions per mg. The weight is therefore:

\[ 12.673 + (12.4 - 10.4) \times 0.001/3.8 = 12.673 + 0.00053 \]

\[ = 12.67353 \text{ g, or 12.6735 g. (to the nearest 0.1 mg.)} \]

(ii) Weighing by the method of short swings. For ordinary analytical work, entirely satisfactory weighings to an accuracy of 0.1 mg. can be made by the method of short swings. The swings observed are so short that the damping effect produced in two successive swings is inappreciable. The zero or rest point is determined by adding together the observed values of two successive swings on either side of the centre of the pointer scale, and taking the mean. The swings may vary from 4 divisions on the pointer scale to the shortest one that is distinctly visible; those from 1 to 2 divisions on either side of the centre of the scale are usually satisfactory. As an example, we may consider two successive swings +2.2 and −2.0; the centre of the scale is here taken as the reference point, values to the right being positive and those to the left negative. The zero point is \((+2.2 - 2.0)/2 = +0.1\). This method of weighing is recommended for all routine work, but is not suitable for the calibration of weights (see Section II, 8).

(iii) Weighing of chemical samples. It will be convenient at this stage to discuss the application of the two methods of direct weighing just described to the weighing of chemical samples. Most chemicals are weighed by difference in order to avoid exposing the sample to the atmosphere, from which dry substances may absorb moisture in varying amounts. If the sample has been dried, it should be placed in a weighing-bottle and kept in a desiccator, containing a suitable drying agent, until required for weighing. The most convenient form of weighing-bottle is that provided with a ground-on cap (Fig. II, 6, 2, a). That with a ground-in stopper is not recommended, particularly for weighing powders; there is always a danger that the small particles may adhere to the ground surface and that when the stopper is pressed into place, they may either tend to cause the stopper to stick or else be forced out and lost. A special type of “duplex” weighing-bottle, together with the relative dimensions, is shown in Fig. II, 6, 2, b. This is fitted
Technique of Quantitative Analysis

with externally ground caps, and possesses many obvious advantages. Among these may be mentioned the flattened side, which gives great stability, the wide mouth, which permits facile addition and removal of solids, the narrow mouth, which allows of easy transfer of solids or liquids into narrow-neck receptacles, and finally the designed slopes, which permit easy access of brush or stream of liquid into and against all parts of the interior.

To weigh a substance by difference, weigh a glass-stoppered weighing-bottle (Fig. II, 6, 2, a) containing the sample. Approximately the desired amount is then transferred into a suitable container (beaker, flask, etc.) by appropriate shaking, and the bottle re-weighed. If desired, the sample may be removed with the aid of a small clean spatula (which should preferably be of platinum) which is kept in the bottle. Sometimes the sample is removed with the aid of a clean spatula, spoon, or scoop, which is not weighed; it is then of the greatest importance that every particle removed from the bottle be transferred to the container. The spatula or scoop should be carefully brushed with a small camel-hair brush.

In the actual transfer of the weights from the box to the balance-pan, it is desirable to place the gram weights in the centre of the pan, the decigram weights to one side, and the centigram pieces to the other side. This will assist in reducing the likelihood of error in recording the weighing. The weights on the pan are noted and their values confirmed by observing the vacant places in the weight box. As a final check, the value of each weight as it is returned to the box is noted. All weights should be recorded in ink in a note-book at the time that they are made; loose sheets of paper should never be used, as they are readily lost.

If the sample is unaffected by exposure to the air, it may be weighed on a watch glass. A clean, dry watch glass is weighed, portions of the sample, which should preferably be in the form of a powder, are added by means of a spatula or scoop until the weight is approximately correct, and the combined weight is then determined. It is often convenient to have a pair of counterpoised watch glasses for this purpose, i.e., a pair of watch glasses which weigh so nearly the same that they can be balanced with the aid of the rider alone. One watch glass is placed on each pan, and weights are placed on the right-hand pan amounting to the desired quantity of the sample; the latter is then added with a spatula or similar apparatus.

Liquids must be weighed in closed weighing-bottles. The most convenient method is to weigh the empty bottle and stopper; the approximate amount of liquid is introduced by a graduated pipette or glass tube, and the bottle is re-weighed. The entire contents of the bottle is then washed into the second container.

Sometimes ignited precipitates are hygroscopic or tend to absorb carbon dioxide from the air. Weighing must then be made as rapidly as possible. These precipitates are ignited to constant weight; the approximate weight is therefore known from a previous ignition. In the final weighing it is perhaps best to adjust the rider to the nearest milligram and then to determine tenths of a milligram by the method of swings.

An experimental point which merits attention is that a vessel should always be weighed filled with the same gas. Thus in the determination
of carbon by combustion in oxygen and the absorption of the resultant carbon dioxide in a U-tube containing soda lime or some other substance, it is important to weigh the absorption tube filled with air both before and after the determination. To get some idea of the error resulting from the neglect of this precaution, let us take the case of a U-tube of, say, 50 ml. capacity. One litre of air at 20° C. and 750 mm. pressure weighs approximately 1·19 g., and 1 litre of oxygen under similar conditions weighs 1·31 g. The difference in weight produced by substituting oxygen for air will be \(1·31 - 1·19\) \times \(50/1000\), or 0·0060 g. Since the weight of carbon dioxide absorbed is usually of the order of 0·1 g., the neglect of this precaution will introduce an error of about 6·0 per cent.

A common procedure in quantitative analysis is to dissolve a known weight of a substance in a definite volume of liquid, which is usually distilled water or distilled water to which a reagent has been added. A graduated flask is generally employed for this purpose. The operation is carried out as follows. Insert a short-stemmed funnel into the neck of the flask. Transfer the required amount of substance from the weighing-bottle to the funnel, taking care that no particles are lost. After the weighing-bottle has been re-weighed, the substance in the funnel is washed down with a stream of the liquid. The funnel is thoroughly washed, inside and out, and then removed from the flask; the contents of the flask are dissolved, if necessary, by shaking or swirling the liquid, and then made up to the mark, if an exact volume is required. If a watch glass is employed for weighing out the sample, the contents are transferred as completely as possible to the funnel; the last traces remaining on the watch glass are transferred by washing. The procedure is then as above.

(b) **Gauss's method of double weighing.** This method will eliminate any errors due to the inequality of the arms. Let us suppose that the lengths of the arms are \(d_1\) and \(d_2\) respectively (see Fig. II, I, 1), and the true mass of the object is \(M_t\). If the object is placed in the left-hand pan and is counter-balanced by weights \(W_1\) on the right-hand pan, we have by the principle of moments:

\[
M_t \times d_1 = W_1 \times d_2 
\]  
(1)

If now the object is placed in the right-hand pan and is counter-balanced by weights \(W_2\) on the left-hand pan, we have:

\[
M_t \times d_2 = W_2 \times d_1 
\]  
(2)

Upon multiplying these two expressions together and cancelling out the common factor \(d_1 d_2\), we obtain:

\[
M_t^2 = W_1 W_2, \text{ or } M_t = \sqrt{W_1 W_2} 
\]  
(3)

i.e., the mass is equal to the square root of the product of the two apparent weights. Since \(d_1\) and \(d_2\) are very nearly equal, it is sufficiently accurate to write:

\[
M_t = (W_1 + W_2)/2 
\]  
(3')

i.e., the true mass is equal to the arithmetic mean of the apparent weights.

(c) **Borda's method of weighing.** This is another method for determining the true mass of an object; it is independent of the inequality of
the balance arms. The object is placed on the right-hand pan, and
counterbalanced or tared by any convenient counterpoise, which may
be the weights of a duplicate set, lead shot, or sand. The rest point
of the balance is determined. The object is then removed and replaced
by weights which give the same rest point. The mass of the object is
thus equal to the mass of the weights on the left-hand pan. This
substitution method is useful for weighing large objects. It is also
employed in the calibration of weights, but the precision is not so great
as in Gauss’s method.

II, 7. Errors in weighing.—The chief sources of error are the
following:

1. Change of the condition of the containing vessel or of the substance
between successive weighings.

2. Inequality of the lengths of the balance arms.

3. Effect of the buoyancy of the air upon the object and the weights.

4. Inaccuracy of the weights.

The first source of error is occasioned by the change in weight of the
containing vessel: (a) by absorption or loss of moisture, (b) by electro-

fication of the surface caused by rubbing, and (c) by its temperature
being different from that of the balance-case. These errors may be
largely eliminated by wiping the vessel gently with a linen cloth, and
allowing it to stand at least 30 minutes in the balance-room before
weighing. The electrification, which may cause a comparatively large
error, particularly if both the atmosphere and the cloth are dry, is slowly
dissipated on standing, but is best removed by placing a piece of pitch-
blende or other radioactive material in the balance-case to ionise the
air. The best method, if practicable, is to use a vessel of similar
dimensions as a tare. Hygroscopic, efflorescent, and volatile substances
must be weighed in completely closed vessels. Substances which have
been heated in an air-oven or ignited in a crucible must be allowed to
cool in a desiccator containing a suitable drying agent. The time of
cooling in a desiccator cannot be exactly specified, since it will depend
upon the temperature and the size of the crucible, as well as upon the
material of which it is composed. Platinum vessels require a shorter
time than those of porcelain, glass, or silica. As a general rule, plati-
num crucibles should be left in the desiccator for 25 minutes, and

The use of drying agents or absorbents for carbon dioxide in the
balance-case is generally of little value except where atmospheric
conditions are such as to otherwise cause serious corrosion of the balance.
These reagents give comparatively little protection during weighing,
for the small surface of absorbent usually exposed cannot quickly purify
the air introduced when the case is opened. However, if reagents are
to be used, soda-lime and fused calcium chloride are satisfactory.

The error due to the inequality of the lengths of the balance arms
may be completely eliminated by Gauss’s method of double weighing
(Section II, 6 (b)) or by Borda’s method of substitution (Section II, 6 (c)).
In a good analytical balance the arms will seldom differ in length by
more than 1 part in 50,000, so that the error introduced by the direct
method of weighing is not large. The error is still further reduced in
routine work in quantitative analysis, where the sample and the ignited
or dried precipitate are weighed on the same balance and on the same
pan. Here absolute weights are not essential, since it is only the ratio
of the weights with which we are concerned. It is clear that if both
the sample and the precipitate are affected by the same small error,
the ratio of the weights will not be appreciably affected. Where
absolute weights are required, as in the calibration of weights or of
volumetric apparatus, one of the two methods mentioned at the
beginning of this paragraph must be used.

Effect of the buoyancy of the air. Reduction of weighings to vacuo. When
a substance is immersed in a fluid, its true weight is diminished
by the weight of the fluid which it displaces. If the object and the
weights have the same density, and consequently the same volume,
no error will be introduced on this account. If, however, as is usually
the case, the density of the object is different from that of the weights,
the volumes of air displaced by each will be different. If the substance
has a lower density than the brass weights, as is usual in analysis, the
former will displace a greater volume of air than the latter, and it will
therefore weigh less in air than in a vacuum. Conversely, if a denser

![Diagram](image)

Fig. II, 7, 1.

material (e.g., one of the precious metals) is weighed, the weight in a
vacuum will be less than in air.

The effect of the relative volumes (and therefore the densities) of
the object and weights is shown diagrammatically in Fig. II, 7, 1.
Two cases arise:

(a) The object has a smaller density, and consequently a greater
volume, than the weights. If the object and weights are exactly
balanced in air and the air is then pumped out of the balance-case,
the object will appear to be heavier: the left-hand pan will sink as the
buoyant effect of the air is removed, and weights must be added to the
right-hand pan to restore the condition of balance. Hence the true
weight (weight in vacuo) is greater than the apparent weight (weight in
air).

(b) The density of the object is greater than that of the weights.
Here the weight in vacuo is greater than the weight in air. It need
hardly be added that if the object and weights are of equal density
and therefore occupy the same volume, removing the air from the
balance-case will not affect the equilibrium, and the weight in air will
be the same as the weight in vacuo.

Let us enquire into the magnitude of the error. First, let us con­sider
the weighing of a litre of water, first in vacuo, and then in air.
It is assumed that the flask containing the water is tared by an exactly
similar flask, that the temperature of the air is 20° C. and the barometric
pressure is 760 mm. of mercury. The weight of 1 litre of water in vacuo
at 20° C. and 760 mm. is 998.23 g. If the water is weighed in air, it will be found that 998.23 g. are too heavy. We can readily calculate the difference. The weight of 1 litre of air displaced by the water is 1.20 g. The brass weights have a density of 8.4, hence they will displace \( \frac{998.23}{8.4} = 116.9 \) ml., or \( 116.9 \times 1.20/1000 = 0.14 \) g. of air. The net difference in weight will therefore be \( 1.20 - 0.14 = 1.06 \) g. Hence the weight in air of 1 litre of water under the experimental conditions named is 998.23 - 1.06 = 997.17 g., a difference of 0.1 per cent from the weight in vacuo.

Let us now extend our enquiry to the case of a solid, such as potassium chloride, under the above conditions. The density of potassium chloride is 1.98. If 2 g. of the salt are weighed, the apparent loss in weight (= weight of air displaced) is \( 2 \times 0.0012/1.98 = 0.0012 \) g. The apparent loss in weight for the brass weights is \( 2 \times 0.0012/8.4 = 0.00029 \) g. Hence 2 g. of potassium chloride will weigh 0.0012 - 0.00029 = 0.00091 g. less in air than in vacuo, a difference of 0.05 per cent.

It must be pointed out that for most analytical purposes where it is desired to express the results in the form of a percentage, the ratio of the weights in air, so far as solids are concerned, will give a result which is practically the same as that which would be given by the weights in vacuo. Hence no buoyancy correction is necessary in these cases. However, where absolute weights are required, as in the calibration of volumetric glassware, corrections for the buoyancy of the air must be made (compare Section II, 20).

Let us now consider the general case. It is evident that the weight of an object in vacuo is equal to the weight in air plus the weight of air displaced by the object minus the weight of air displaced by the weights. It can easily be shown that if \( W_v = \) weight in vacuo, \( W_a = \) apparent weight in air, \( d_a = \) density of air, \( d_w = \) density of the weights, and \( d_b = \) density of the body, then:

\[
W_v = W_a + d_a \left( \frac{W_s}{d_b} - \frac{W_a}{d_a} \right)
\]  

The density of the air will depend upon the humidity, the temperature, and the pressure. For an average humidity (50 per cent) and average conditions of temperature and pressure in a laboratory, the density of the air will rarely fall outside the limits 0.0011 and 0.0013 g./ml. It is therefore permissible for analytical purposes to take the weight of 1 ml. of air as 0.0012 g.

Since the difference between \( W_v \) and \( W_a \) does not usually exceed 1 to 2 parts per thousand, we may write:

\[
W_v = W_a + d_a \left( \frac{W_s}{d_b} - \frac{W_a}{d_a} \right)
\]  

\[
= W_a + W_a \left( \frac{1}{d_b} - \frac{1}{d_a} \right) \text{ [for brass weights, } d_w = 8.4] 
\]

\[
= W_a + kW_a/1000
\]

where

\[
k = 1.20 \left( \frac{1}{d_b} - \frac{1}{d_a} \right)
\]

The values of \( k \) for \( d_a = 0.0012 \) and \( d_w = 8.4 \) have been calculated and
are collected in the following table. If a substance of density $d_b$ weighs $W_a$ grams in air, then $W_a \cdot k$ milligrams are to be added to the weight in air in order to obtain the weight in vacuo. The correction is positive if the substance has a density lower than that of brass, and negative if the density of the substance is greater than that of brass.

**Table I. Reductions of Weighings Made in Air with Brass Weights to Vacuo**

<table>
<thead>
<tr>
<th>$d_b$</th>
<th>$k$</th>
<th>$d_a$</th>
<th>$k$</th>
<th>$d_v$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>+2.28</td>
<td>1.9</td>
<td>+0.49</td>
<td>11.0</td>
<td>-0.03</td>
</tr>
<tr>
<td>0.6</td>
<td>+1.86</td>
<td>2.0</td>
<td>+0.46</td>
<td>12.0</td>
<td>-0.04</td>
</tr>
<tr>
<td>0.7</td>
<td>+1.57</td>
<td>2.5</td>
<td>+0.34</td>
<td>13.0</td>
<td>-0.05</td>
</tr>
<tr>
<td>0.8</td>
<td>+1.38</td>
<td>3.0</td>
<td>+0.25</td>
<td>14.0</td>
<td>-0.06</td>
</tr>
<tr>
<td>0.9</td>
<td>+1.19</td>
<td>3.5</td>
<td>+0.20</td>
<td>15.0</td>
<td>-0.07</td>
</tr>
<tr>
<td>1.0</td>
<td>+1.06</td>
<td>4.0</td>
<td>+0.16</td>
<td>16.0</td>
<td>-0.07</td>
</tr>
<tr>
<td>1.1</td>
<td>+0.95</td>
<td>4.5</td>
<td>+0.13</td>
<td>17.0</td>
<td>-0.07</td>
</tr>
<tr>
<td>1.2</td>
<td>+0.86</td>
<td>5.0</td>
<td>+0.10</td>
<td>18.0</td>
<td>-0.08</td>
</tr>
<tr>
<td>1.3</td>
<td>+0.78</td>
<td>5.5</td>
<td>+0.08</td>
<td>19.0</td>
<td>-0.08</td>
</tr>
<tr>
<td>1.4</td>
<td>+0.72</td>
<td>6.0</td>
<td>+0.06</td>
<td>20.0</td>
<td>-0.09</td>
</tr>
<tr>
<td>1.5</td>
<td>+0.66</td>
<td>7.0</td>
<td>+0.03</td>
<td>21.0</td>
<td>-0.09</td>
</tr>
<tr>
<td>1.6</td>
<td>+0.61</td>
<td>8.0</td>
<td>+0.01</td>
<td>22.0</td>
<td>-0.09</td>
</tr>
<tr>
<td>1.7</td>
<td>+0.58</td>
<td>9.0</td>
<td>-0.01</td>
<td>23.0</td>
<td>-0.09</td>
</tr>
<tr>
<td>1.8</td>
<td>+0.52</td>
<td>10.0</td>
<td>-0.02</td>
<td>24.0</td>
<td>-0.09</td>
</tr>
</tbody>
</table>

In volumetric analysis we are frequently concerned with the calibration of volumetric apparatus, and hence a knowledge of the weight in vacuo of 1 ml. of water is required for the calculation of the weight in air by equation (2) or (3). The necessary data are collected in Table II.

**Table II. Weight in Vacuo of 1 ml. of Water**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.00000</td>
<td>21</td>
<td>0.99802</td>
</tr>
<tr>
<td>10</td>
<td>0.99732</td>
<td>22</td>
<td>0.99750</td>
</tr>
<tr>
<td>11</td>
<td>0.99635</td>
<td>23</td>
<td>0.99756</td>
</tr>
<tr>
<td>12</td>
<td>0.99580</td>
<td>24</td>
<td>0.99732</td>
</tr>
<tr>
<td>13</td>
<td>0.99490</td>
<td>25</td>
<td>0.99707</td>
</tr>
<tr>
<td>14</td>
<td>0.99376</td>
<td>26</td>
<td>0.99781</td>
</tr>
<tr>
<td>15</td>
<td>0.99193</td>
<td>27</td>
<td>0.99654</td>
</tr>
<tr>
<td>16</td>
<td>0.98907</td>
<td>28</td>
<td>0.99628</td>
</tr>
<tr>
<td>17</td>
<td>0.98880</td>
<td>29</td>
<td>0.99597</td>
</tr>
<tr>
<td>18</td>
<td>0.98857</td>
<td>30</td>
<td>0.99567</td>
</tr>
<tr>
<td>19</td>
<td>0.98843</td>
<td>40</td>
<td>0.99254</td>
</tr>
<tr>
<td>20</td>
<td>0.98823</td>
<td>50</td>
<td>0.99807</td>
</tr>
</tbody>
</table>

II. 8. Calibration of weights.—All weights should be calibrated in order to detect any inaccuracies amongst the weights themselves. This calibration should be repeated at least once a year, because changes may occur owing to wear, corrosion, or other causes. In all good sets of weights the duplicate and triplicate weights are distinguished by the marking of one * or two ** asterisks on the surface. If this is not the case, the set should either be returned to the makers or the markings made with a suitable punch by a qualified mechanic in the instrument workshop of the Institution.
The simplest and best method of calibration is to check each piece of a set against a corresponding piece of a set calibrated by a nationally recognised laboratory.* The method of substitution is employed. A third or subsidiary set of weights is also required. First, place the smallest weight of the set to be calibrated on the right-hand pan and balance it by the corresponding piece of the subsidiary box of weights placed on the left-hand pan. Ascertain the rest point by the method of swings. Remove the weight from the right-hand pan and replace it by a piece of the same denomination from the standard set of weights, and determine the rest point again. The error in the weight can then be computed from the difference in the rest point in the two weighings and the known sensitivity of the balance for the load in question. This process is repeated for every piece in the box of weights. Finally a table is constructed showing the absolute error for each weight.

Complete sets of standard weights are not always available. A modification of the method due to T. W. Richards (1900), which is essentially a calibration of the weights relative to one another, is then employed. Here also the substitution method of weighing is utilised; an extra set of weights, to act as a tare, is also required. The principle of the method is to assume that the smallest weight in the set, say one of the 10-mg. pieces, is correct, and the value of every other weight in the set is obtained in terms of it. The weighings must be made by the method of swings. The values for the larger weights are found to differ considerably from the nominal values because such a small standard was used. It is therefore usual to change the relative standard to one of the larger weights, say, to a nominal 10-g. piece, and to express all the other pieces in terms of the larger standard. The differences will then be much smaller. If the absolute value of the new standard can be determined by comparison with a similar standard weight (calibrated by the N.P.L., Bureau of Standards, etc.), we can then readily calculate the absolute values of all the other weights, since the ratio of the 10-g. weight to all the others in the set has been determined.

The detailed procedure is as follows. The sensitivity of the balance at different loads must be known. If this is not the case, it must be determined as described in Section II, 6 (a). Leave the weights for at least 30 minutes before commencing the calibration. Place one of the 10-mg. weights, temporarily assumed as exactly 10 mg., on the right-hand scale pan, and counterpoise it with the corresponding weight from the subsidiary set on the left-hand pan. Determine the rest point by the method of swings; this should be near the centre of the scale (division 10 in Fig. II, 2, 1). Repeat the determination of the rest point for the other two 10-mg. weights (0.01* and 0.01**), retaining the original tare on the left-hand pan. Any difference in their weights can be calculated from the known sensitivity of the balance. Next place the two 0.01-g. pieces (say, 0.01 and 0.01*) on the right-hand pan, and counterbalance them with a 0.02-g. weight from the extra set. Determine the rest point. Repeat with the 0.02-g. weight from the set, using the same tare. The calibration correction for the 0.02-g. weight can then be determined, knowing that for the 0.01 g. and 0.01* g.

Continue the comparison until the complete set is calibrated. The

* For the British Empire, this is the National Physical Laboratory; for U.S.A., the Bureau of Standards, etc.
following comparisons will be made: 0·01* g. against 0·01 g., 0·01** g. against 0·01* g.; 0·02 g. against (0·01 + 0·01*) g.; 0·05 g. against 
(0·02, 0·01, 0·01*, 0·01**) g. = Σ 0·05; 0·1 g. against (0·05 + Σ 0·05) = Σ 0·1 g.; 0·1* g. against 0·1 g.; 0·2 g. against (0·1 + 0·1*) g.; 0·5 g. against 
(0·2 + 0·1 + 0·1* + Σ 0·1) g. = Σ 0·5; 1 g. against (0·5 + Σ 0·5) g.; 1* g. against 1 g.; 1** g. against 1* g.; 2 g. against (1 + 1*) g.; 5 g. against 
(2 + 1 + 1* + 1**) g.; 10 g. against (5 + 2 + 1 + 1* + 1**) g.; 10* g. against 10 g.; 20 g. against (10 + 10*) g.; 50 g. against (20 + 10 + 10* + 5 + 2 + 1 + 1* + 1**) g.

It is generally advisable to calibrate the rider also. Let us suppose this is of 10 mg. denomination. The rider is placed on position 10 of the beam and comparison is made directly with the 0·01 g., the assumed temporary standard placed on the left-hand pan. In some sets of weights there are only two 10-mg. pieces; in such cases the rider is kept at position 10 during the calibration.

The results should be tabulated as shown in Table III. This also illustrates the exact method of computation. The method of calculation of the relative values taking the 0·01 g. as correct is obvious. Column 7, the ideal calibration value, is most simply obtained by assuming that the 10-g. weight actually possesses the weight of 10·0385 g. (see Table) and taking this as the permanent standard; there is therefore no correction for this weight. The 5-g. pieces on this basis should weigh 5 × 10·0385/10 = 5·0193 g.; the other ideal calibration values are calculated in the same manner. The differences between columns 6 and 7 give the corrections to be added to or subtracted from the nominal values of the weights. A table should be constructed showing the correction to be applied to each weight: the table may also contain the corrections for various combinations of weights.

The absolute values of the weights are required for the calibration of volumetric apparatus and, strictly speaking, for the preparation of standard solutions where it is desired to express the concentration of the reagent in terms of normality or molarity. Many of the determinations of quantitative inorganic analysis are derived from the ratios of weights, and a knowledge of the absolute values of the weights used is unnecessary. It is of the utmost importance, however, that the weights should agree among themselves, e.g., the 2-g. piece should be exactly twice that of the 1-g. weight, etc. Except for the most expensive sets of brass weights (such as the Oertling first quality) it is rarely found that these adjustments have been carried out with sufficient accuracy. Hence it is imperative that all sets of weights should be calibrated or standardised by one of the methods outlined above. Analytical weights of "nickel–chromium alloy" (Oertling) or of "permas," "an alloy containing more than 50 per cent non-ferrous constituents, i.e., nickel, chromium, etc." (Fisher Scientific Co.), are marketed; these essentially stainless-steel weights are said to be harder than brass and therefore possess greater resistance to wear and abrasion, to be more resistant to corrosion, are not lacquered, and are non-magnetic. Fractional weights (500–50 mg.) of tantalum are also obtainable.

Attention is directed to the fact that the appropriate value of the density of the alloy must be employed in applying the correction for the buoyancy of the air (see Section II, 7, equation (3)).

The National Physical Laboratory at Teddington undertakes the certification of weights, and it recognises two classes of weights, Class
A and Class B. A Class A certificate, with calibration errors, enables weighings to be corrected to an order of accuracy of about 1 part in 1 million. A Class A tolerance certificate (weight-in-air basis) enables weighings to be made to an order of accuracy of about 1 part in 100,000 without the necessity of applying corrections for the individual errors of the weights, and suffices for most work in quantitative analysis. For work where less precision suffices, a Class B tolerance certificate is supplied, giving an accuracy of about 1 part in 20,000. The accuracy of certification and the tolerance for both classes of weights are given in Table IV.
The U.S. Bureau of Standards at Washington recognises three classes of weights, M, S, and S-2. Class M weights are employed as primary reference standards against which all weights may be checked and are of one-piece construction. Class S weights are used for routine accurate work in scientific laboratories; they may be of two-piece construction with a screw knob, so that exact adjustment of mass may be made by placing a small piece of a suitable metal within the cavity beneath the knob. The tolerances for Class M and Class S weights are identical. Class S-2 weights have tolerances five times those permitted for Class S weights, and are adequate for most student requirements. The precision of correction and tolerances are collected in Table V.

| Denomination | Class A | | Class M or S. | | Class S-2. |
|--------------|---------|------------------|------------------|------------------|
|              | Accuracy of Certificate (mg.) | Tolerance (mg.) | Precision of Correction (mg.) | Tolerance (mg.) | Tolerance (mg.) |
| 100 g.       | 0.1     | 1                | 0.05             | 0.5              | 2.5             |
| 50 g.        | 0.05    | 0.5              | 0.1              | 0.2              | 1.0             |
| 20 g.        | 0.02    | 0.2              | 0.05             | 0.15             | 0.75            |
| 10 g.        | 0.05    | 0.15             | 0.05             | 0.10             | 0.50            |
| 5 g.         | 0.01    | 0.10             | 0.01             | 0.05             | 0.25            |
| 2 g.         | 0.01    | 0.05             | 0.01             | 0.03             | 0.15            |
| 1 g.         | 0.01    | 0.03             | 0.01             | 0.02             | 0.10            |
| 500 mg.      | 0.01    | 0.02             | 0.01             | 0.01             | 0.05            |
| 200 mg.      | 0.01    | 0.01             | 0.01             | 0.01             | 0.05            |
| 100 mg.      | 0.01    | 0.01             | 0.01             | 0.01             | 0.05            |
| 50 mg.       | 0.01    | 0.01             | 0.01             | 0.01             | 0.05            |
| 20 mg.       | 0.01    | 0.01             | 0.01             | 0.01             | 0.05            |
| 10 mg.       | 0.01    | 0.01             | 0.01             | 0.01             | 0.05            |
| 5 mg.        | 0.01    | 0.01             | 0.01             | 0.01             | 0.05            |
| 2 mg.        | 0.01    | 0.01             | 0.01             | 0.01             | 0.05            |
| 1 mg.        | 0.01    | 0.01             | 0.01             | 0.01             | 0.05            |
II, 9. Other types of balances.—The instrument described in Section II, 2 is the common form of a chemical balance (e.g., Oertling No. 48/SB), and is the type that is most widely used for analytical work in teaching institutions. Changes have, however, been made in the design of balances, chiefly with the object of rendering the operation of weighing more convenient and more rapid—a consideration of great importance for routine weighing in industrial laboratories. Some of these will be discussed below.

A. The chainomatic balance. This balance is similar to an ordinary

![Diagram of a chainomatic balance]

balance in general construction, but differs from it in that the use of fractional weights is entirely eliminated. A diagram of a typical chainomatic balance* (case not shown) constitutes Fig. II, 9, 1. A rolled-gold or gold chain is attached at one end to the beam of the balance and at the other end to a small vernier movable along a vertical column, graduated in mms., and situated at the right of the balance beam. The device is operated by turning a handle outside the balance.

* Manufactured by L. Oertling, Ltd., 110 Gloucester Place, London, W.1, England. The balance illustrated is the "Aperiodic Null-point Gram-chain Balance," Model 101; it has a capacity of 200 g. in each pan, and is provided with a magnetic damping device; the magnet is easily withdrawn to provide a normal free-swinging instrument.
case. The weight of the chain is carried both by the beam and the vernier block; the higher the latter, the smaller is the proportion of the weight carried by the beam. The column is graduated to read directly in mg, up to 100 mg., and readings can easily be made to 0.1 mg. with the aid of the vernier block. In the balance illustrated, the beam is serrated into 10 parts from “0” on the left to “10” on the right and is adjusted with a 5-decigram rider at zero, each serration being equivalent to 1 decigram, thus giving a total displacement of 1 g.

The chief advantages of chainomatic balances are:

(i) Weights less than 1 g. are unnecessary.

(ii) The frequent opening and closing of the balance-case towards the end of a weighing are thus avoided; the chainomatic mechanism can be operated whilst the balance is swinging.

(iii) The weighings can be carried out rapidly.

B. The air-damped balance. An oscillating system, such as a balance, is said to be damped if it is subject to some force which restrains its motion and decreases the amplitude of its swings. All balances are damped to a slight extent, since friction cannot be entirely eliminated. In the air-damped balance, large light pistons attached to the pans or to the beam move loosely in large cylinders. The resultant damping is so great that the pointer swings slowly from the centre to the rest point within 10–15 seconds. The sensitivity of the balance is not decreased by damping. In weighing it is therefore only necessary to note the point of rest. Some balances (e.g., Bunge) have a scale which is graduated so that each division corresponds to 1 mg., and the rest point is observed through a microscope. In other balances (e.g., Oertling No. 52 F.M.) a finely divided graticule is attached to the end of the pointer, and an enlarged reflection of the scale is projected on to an illuminated screen situated in a convenient position at the top of the balance-case. The graticule is divided into 1000 equal parts corresponding to 0.001 g., thus permitting readings to 0.1 mg. Weights smaller than 1 decigram are not required. An air-damped (or aperiodic) balance is also available (Oertling No. 62/FM) provided with a “multiweight carrier”; the latter is a special attachment fitted to the right-hand side of the balance-case, consisting of rotating dials which can be moved in either direction, working in conjunction with a series of lever arms by means of which varying weights up to a total of 0.99 g. may be added to the right arm of the beam; here the illuminated graticule, graduated in 50 divisions from “0” to “100,” covers the value of 0.01 g. and therefore permits of facile reading to 0.1 mg. The general arrangement is similar to Fig. II, 9, 7.

C. The magnetically damped balance. Damping can also be effected by suitably suspending a small aluminium plate from the right-hand stirrup of the balance; a counterpoise, usually of brass, is suspended from the left-hand stirrup. The aluminium plate moves between but does not quite touch, the poles of a powerful permanent horseshoe magnet, which is attached rigidly to a support, which may be mounted on the central pillar or independently. The effect is very similar to the air-damped balance. It has been stated that ferrous materials can be weighed on this balance without appreciable error. The sensitivity of a balance is unaffected by damping in either of the above ways.

D. The multiple-rider or multiple-weight balance. Reference has already
been made under B to the Oertling "multiple-weight" device which eliminates the use of all fractional weights. Balances are now available which completely eliminate the use of weights; the "weights," some of which are constructed in the form of riders, are put into place by means of levers. The advantages of this type of construction are the speed of operation, the precision with which the "weights" may be placed in the same positions, and the only slight wear on the "weights." The Stanton B.A.5 balance * is shown in Fig. II, 9, 2; it has a capacity of 100 or 200 g., and is sensitive to 0·1 mg. The rider weights are of stainless steel and are adjusted to N.P.L. Class A tolerances. The lowest of three circular control knobs actuates seven weights ranging from 10 to 90 g. so arranged that the load is carried evenly at all times; thus when the control knob is turned to 10 g., two 5-g. weights are added, one at each end of the carrier bar; for 20 g., the two 5-g. weights are raised and simultaneously two 10-g. weights are placed on; for 90 g., the centre arm controls the 50-g., and four 10-g. weights (two on each side of the centre arm) are placed in position with the same movement. The central control knob is similar, and here the weights range from 1 to 9 g. The top series of weights is controlled by two concentric knobs, the outer one dealing with a series of rider weights 0·5, 0·2, 0·2, and 0·1 g., and the inner one with 0·05, 0·02, 0·02, and 0·01 g.: the rider weights are loaded on to a double rider bar which prevents weights swinging when placed in position.

Weights below 10 mg. are determined from the illuminated graticule at the foot of the column, numbered 0–10 mg. and divided into fifty divisions.

The Voland "Speedigram" balance, model 750-D,* is illustrated in Fig. II, 9, 3; a simple mechanism places stainless-steel and aluminium weights, adjusted to U.S. Bureau of Standards Class S tolerances, on a specially designed hanger as selected. The three dials which control these weights read directly up to 99.9 g. The final 100 mg. are controlled by rotating the "visiglam" wheel located at the right-hand side of the balance; the weight corresponding to the amount of chain deposited on the beam is read on the counter (top right-hand corner of the balance). Readings are made directly across the dial and counter without computation or interpolations. A 100-g. weight is furnished in a special compartment in the cabinet for use when the entire capacity of the balance is required. A built-in adjustable magnetic damper is provided.

E. The Mettler gram-atomic balance. This balance, manufactured by E. Mettler of Küsnacht-Zurich, Switzerland,† represents an advance in design and also in the technique of precise, rapid weighing. The balance has but one pan and two knife edges: all weighings are made under constant load, because weights are removed, not added, as required by the sample. The main features of the balance will be evident from the schematic diagram and key given in Fig. II, 9, 4 (kindly supplied by the Fisher Scientific Company). The area of the

* Voland and Sons Inc., 32 Relyea Place, New Rochelle, New York, N.Y., U.S.A.
† Marketed in the U.S.A. and Canada by the Fisher Scientific Co., of Pittsburgh, Pa., and termed the gram-atomic balance.
plates 9 on the air-damping device is made equal to the area of the pan and, in consequence, any errors due to moisture condensation are equalised. The actual balance is shown in Fig. II, 9, 5. The weights are adjusted to a tolerance of \( \pm 0.03 \) mg., and the accuracy of the balance, capacity 200 g., is \( \pm 0.05 \) mg. independent of load. The gold-plated weights, from 100 to 0.1 g., are suspended from hard stainless-steel hoops which rest on rods suspended from the balance beam; they are transferred rapidly by means of knobs on the panel.

The upper left-hand knob controls the 100-g. weight; the lower left-hand knob controls tens of grams; the upper right-hand knob deals with grams, and the lower right-hand knob controls tenths of a gram. The counter in the centre of the control panel automatically records the weight to the nearest decigram. Upon now operating the pan-release lever on the left of the balance, the figures to the nearest tenth of a milligram automatically appear, by optical projection, on the scale. An enlarged "mechanical and optical weight scale with vernier" is shown in Fig. II, 9, 6: the weight shown is 162.4312 g. The zero point is determined by turning a knob, situated in the right-hand side of the instrument, which moves a plane prism in the optical system. The zero line of the projected scale and the zero line of the vernier can be made to coincide in this manner. It is claimed that the entire sequence of operations, including the placing of the object on the
balance-pan, requires 21 seconds in the hands of a technician with limited experience in handling the new balance.

It must be pointed out that the balances described under D and E suffer from the disadvantage that it is impossible to provide a tare of equal volume for the object being weighed: this is of little moment when dealing with routine weighings by difference.

F. Semimicro balances. These are balances with a sensitivity of 0·01 mg. and are becoming increasingly popular for many types of analytical work in which minute quantities of materials are involved. The Oertling "semimicro chemical balance, No. 141" ("Aperiodic Micro Balance"), illustrated in Fig. II, 9, 7, is a typical example of a high-grade instrument. The maximum load is 30 g. Rapid weighing is ensured by air damping. Fractional weights, up to a total of 0·09 g., are added by means of a mechanical-loading device fitted to the right-hand side of the case; it can be turned in both directions and is direct reading. The rider bar is serrated into ten parts from "0" on the
left to "10" on the right for use with a 5-mg. rider adjusted at zero.
The illuminated graticule is divided "0-100" with zero reading at
"0": one division represents 0·01 mg. A total displacement of 0·1 g.
is thus provided for without opening the case: larger weights are

![Diagram of a balance instrument](image)

added to the balance-pan in the usual way. A glass division separates
the beam compartment.

An excellent semimicro balance, provided with a chainomatic column
and a built-in magnetic damper, is made by the American Balance
Corporation * (type SM-1012): the capacity is 100 g.

A Mettler semimicro gram-atic balance, load 100 g. and sensitive to
0·02 mg., is available.

* Manufactured by American Balance Corporation, 48 Potter Avenue, New Rochelle,
N.Y., U.S.A.
In the following pages an account will be given of the general apparatus and reagents of quantitative analysis. Apparatus which is confined either to volumetric or gravimetric analysis will be described in the Sections devoted to these.

II, 10. General apparatus.—A. Burners. The ordinary Bunsen burner is widely employed for the attainment of moderately high temperatures. It is important that the air regulator should be in working order. The maximum temperature is attained by adjusting the regulator so as to admit rather more air than is required to produce a non-luminous flame; too much air gives a noisy flame, which is unsuitable.

An improvement in the design has been effected in burners in which both the gas and air supply can be regulated. The flow of gas is controlled at the base of the burner by means of a screw which operates a needle valve; the supply of air is regulated by screwing the tube of the burner up or down and thus allowing more or less air to enter through the holes at the base. The Pittsburgh universal burner *(sometimes termed a Tirril burner) and one of the Fletcher burners † are of this type. A temperature of 1050–1150° C. in a covered platinum crucible or 600–700° C. in a covered porcelain crucible can be attained with these burners.

With a Méker burner † a temperature of 1100–1200° C. is said to be reached in a covered platinum crucible and 800–900° C. in a covered porcelain crucible. The volume of air passing through a fully aerated ordinary Bunsen burner is about 2.5 times the volume of the gas; for the complete combustion of coal gas about 6 volumes of air are necessary. If a mixture of coal gas and air in the latter proportions were ignited at an ordinary Bunsen burner, the flame would "strike back" and burn at the bottom of the tube. In the Méker burner (Fig. II, 10, 1, a) the holes for the admission of air are large enough to pass sufficient air for the complete combustion of the gas, and the tube is narrowest near the base and widens out near the top, thus resulting in a more

* Manufactured by the Fisher Scientific Company, 711–723 Forbes Street, Pittsburgh, Pa., U.S.A.
† Manufactured by Fletcher, Russell and Co., Ltd., Palatine Works, Warrington, England.
perfect mixing of the gas with air; a nickel grid is fitted into the top of the burner in order to prevent the flame striking back. The gas burns in many small flames, with the top of each inner reducing cone about 1 mm. above the top of the burner. The numerous small flames combine to give a very hot and highly concentrated flame, which is oxidising in character except below the tips of the tiny flames; the maximum temperature is attained just a little above the small flames, i.e., about 2–3 mm. from the top of the burner. The burner is used for the ignition of precipitates that require a high temperature for conversion into a weighable form, and also for some fusions. A blow-pipe flame or “blast lamp” is sometimes used for these purposes, but in most cases equally satisfactory results are obtained with the Méker burner. An improved form of the ordinary Méker burner (e.g., in the Fisher “high-temperature” burner, Fig. II, 10, 1, b) contains an arrangement for adjusting both the gas and air supplies as in the Pittsburgh universal burner already described.

The “Amal” burner* attempts to combine the chief features of the improved Bunsen burner and the Méker burner. The flame can be turned down very low without flashing back, and it also furnishes a very hot flame. This is a very useful burner, but is comparatively expensive.

B. Wash bottles. A wash bottle is a flat-bottomed flask fitted up to deliver a fine stream of distilled water or other liquid for use in the transfer and washing of precipitates. A convenient size is a 500–750-ml. flask of Pyrex or other resistance glass; it should be fitted up as shown in Fig. II, 10, 2. A rubber bung is used, and the glass tubes above the bung should be in the same straight line and lie in the same plane. The jet should deliver a fine stream of water; a suitable diameter of the orifice is 1 mm. All glass tubing must be rounded in the Bunsen flame after cutting. Thick string, asbestos string, thin sheet cork, or other insulating material, held in place by copper wire, should be wrapped round the neck of the flask in order to protect the hand when hot water is used. Asbestos paper is best applied wet and allowed to dry overnight: there is sufficient adhesive material in the paper to make it cling tightly. In order to protect the mouth from scalding by the back rush of steam through the mouth-piece when the blowing is stopped, it is convenient to use a three-holed rubber stopper; a short piece of glass tubing open at both ends is inserted in the third hole. The thumb is kept over this tube whilst the water is being blown out, and is removed immediately before the mouth pressure is released.

All-glass wash bottles, fitted with ground-glass joints, can be purchased. They should be used with organic solvents that attack rubber.

C. Distilled water. Distilled water must be employed in all analytical work. Various forms of still are in common use. It is important that the vessel containing the boiling water, which may be of almost any material, should be so separated from the condenser that there is little or no danger of spray entering the latter. The condenser should be of pure tin or, if this is not possible, be heavily plated with tin. The dis-

tilled water thus prepared may contain small quantities of dissolved ammonia and carbon dioxide. For water analysis and other purposes requiring highly purified water, the distilled water should be re-distilled from alkaline potassium permanganate, and the head and tail fractions rejected; most of the dissolved ammonia is removed by this process. The most convenient method for the preparation of highly purified water (the so-called conductivity water) is to employ a mixture of two ion-exchange resins, a strong-acid resin and a strong-base resin. The strong-acid resin will remove cation impurities in the water supply and exchange them for hydrogen ions, and the latter ions are immediately neutralised by the basic resin: anions are removed by the strong-base resin in the same way. An intimate mixture of 2 parts of Permutit “De-acidite FF” and 1 part of Permutit “Zeo-Karb 225,”* occupying a volume of about 200 ml., is placed in a Pyrex tube of 1 in. diameter and 24 in. long. The column is washed with distilled water until the conductivity of the water emerging is the same as that entering. Such a column will deliver upwards of one thousand times its own volume of conductivity water. In practice, it is usually more convenient to use Permutit “Bio-Deminrolit,” which is a mixture of “De-acidite FF” and “Zeo-Karb 225” with both the resins regenerated and washed so that the mixture is ready for use. The single resin gives, with very little washing, conductivity water of specific conductivity 0.1–0.2 × 10^{-6} reciprocal ohms: the specific conductivity of this water rises to that of “equilibrium” water (0.8–1.0 × 10^{-6} reciprocal ohms) on exposure to air unless precautions are taken to exclude carbon dioxide. Similar results are obtained with the Rohm and Haas resins “Amberlite IR-120” and “Amberlite IRA-400,” † which must be freshly regenerated; a volume of 30–50 ml. of total resins, packed in a Pyrex tube of 30 cm. length and fed with boiled-out distilled water, will produce many hundreds of litres of conductivity water (C. W. Davies and C. H. Nancollas, 1950).

**D. Glassware.** In order to avoid the introduction of impurities during analysis, resistance-glass apparatus should be employed. For most purposes Pyrex glass (a boro-silicate glass) is to be preferred. Chance’s Hyasil glass is also satisfactory. As a rule glassware should not be heated with a naked flame; a wire gauze, preferably with an asbestos centre, should be interposed between the flame and the glass vessel.

The most satisfactory beakers for general use are those provided with a spout. The advantages of this form are: (a) convenience of pouring, (b) the spout forms a convenient place at which a stirring rod may protrude from a covered beaker, and (c) the spout forms an outlet for steam or escaping gas when the beaker is covered with an ordinary clock glass. The size of a beaker must be selected with due regard to the volume of the liquid which it is to contain. The most useful sizes are from 250 to 600 ml. For evaporations with high-boiling-point liquids, e.g., sulphuric acid, the shallow, squat type of beaker (e.g., Chance’s Baco type) is preferable.

Conical (or Erlenmeyer’s) flasks of 200–500-ml. capacity find many applications, for example, in titrations.

* Manufactured by The Permutit Company, Ltd., Gunnersbury Avenue, London, W.4, England; the regenerated resins should be used.
Funnels should enclose an angle of 60°. The most useful sizes for quantitative analysis are those with diameters of 5-5, 7, and 9 cm. The stem should have an internal diameter of about 4 mm. and should not be more than 15 cm. long. For filling burettes and transferring solids to graduated flasks, a short-stem, wide-necked funnel is useful.

E. Porcelain apparatus. Porcelain is generally employed for operations in which hot liquids are to remain in contact with the vessel for prolonged periods. It is usually considered to be more resistant to solutions, particularly alkaline solutions, than glass, although this will depend primarily upon the quality of the glaze. Shallow porcelain basins with lips are employed for evaporations. Casseroles are lipped, flat-bottomed porcelain dishes provided with handles; they are more convenient to use than dishes.

Porcelain crucibles are very frequently utilised for igniting precipitates and heating small quantities of solids because of their cheapness and their ability to withstand high temperatures without appreciable change. Some reactions, such as fusion with sodium carbonate or other alkaline substances, and also evaporations with hydrofluoric acid cannot be carried out in porcelain crucibles owing to the resultant chemical attack. A slight attack of the porcelain also takes place with pyrosulphate fusions.

F. Fused-silica apparatus. Two varieties of silica apparatus are available commercially, the translucent and the transparent grades. The former is much cheaper and can usually be employed instead of the transparent variety. The advantages of silica ware are: (a) its great resistance to heat shock because of its very small coefficient of expansion, (b) it is not attacked by acids at a high temperature, except by hydrofluoric acid and phosphoric acid, and (c) it is more resistant to pyrosulphate fusions than is porcelain. The chief disadvantages of silica are: (a) it is attacked by alkaline solutions and particularly by fused alkalis and carbonates, (b) it is more brittle than ordinary glass, and (c) it requires a much longer time for heating and cooling than does, say, platinum apparatus.

G. Platinum apparatus. This is discussed fully in Section II, 37. Mention may, however, be made here of the resistance of platinum ware to fusions with sodium carbonate and/or potassium carbonate, and to evaporations with hydrofluoric acid and other single acids. A great advantage is its high thermal conductivity: a red-hot platinum crucible placed in a desiccator to cool is ready for weighing after about 25 minutes.

H. Silver apparatus. The chief uses of silver crucibles and dishes in the laboratory are in the evaporation of alkaline solutions and for fusions with caustic alkalis; in the latter case, the silver is slightly attacked. Silver melts at 960°C, and care should therefore be taken when it is heated over a bare flame.

I. Nickel ware. Crucibles and dishes of nickel are employed for fusions with alkalis and with sodium peroxide. In the peroxide fusion a little nickel is introduced, but this is usually not objectionable. No metal entirely withstands the action of fused sodium peroxide. Nickel oxidises in air, hence nickel apparatus cannot be used for operations involving weighing.

J. Iron ware. Iron crucibles may be substituted for those of nickel in sodium peroxide fusions. They are not so durable, but are much cheaper.
K. Bakelite apparatus. This synthetic resin is unaffected by hydrofluoric acid at the ordinary temperature. Bakelite funnels, measuring cylinders, etc., are available for use with this acid.

L. Stirring-rods. These are made from glass rod 3–5 mm. in diameter, cut into suitable lengths. Both ends should be rounded by heating in the Bunsen or blowpipe flame. The length of the stirring-rod should be suitable for the size and the shape of the vessel for which it is employed, e.g., for use with a beaker provided with a spout, it should project 3–5 cm. beyond the lip when in a resting position.

A stirring-rod of convenient size should be provided with a short piece of rubber tubing fitted tightly over one end. This is the so-called policeman; it is used for detaching particles of a precipitate adhering to the side of a vessel which cannot be removed by a stream of water from a wash bottle; it should not, as a rule, be employed for stirring, nor should it be allowed to remain in a solution.

M. Boiling-rods. Boiling liquids and liquids in which a gas, such as hydrogen sulphide, sulphur dioxide, etc., has to be removed by boiling can be prevented from superheating and "bumping" by the use of a boiling-rod (Fig. II, 10, 3). This consists of a piece of glass tubing closed at one end and sealed approximately 1 cm. from the other end; the latter end is immersed in the liquid. When the rod is removed, the liquid in the open end must be shaken out and the rod rinsed with a jet of water from a wash bottle. This device should not be used in solutions which contain a precipitate.

N. Desiccators. An ordinary Scheibler-type of desiccator (Fig. II, 10, 4, A) is used for maintaining a dry atmosphere in which to place objects that might be affected by moisture or carbon dioxide. The drying agent (usually calcium chloride in elementary work) is placed in the lower compartment, and the upper compartment is fitted up for the accommodation of crucibles, weighing-bottles, etc. For small desiccators, a silica triangle with wire ends is bent so that the ends are perpendicular to the plane of the triangle, and then the wire ends spread out sufficiently so that they press against the walls and floor of the compartment and are thus held firmly into position. With large desiccators, a porcelain plate on feet (Fig. II, 10, 4, A), provided with apertures for crucibles, etc., is to be preferred: it should be wedged into the sides, if necessary, with cork or some other material. The ground edge of the desiccator should be lightly coated with white vaseline or a special grease in order to make it air-tight; too much grease may permit the lid to slide.
When a hot object is placed in a desiccator, about 5–10 seconds should elapse for the air to become heated and expanded before putting the cover in place. In removing the object, the cover should be slid open very gradually in order to prevent any sudden inrush of air due to the partial vacuum which exists owing to the cooling of the expanded gas content of the desiccator and to desiccation, and thus prevent the precipitate being blown out of the crucible.

A desiccator is also employed for thorough drying of solids for analysis and other purposes. A very convenient type is portrayed in Fig. II, 10, 4, B, a form of "vacuum" desiccator; these are made of thick glass and should be tested by the manufacturers for use with a high vacuum. Large surfaces of the solid can be exposed, and the whole can be evacuated; drying is thus much more rapid than in the ordinary Scheibler desiccator. Pyrex-glass desiccators, both plain and for "vacuum" work, are marketed: these are made of heavy Pyrex glass, and will withstand greater mechanical and thermal shock than those made of soda glass. Phoenix-glass desiccators (a heat-resisting glass)* are cheaper than those of Pyrex glass, and are satisfactory for general student use; the parts are standard, so that a broken cover, for example, can be readily replaced.

Attention is directed to an all-aluminium desiccator (the Fisher "desicooler") which is now marketed.† It is fitted with a shelf containing three holes to accommodate three sizes of crucible, and employs activated alumina as the desiccant (corrosion of the aluminium may occur with other desiccants). The charge of about 60 g. of activated alumina may be reactivated when exhausted by simply heating to 175° C. This desiccator should prove useful for general students' use since it is unbreakable and inexpensive. Larger aluminium desiccators (4-5 in. and also 8 in. diameter) of more robust construction are also available.

The most commonly used desiccant is granular, fused calcium chloride; the 3–8-mesh size is very suitable, but the fused lumps are often employed on account of cheapness. In point of fact, the so-called anhydrous calcium chloride (the hydrated crystalline variety is useless for this purpose) is not a very efficient drying agent (it usually contains about \( \frac{1}{2} \) molecule of water), but it is satisfactory for most purposes. Phosphorus pentoxide is the most powerful common desiccant known; it should be used only when it is absolutely necessary, and must be renewed as soon as a crust forms over its surface. Concentrated sulphuric acid is better than calcium chloride; it should be poured over pumice or broken glass or glass beads, and should not cover the solid completely, thereby reducing the danger of splashing of the liquid on to the bottom of objects in the desiccator: the acid must be replaced as soon as it shows signs of darkening. Re-sublimed iodine must not be dried over sulphuric acid. Anhydrous magnesium perchlorate (anhydrole or dehydrite) and magnesium perchlorate dihydrate have found wide application; they are comparatively expensive for use in desiccators, but the former is extensively employed in the quantitative absorption of water. Anhydrole rivals phosphoric oxide in its power of desiccation; it can absorb about 50 per cent of its weight of water, and can be regenerated by suitable means. Anhydrous calcium

* Supplied by Jencons (Scientific), Ltd., Rosebank Way, Aston, London, W.3,
† Obtainable from the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.
sulphate (marketed in a porous form as drierite) is a very useful and relatively inexpensive desiccant. The relative efficiencies of various drying agents will be evident from the data presented in Table VI.

**TABLE VI.—COMPARATIVE EFFICIENCY OF DRYING AGENTS**

<table>
<thead>
<tr>
<th>Drying Agent</th>
<th>Residual Water per Litre of Air in Mg.</th>
<th>Drying Agent</th>
<th>Residual Water per Litre of Air in Mg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO(_4)</td>
<td>2·8</td>
<td>KOH (stick)</td>
<td>0·014</td>
</tr>
<tr>
<td>ZnCl(_2) (sticks)</td>
<td>1·0</td>
<td>Al(_2)O(_3)</td>
<td>0·005</td>
</tr>
<tr>
<td>CaCl(_2) (gran. “anhyd.” tech.)</td>
<td>1·5</td>
<td>CaSO(_4)</td>
<td>0·005</td>
</tr>
<tr>
<td>NaOH (sticks)</td>
<td>0·8</td>
<td>H(_2)SO(_4)</td>
<td>0·003</td>
</tr>
<tr>
<td>H(_2)SO(_4) (95 %)</td>
<td>0·3</td>
<td>Mg(ClO(_4))(_2)</td>
<td>0·002</td>
</tr>
<tr>
<td>Silica gel</td>
<td>0·03</td>
<td>BaO</td>
<td>0·0007</td>
</tr>
<tr>
<td>Mg(ClO(_4))(_2),2H(_2)O</td>
<td>0·03</td>
<td>P(_2)O(_5)</td>
<td>0·00002</td>
</tr>
</tbody>
</table>

It is clear from the table that a hygroscopic material such as ignited alumina should not be allowed to cool over “anhydrous” calcium chloride; anhydrite is satisfactory.

**O. Test papers.** With the development of more refined methods of quantitative analysis, the use of litmus paper as a rough indicator for determining the acidity and alkalinity of solutions has become obsolete. Paper strips coated with indicators are available commercially in books or cork-stoppered glass vials. These include the following (the p\(\text{H}\) ranges are given in parentheses): thymol blue (1·2-2·8); bromo-phenol blue (2·8-4·6); congo red (3·0-5·0); bromo-cresol green (3·8-5·4); methyl red (4·2-6·3); chloro-phenol red (5·2-6·6); bromo-cresol purple (5·2-6·8); bromo-thymol blue (6·0-7·6); phenol red (6·8-8·4); phenolphthalein (8·6-10·2); and thymol phthalein (9·3-10·5).

An important advance is the introduction of “wide range” or “universal” indicator test papers* which give the approximate hydrogen-ion concentration over the p\(\text{H}\) range 1-2 to 10 to about 1-2 p\(\text{H}\) units. The B.D.H. or Johnsons “narrow range” indicator test papers enable the p\(\text{H}\) to be defined to ± 1 p\(\text{H}\) unit. Colour charts are supplied with all these test papers. Such terms as strongly acid, weakly acid, strongly alkaline, or weakly alkaline now possess real significance when “universal” test papers are employed.

**P. Centrifuge.** A small electrically-driven centrifuge is a useful apparatus for an analytical laboratory. It may be employed for removing the mother liquor from recrystallised salts, for collecting difficultly filterable precipitates, and for the washing of certain precipitates by decantation (see also Section IX, 3, K).

**II, 11. Reagents.—**The purest available reagents, both liquid and solid, should be used for quantitative analysis. The analytical reagent quality (A.R.) is generally employed. In Great Britain A.R. chemicals from British Drug Houses Ltd. and from Hopkin and Williams, Ltd., are similar.

Technique of Quantitative Analysis

conform to the specifications given in their handbook ‘AnalR’ Standards for Laboratory Chemicals (Fourth Edition, 1949). In the U.S.A. the American Chemical Society Committee on Analytical Reagents has established standards for certain reagents,* and manufacturers (e.g., Mallinckrodt, Merck, J. T. Baker, and Coleman and Bell) supply reagents which are labelled “Conforms to A.C.S. Specifications.” In addition, these manufacturers market chemicals, not yet included in the A.C.S. specifications, of high purity, and each package of these analysed chemicals has a label giving the manufacturer’s limits of certain impurities.

It must be remembered that the label on a bottle is not an infallible guarantee of the purity of a chemical, for the following reasons:

(i) Some impurities may not have been tested for by the manufacturer.

(ii) In spite of the greatest care exercised in packing, foreign materials, such as dust, small pieces of cork, paper, etc., may be accidentally introduced.

(iii) The reagent may have been contaminated after its receipt from the manufacturers either by the stopper having been left open for some time, with the consequent exposure of the contents to the laboratory atmosphere or by the innocent return of an unused portion of the reagent to the bottle.

(iv) In the case of a solid reagent, it may not be sufficiently dry. This may be due either to insufficient drying by the manufacturers or to leakage through the stoppers during storage, or to both of these causes.

However, if the analytical reagents be purchased from a manufacturing firm of repute, and instructions given (a) that no bottle is to be opened for a longer time than is absolutely necessary, and (b) that no reagent is to be returned to the bottle after it has been removed, the likelihood of any errors arising from some of the above possible causes is considerably reduced. Liquid reagents should be poured from the bottle; a pipette should never be inserted into the reagent bottle. Particular care should be taken to avoid contamination of the stopper of the reagent bottle. When a liquid is poured from a bottle, the stopper should never be placed on the shelf or on the working bench; some chemists hold the stopper between two fingers of the right hand so that the plug projects from the back of the hand. The exact mode of drying, if required, will vary with the reagent; details are given in the text in connexion with their use. In all cases of doubt as to the purity of the reagents used, they should be tested by standard methods† for the impurities that might cause errors in the determinations. It may be mentioned that not all chemicals employed in quantitative analysis are available in the form of analytical reagents; the purest commercially available products should, if necessary, be purified by known methods, some of which are given below.

For expressing concentrations of reagents, the molar system is universally applicable, i.e., the number or fraction of gram-molecular weights present in 1 litre of solution. Concentrations may also be

expressed in terms of normality if no ambiguity is likely to arise (compare Section I, 23). All reagent bottles should be kept scrupulously clean, particularly round the neck and mouth. The stopper should never be laid on the bench, but should be held between the fingers or placed upon a clean watch-glass; it should be returned to its bottle immediately after the reagent has been removed.

II, 12. Purification of substances.—Space does not permit more than a short discussion of a few of the most important methods of purification which are likely to be employed by the student.

A. Recrystallisation of solids. This is the commonest method of purification; the usual solvent is water. A known weight of the solid is dissolved in a volume of water sufficient to give a saturated or nearly saturated solution at the boiling point: a beaker, conical flask or porcelain dish may be used. The hot solution is filtered through a fluted filter-paper placed in a funnel with a short stem, and the filtrate collected in a beaker; this process will remove insoluble material which is usually present. If the substance crystallises out in the funnel, it should be filtered through a hot-water funnel. In the latter, the conical portion of the funnel is surrounded by a double-walled copper vessel containing water, which can be heated either by placing a Bunsen burner beneath a hollow projection in direct communication with the copper jacket or, better, electrically. The clear hot filtrate is cooled rapidly by immersion in a dish of cold water or in a mixture of ice and water, according to the solubility of the solid; the solution is constantly stirred in order to promote the formation of small crystals, which occlude less mother liquor than larger crystals.

The solid is then separated from the mother liquor by filtration. The various funnels which may be employed for this purpose are shown diagrammatically in Fig. II, 12, 1. (a) is the ordinary porcelain Buchner funnel; (b) is the Jena Buchner “slit sieve” glass funnel. In both cases, one or, better, two good-quality filter papers are placed on the plate; the Jena type is preferable since it is transparent and it is easy to see whether the funnel is perfectly clean. (c) is a Pyrex Buchner funnel with a sintered glass plate; no filter paper is required; strongly acid and weakly alkaline solutions can be readily filtered with this funnel. In all cases the funnel of appropriate size is fitted into a filter flask (d), and the filtration conducted under the diminished pressure provided by a filter pump or vacuum line. The solid may be pressed down on the funnel with a wide glass stopper, sucked as dry as possible, and then washed with small portions of the original solvent to remove the adhering mother liquor. The recrystallised solid is dried upon clock glasses at or above the laboratory temperature according to the
nature of the material; care must of course be taken to exclude dust. Various methods for drying at temperatures above that of the room are described below. The dried solid is preserved in glass-stoppered bottles. It should be noted that unless great care is taken there is a danger of introducing a little filter paper with funnels (a) and (b), and small particles of glass with funnel (c) when the solid is removed.

Some solids are either too soluble, or the solubility does not vary sufficiently with temperature, in a given solvent for direct crystallisation to be practicable. In many cases, the solid can be precipitated from, say, a concentrated aqueous solution by the addition of a liquid, miscible with water, in which it is less soluble. Alcohol, in which most inorganic compounds are almost insoluble, is generally used. Care must be taken that the amount of alcohol or other solvent added is not so large that the impurities are also precipitated. Potassium bicarbonate and tartar emetic (potassium antimonyl tartrate) may be purified by this method.

B. Sublimation. This process is employed to separate volatile substances from non-volatile impurities. Iodine, arsenious oxide and ammonium chloride can be purified in this way. The substance is placed in a porcelain dish or casserole; the latter is gently heated with a small flame and the vapour condensed upon a cool surface, such as a large inverted glass funnel containing a plug of glass wool at the apex, or, preferably, a flask containing cold water.

Pure iodine is required in volumetric analysis, and details for its purification will not be out of place here. Grind together 10 g. of iodine with 4 g. of potassium iodide (the latter to retain any chlorine or bromine present as the non-volatile potassium salts) and transfer the mixture to a casserole; place a flask almost filled with cold water on the casserole (Fig. II, 12, 2). Heat very gently until sufficient iodine has sublimed on to the bottom of the flask, allow to cool, and remove the flask with the iodine adhering to it. Pass a rapid stream of cold water through the flask; this will cause the glass to contract somewhat and the whole of the crust can then be removed by scraping with a clean glass rod and is collected on a clock glass. Break up the large pieces, and repeat the sublimation without the addition of potassium iodide. Remove the second sublimate as before, and grind the iodine in a glass mortar. Dry in a desiccator containing calcium chloride; no grease whatever should be exposed on the inside, since iodine vapour attacks grease forming hydrogen iodide.

II, 13. Heating apparatus.—A. Steam baths. These are used for the slow evaporation of liquids, digestion of precipitates, etc. The simplest form is a lipped beaker in which water is boiled, the vessel being supported on the rim. Generally, a copper vessel, about half-filled with water and heated by a Bunsen burner, is employed. The upper portion is fitted with a series of flat, sheet copper rings of gradually diminishing diameter so that vessels of various sizes can be accommodated. If the water-bath is a large one, the upper portion is fitted with a cover containing holes of various sizes, and each aperture may be provided with its own series of concentric rings or with an individual cover:
vessels of various dimensions can thus be heated at the same time. It is advantageous to fit a constant-level device to the water bath; the danger of running dry and consequent overheating is thus eliminated. In some laboratories, the water bath may be connected to a direct steam supply. Electrically-heated water baths, fitted with a cut-out switch to prevent overheating if the water supply should fail, may be purchased.

**B. Steam ovens.** A steam oven is usually made of copper and, with the exception of the door, is double-cased throughout. The casing is filled to about one fourth of its height with water and is heated by means of a Bunsen or other burner. The water is kept boiling gently and the steam is condensed by a suitable condenser and returned as water to the oven. In many laboratories the heating of steam ovens is carried out simultaneously with the distillation of water in the so-called combined steam oven and still. The temperature inside a steam oven usually does not exceed 90–95°C.

**C. Electric ovens.** The most convenient type is an electrically heated, thermostatically controlled drying oven having a temperature range from room temperature to about 250–300°C. These are comparatively inexpensive and should form part of the normal equipment of every analytical laboratory. The temperature can be controlled to within ±1–2°C. They are used principally for drying precipitates or solids at comparatively low controlled temperatures.

**D. Muffle furnaces.** An electrically heated furnace of muffle form should be available in every well-equipped laboratory. The maximum temperature should be about 1200°C. If possible, a thermo-couple and indicating pyrometer should be provided; otherwise the ammeter in the circuit should be calibrated, and a chart constructed showing ammeter and corresponding temperature readings. Gas-heated muffles may also be used, but are not so convenient in practice; the maximum temperature is about 1000°C.*

**E. Hot plates.** The electrically-heated hot plate, preferably provided with three controls, "Low," "Medium," and "High," is almost indispensable for analytical laboratories. The heating elements and the internal wiring should be totally enclosed; this protects them from fumes and spilled liquids. The three-heat rectangular type is particularly suitable where a number of evaporations are to be carried out simultaneously.

**F. Air baths.** For drying solids and precipitates at temperatures up to 250°C in which acid or other corrosive vapours are evolved, an electric oven should not be used. An air bath may be constructed from a circular metal (copper, iron, or nickel) vessel, lined round the sides and at the bottom with two thicknesses, $\frac{1}{3}$ in. thick, of asbestos board; it is advisable to soak the asbestos in water before placing it in position. The cover consists of an asbestos board, $\frac{1}{4}$ in. thick, provided with a hole for the insertion of a thermometer supported upon a cork. A silica triangle, the legs of which are appropriately bent, is inserted inside the bath for supporting a clock glass, etc. The whole is heated by a Bunsen flame, which is shielded from draughts; the temperature

* Two excellent gas-heated muffle furnaces are marketed: (i) the Gas, Light and Coke Co. pattern, manufactured by Baird and Tatlock (London), Ltd., Freshwater Road, Chadwell Heath, Essex, and (ii) the Fletcher pattern, manufactured by Fletcher, Russell and Co., Ltd., Warrington.
can be readily maintained constant within 2–3° C. An air bath of similar construction, but with special heat-resistant glass sides (Fig. II, 13, 1) has been introduced; this possesses the obvious advantage of visibility inside the air bath.

A form of air bath, which is very useful for the speedy evaporation of liquids (including concentrated sulphuric acid) at almost any temperature and also for the dehydration of many solids, is known as a radiator. It is constructed of sheet iron or nickel bent into the form of a cone (Fig. II, 13, 2, A); the bottom B, also of nickel or iron, but best of platinum, is fixed to the cone by bending the notched edges over one another. A convenient size is 7 cm. high, 7 cm. wide at the top and 5 cm. at the bottom. A triangle of silica, porcelain or platinum is suspended inside the radiator either by cutting three narrow slits to a suitable depth and placing the wire ends of the triangle through these (as in Fig. II, 13, 2, C) or the wire ends may be bent over the upper rim of the cone.* The crucible or dish is supported on the triangle. The radiator is mounted on a tripod and heated directly by a burner; alternatively, it may be heated on a hot plate. Evaporations may thus be carried out speedily without bumping. When very rapid evaporation is required, a metal ring with an opening somewhat larger than the mouth of the crucible, etc., is placed upon the top of the radiator.

Another device of similar character is due to J. J. Moroney. It consists of a metal cylinder, which is usually made of a cast-aluminium alloy; the inside bottom is provided with three small projections upon which the beaker rests. There is only a small clearance around the beaker and the evaporator (Fig. II, 13, 2, D). The beaker is thus heated on the sides as well as the bottom, and has three small hot spots on the bottom at which points the bubbles form when boiling takes place. The general superheating of the bottom is thus eliminated, together with the attendant "bumping." The Moroney evaporator is available commercially; it eliminates the bumping experienced in evaporating heavy solutions, or hydroxides, sulphuric acid, and solutions containing a precipitate.

**Fig. II, 13, 1.**

**Fig. II, 13, 2.**

**II, 14. Sampling of solids.—** Sampling is the process of extracting from a large quantity of material a small portion which is truly representative of the composition of the whole material. This process is of great importance since, if it is not satisfactorily done, the labour and time

* The apparatus, known as the Hillebrand-Willard crucible radiator, is commercially available. It is constructed from one piece of monel metal, and is marketed by the Central Scientific Co., 1700 Irving Park Blvd., Chicago, Ill., U.S.A.
† Obtainable from the Fisher Scientific Company, Pittsburgh, U.S.A.
spent in making a careful analysis of the sample may be completely wasted. If the material is more or less homogeneous, sampling is comparatively simple. If, however, the material is bulky and heterogeneous, sampling must be carried out with great care, and the method will vary somewhat with the nature of the bulk solid. A detailed discussion of the methods of sampling is outside the scope of this book.*

The underlying principle of the sampling of material in bulk, say, of a truck load of coal or iron ore, is to select a large number of portions in a systematic manner from different parts of the bulk and then to combine them. This large sample of the total weight is crushed mechanically, if necessary, and then shovelled into a conical pile. Every shovelful must fall upon the apex of the cone and the shoveller must walk around the cone as he shovels; this ensures a comparatively even distribution. The top of the cone is then flattened out and divided into quarters. Opposite quarters of the pile are then removed, mixed to form a smaller conical pile, and again quartered. This process is repeated, further crushing being carried out if necessary, until a sample of suitable weight (say, 200–300 g.) is obtained.

If the quantity of material is of the order of 2–3 kilos or less, intermixing may be accomplished by the method known as “tabling.” The finely divided material is spread on the centre of a large sheet of oil-cloth or similar material. Each corner is pulled in succession over its diagonal partner, the lifting being reduced to a minimum; the particles are thus caused to roll over and over on themselves, and the lower portions are constantly brought to the top of the mass and thorough intermixing ensues. The sample may then be rolled to the centre of the cloth, spread out, and quartered as before. The process is repeated until a sufficiently small sample is obtained. The final sample for the laboratory, which is usually between 25 and 200 g. in weight, is placed in an air-tight bottle.

The sampling of metals and alloys is best effected by drilling holes, preferably right through the central portion, of a representative test piece; all the material from the hole must be analysed, as the fine dust may differ in composition from the more ductile drillings.

Before analysis the representative sample is usually dried at 105–110°C, or at some higher specified temperature if necessary, to constant weight. The results of the analysis are then reported on the “dry” basis, viz., on a material dried at a specified temperature. The loss in weight on drying may be determined, and the results may be reported, if desired, on the original “moist” basis; these figures will only possess real significance if the material is not appreciably hygroscopic and no chemical changes, other than the loss of water, take place on drying.

In a course of systematic quantitative analysis, such as that with which we are chiefly concerned in the present book, the unknowns supplied for analysis are usually portions of carefully analysed samples which have been finely ground until uniform.

**II, 15. Crushing and grinding.**—If the material is hard (e.g., a sample of rock), it is first broken into small pieces on a hard steel plate with a hardened hammer. The loss of fragments is prevented by covering the plate with a steel ring, or in some other manner. The small lumps may be broken in a "percussion" mortar (also known as a "diamond" mortar) (Fig. II, 15, 1). The mortar and pestle are constructed entirely of hard tool steel. One or two small pieces are placed in the mortar, and the pestle inserted into position; the latter is struck lightly with a hammer until the pieces have been reduced to a coarse powder. The whole of the hard substance may be treated in this manner. The coarse powder is then ground in an agate mortar in small quantities at a time. A mortar of mullite * is claimed to be superior to one of agate: mullite is a homogeneous ceramic material that is harder, more resistant to abrasion and less porous than agate. A synthetic sapphire mortar and pestle * (composed essentially of a specially prepared form of pure aluminium oxide) is marketed; it is extremely hard (comparable with tungsten carbide) and will grind materials not readily reduced in ceramic or metal mortars.

**II, 16. Solution of the sample.**—Most of the synthetic samples employed in the teaching of elementary quantitative analysis are soluble in water or in dilute acids. Naturally occurring minerals and ores, various alloys, etc., must usually be treated with various reagents in order to bring them into solution. In such cases, the qualitative analysis will have revealed the best procedure to adopt. Each case must be considered on its merits; no attempt at generalisation will therefore be made. We can, however, discuss the experimental technique of the simple process of solution of a substance in water or in acids, and also of insoluble substances.

The sample is weighed out into a beaker, and the beaker immediately covered with a clock glass of suitable size (its diameter should not be more than about 1 cm. larger than that of the beaker) with its convex side facing downwards. The beaker should have a spout in order to provide an outlet for the escape of steam or gas. The solvent is then added by pouring it carefully down a glass rod, the lower end of which rests against the wall of the beaker; the clock glass is displaced somewhat during this process. If a gas is evolved during the addition of the solvent (e.g., acids with carbonates, metals, alloys, etc.), the beaker must be kept covered as far as possible during the addition. The reagent is then best added by means of a pipette or by means of a funnel with a bent stem inserted beneath the clock glass at the spout of the beaker; loss by spitting or spray is thus prevented. When the evolution of gas has ceased and the substance has completely dissolved, the under side of the clock glass is well rinsed with a stream of water from a wash bottle, care being taken that the washings fall on to the side of the beaker and not directly into the solution. If warming is necessary, it is usually best to carry out the entire operation of solution in a conical (Erlenmeyer) flask with a small funnel in the mouth (Fig. II, 16, 1, a); loss of liquid by spitting is thus prevented and the escape of gas is not hindered.

* Available from the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.
It may often be necessary to reduce the volume of a solution, or sometimes to evaporate it completely to dryness. Wide and shallow vessels are most suitable, since a large surface is thus exposed and evaporation is thereby accelerated. We may employ shallow beakers of resistance glass (e.g., Chance’s “Baco” beakers), Pyrex evaporating dishes, porcelain basins or casseroles, silica or platinum basins; the material selected will depend upon the extent of attack of the hot liquid upon it and upon the constituents being determined in the subsequent analysis. Evaporations should be carried out on the steam bath or upon a low-temperature hot plate; slow evaporation is preferable to vigorous boiling, since the latter may lead to some mechanical loss in spite of the precautions to be mentioned below. During evaporations, the vessel must be covered by a clock glass of slightly larger diameter than the vessel, and supported either on a large all-glass triangle or upon three small U-rods of glass hanging on the rim of the container. A device known as Fisher’s “speedy-vap” beaker cover *(Fig. II, 16, 1, b) is an improvement on the ordinary watch or clock glass and is of value for simple evaporations. It consists of a clock glass of resistance glass provided with three fused-on glass ribs. Needless to say, at the end of the evaporation the sides of the vessel, the lower side of the clock glass (simple or modified forms), and the triangle and glass hooks (if employed) should be rinsed with distilled water into the vessel.

For evaporation at the boiling point either a conical flask with a short funnel in the mouth or a round-bottomed flask inclined at an angle of about 45° (Fig. II, 16, 1, c) may be employed; in the latter the drops of liquid, etc., thrown up by the ebullition or by effervescence will be retained by striking the inside of the flask, whilst gas and vapour will escape freely.

Substances which are insoluble or only partially soluble in acids are brought into solution by fusion with the appropriate reagent. The most commonly used fusion reagents, or fluxes as they are called, are anhydrous sodium carbonate either alone or, less frequently, mixed with potassium nitrate or sodium peroxide, potassium, or sodium pyrosulphate, sodium peroxide, sodium or potassium hydroxide. The flux employed will depend upon the nature of the insoluble substance. The vessel in which fusion is effected must be carefully chosen; platinum crucibles are employed for sodium carbonate and potassium pyrosulphate; nickel or silver crucibles for sodium or potassium hydroxide; nickel, gold, silver, or iron crucibles for sodium carbonate and/or sodium peroxide; nickel crucibles for sodium carbonate and potassium nitrate (platinum is slightly attacked). To carry out the fusion, a layer of

* Marketed by the Fisher Scientific Co., of Pittsburgh, U.S.A.
the flux is placed at the bottom of the crucible, and then the intimate mixture of the flux and the finely-divided substance added; the crucible should be about half-full, and should, generally, be kept covered during the whole process. The crucible is very gradually heated at first, and the temperature slowly raised to the required temperature. The final temperature should not be higher than is actually necessary; any possible further attack of the flux upon the crucible is thus avoided. When the fusion, which usually takes 30–60 minutes, has been completed, the crucible is grasped by means of the crucible tongs (see Section II, 37) and gently rotated and tilted so that the molten material distributes itself around the walls of the container and solidifies there as a thin layer. This procedure greatly facilitates the subsequent detachment and solution of the fused mass. When cold, the crucible is placed in a casserole, porcelain dish, platinum basin, or Pyrex beaker (according to the nature of the flux) and covered with water. Acid is added, if necessary, and the vessel is covered with a clock glass (preferably of the “speedy-vap” type), the temperature raised to 95–100° C., and maintained until solution is achieved.

Full experimental details for effecting fusions with sodium carbonate and potassium pyrosulphate are given in the analysis of silicates, felspar, etc., in Chapter IV.

**Technique of Volumetric Analysis**

II, 17. Unit of volume.—The fundamental unit employed in measuring the volume of a liquid is the litre. The litre is defined as the volume occupied by one kilogram of water at the temperature of its maximum density (4°C) and subjected to normal atmospheric pressure. It should be noted that the quantity of water which occupies one litre at 4°C has a mass of one kilogram, and not an apparent weight in air of one kilogram. The apparent weight in air of one litre of water at 4°C will be less than one kilogram by the buoyancy effect of the air (compare Section II, 7); if the weighing is made at the ordinary temperature, the apparent weight will be still less because of the lower density of water at temperatures above 4°C. Likewise the volume of water will depend, but to a lesser degree, upon the pressure to which it is subjected. These factors must be allowed for when determining the volume of a piece of apparatus by weighing the water that it contains or delivers.

The millilitre (ml.) is the thousandth part of a litre. This is the most convenient unit for expressing the capacity of volumetric glass ware.

The cubic centimetre (c.c., cm.³) is the volume occupied by a cube each of whose edges is one centimetre in length. The most recent determinations have shown that the relationship between the millilitre and the cubic centimetre is:

\[ 1000 \text{ ml.} = 1000.028 \text{ c.c.} \]

In this book the unit of volume will be taken as the millilitre, in accordance with the recommendation of the National Physical Laboratory in their pamphlets of September 1924 and April 1934, and now almost universally adopted. It is true that the difference between the ml. and c.c. is only 28 parts per million, and therefore well within the limits of error of most volumetric determinations; for this reason many still use the terms c.c. and ml. synonymously. It must be
remembered, however, that the ultimate unit of volume is the litre, which is based upon a determination of mass; it is therefore more logical to adhere to the millilitre for expressing capacities.

II, 18. Standard temperature.—Prior to 1934, the standard temperature in Great Britain was 15° C., but since the issue in 1934 of the “Report on Standard Temperature of Volumetric Glassware” (No. 554) by the British Standards Institution a standard temperature of 20° C. has been almost universally adopted. The latter standard temperature is employed in America and on the continent of Europe. This temperature most nearly represents the average temperature of the laboratory, or at least a temperature which is readily attainable.

If we take the coefficient of cubical expansion of glass as 0.000026 ml. per ml. per degree Centigrade, the following table gives the correction to be added when the sign is +, or subtracted when the sign is —, to or from the capacity of a 1000-ml. flask correct at 20° C. in order to obtain the capacity at other temperatures.

<table>
<thead>
<tr>
<th>Degrees C.</th>
<th>5°</th>
<th>10°</th>
<th>15°</th>
<th>20°</th>
<th>25°</th>
<th>30°</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML.</td>
<td>—0.39</td>
<td>—0.26</td>
<td>—0.13</td>
<td>0.00</td>
<td>+0.13</td>
<td>+0.26</td>
</tr>
</tbody>
</table>

In the actual use of volumetric glassware for the measurements of liquids, the expansion of the liquid must also be taken into consideration if temperature corrections are to be made. Table VIII gives the corrections to be added or subtracted in order to obtain the volume occupied at 20° C. by a volume of water which at the tabulated temperature is contained in an accurate 1000-ml. flask having a standard temperature of 20° C. It will be seen that the allowance for the expansion of water is considerably greater than that for the expansion of the glass.

<table>
<thead>
<tr>
<th>Degrees C.</th>
<th>5°</th>
<th>10°</th>
<th>15°</th>
<th>20°</th>
<th>25°</th>
<th>30°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correction (ml.)</td>
<td>+1.37</td>
<td>+1.24</td>
<td>+0.77</td>
<td>0.00</td>
<td>—1.03</td>
<td>—2.30</td>
</tr>
</tbody>
</table>

II, 19. Volumetric apparatus.—The most commonly used apparatus in volumetric analysis are measuring flasks, burettes, and pipettes. Graduated cylinders and weight pipettes are less widely employed. Each of these will be described in turn, together with the methods of use, calibration, and tolerances allowed by the National Physical Laboratory.

* The discovery of deuterium oxide D₂O ("heavy water"), which has a specific gravity at 20° C. of 1.1059 and a temperature of maximum density of 11°-6° C., introduces a complicating factor. The normal proportion of deuterium oxide in ordinary water is about 1 part in 5,000; this will result in a difference of about 22 parts per million in density from that of pure protium oxide H₂O. Fortunately, the proportion of deuterium oxide does not vary appreciably with all ordinary samples of water, but it is evident that a precise definition of volume must specify the proportion of this constituent.
Cleaning of glass apparatus. Before describing volumetric apparatus in detail, reference must be made to the important fact that all such glassware must be perfectly clean and free from grease, otherwise the results will be unreliable. The test for cleanliness of glass apparatus is that on being filled with distilled water and the water withdrawn, only an unbroken film of water remains. If the water collects in drops, the vessel is dirty and must be cleaned. Various methods are available for cleaning. The method which is most frequently used consists in filling the apparatus with "cleaning mixture," a solution of powdered sodium or potassium dichromate in concentrated sulphuric acid, and allowing it to stand for several hours, but preferably overnight; the acid is then poured off, the apparatus thoroughly rinsed with distilled water, and allowed to drain until dry. (It may be mentioned that potassium dichromate is not very soluble in concentrated sulphuric acid (about 1.5 g. per litre), whereas sodium dichromate \( \text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O} \) is much more soluble (about 70 g. per litre); for this reason, as well as the fact that it is much cheaper, the latter is usually preferred for the preparation of "cleaning mixture." From time to time it is advisable to filter the sodium dichromate–sulphuric acid mixture (ca. 70 g. sodium dichromate per litre) through a little glass wool placed in the apex of a glass funnel: small particles or sludge, which are often present and may block the tips of burettes, are thus removed.) A more expeditious method of drying is to rinse the apparatus with pure acetone after draining off the water and then to blow or draw air through it. Apparatus of borosilicate glass, e.g., Pyrex, may be dried in an oven at 100–120°. A more efficient cleaning liquid is a mixture of concentrated sulphuric acid and fuming nitric acid; this may be used if the vessel is very greasy and dirty. Grease may also be removed by filling the apparatus with warm soap solution, leaving for 15 minutes, rinsing with water, followed by concentrated hydrochloric acid, and finally with distilled water.

\[ \text{Measuring flasks.*} \text{A measuring flask is a flat-bottomed, pear-shaped, or spherical vessel with a long narrow neck (Fig. II, 20, 1).} \]

A thin line etched around the neck indicates the volume that it holds at a certain definite temperature, usually 20° C. (both the capacity and the temperature are clearly marked on the flask); the flask is then said to be graduated to contain. Flasks with one mark are always taken to contain the volume specified. A flask may also be marked to deliver a specified volume of liquid under certain definite conditions; these are, however, not suitable for exact work. Vessels standardised at the National Physical Laboratory are marked with a letter \( D \) when they are meant to deliver; if they are intended both to contain and to deliver, the letter \( D \) is placed above the upper mark and the letter \( C \) below the lower mark.

The mark extends completely around the neck in order to avoid errors due to parallax when making the final adjustment; the lower edge of the meniscus should be tangential to the graduation mark, and both the front and the back of the mark should be seen as a single line. The neck is made narrow so that a small change in volume will have a large effect upon the height of the meniscus; the error in adjustment of the meniscus is accordingly small. Volumetric flasks should be fitted

* These are sometimes known as volumetric flasks.
with ground-glass stoppers, and both the stopper and the flask should be numbered.

Measuring flasks are ordinarily made of 25, 50, 100, 250, 500, 1000, and 2000-ml. capacity. They are employed in making up standard solutions to a given volume; they can also be used for obtaining, with the aid of pipettes, aliquot portions of the substance to be analysed.

**Calibration.** A large balance, which will carry about a kilogram in each pan and which has a sensitivity when fully loaded of about 5 mg., is required. The flask is first thoroughly cleaned and dried; it is then weighed on the large balance. The flask is then filled with distilled water, which has been standing in the balance room for at least an hour before use, to a few millimetres above the mark: care is taken to avoid wetting the neck above the water surface. The lowest point of the water meniscus is then adjusted to the graduation mark by withdrawing small quantities of water with a capillary tube or with a narrow tube drawn out to a jet at the lower end. The flask is then weighed, and the temperature of the water noted. The true volume of the water filling the flask to the graduation mark can be calculated with the aid of the above table. The values in the table have been obtained by making allowance for (a) the difference in volume of the glass vessel at the calibration temperature and at 20° C., (b) the density of water at the temperature of the calibration, and (c) the effect of buoyancy of the air upon the water and the brass weights. The figures apply to an atmospheric pressure of 760 mm. of mercury and a relative humidity of the air of 50 per cent; the usual deviation from these figures will affect

**TABLE IX.—WEIGHT OF WATER (BRASS WEIGHTS IN AIR) TO GIVE ONE LITRE AT 20° C.**

<table>
<thead>
<tr>
<th>Temp. (° C.)</th>
<th>Weight (g.)</th>
<th>Volume of 1 g. of Water (ml.)</th>
<th>Temp. (° C.)</th>
<th>Weight (g.)</th>
<th>Volume of 1 g. of Water (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>998.39</td>
<td>1.0016</td>
<td>23</td>
<td>996.60</td>
<td>1.0034</td>
</tr>
<tr>
<td>11</td>
<td>998.32</td>
<td>1.0017</td>
<td>24</td>
<td>996.33</td>
<td>1.0036</td>
</tr>
<tr>
<td>12</td>
<td>998.23</td>
<td>1.0018</td>
<td>25</td>
<td>996.17</td>
<td>1.0038</td>
</tr>
<tr>
<td>13</td>
<td>998.14</td>
<td>1.0018₃</td>
<td>26</td>
<td>995.93</td>
<td>1.0041</td>
</tr>
<tr>
<td>14</td>
<td>998.04</td>
<td>1.0019</td>
<td>27</td>
<td>995.69</td>
<td>1.0043</td>
</tr>
<tr>
<td>15</td>
<td>997.93</td>
<td>1.0021</td>
<td>28</td>
<td>995.44</td>
<td>1.0046</td>
</tr>
<tr>
<td>16</td>
<td>997.80</td>
<td>1.0022</td>
<td>29</td>
<td>995.18</td>
<td>1.0048</td>
</tr>
<tr>
<td>17</td>
<td>997.68</td>
<td>1.0023</td>
<td>30</td>
<td>994.91</td>
<td>1.0051</td>
</tr>
<tr>
<td>18</td>
<td>997.51</td>
<td>1.0025</td>
<td>31</td>
<td>994.64</td>
<td>1.0054</td>
</tr>
<tr>
<td>19</td>
<td>997.35</td>
<td>1.0026</td>
<td>32</td>
<td>994.35</td>
<td>1.0057</td>
</tr>
<tr>
<td>20</td>
<td>997.18</td>
<td>1.0028</td>
<td>33</td>
<td>994.06</td>
<td>1.0060</td>
</tr>
<tr>
<td>21</td>
<td>997.00</td>
<td>1.0030</td>
<td>34</td>
<td>993.75</td>
<td>1.0063</td>
</tr>
<tr>
<td>22</td>
<td>996.80</td>
<td>1.0032</td>
<td>35</td>
<td>993.45</td>
<td>1.0066</td>
</tr>
</tbody>
</table>

*Note.—For the calibration of flasks of capacity other than 1 litre, the corresponding multiple or sub-multiple of the above values is taken.*

water meniscus is then adjusted to the graduation mark by withdrawing small quantities of water with a capillary tube or with a narrow tube drawn out to a jet at the lower end. The flask is then weighed,* and the temperature of the water noted. The true volume of the water filling the flask to the graduation mark can be calculated with the aid of the above table. The values in the table have been obtained by making allowance for (a) the difference in volume of the glass vessel at the calibration temperature and at 20° C., (b) the density of water at the temperature of the calibration, and (c) the effect of buoyancy of the air upon the water and the brass weights. The figures apply to an atmospheric pressure of 760 mm. of mercury and a relative humidity of the air of 50 per cent; the usual deviation from these figures will affect

* If a precision type of balance is not available, or the equality of the length of the balance arms is suspect, it is best to weigh by the method of substitution (Section II, 60). Counterpoise the empty flask either by adding lead shot into a beaker placed on the right-hand pan and/or another set of weights; observe the rest point. Remove the flask and replace it by weights sufficient to bring the balance to the same rest point. Record the weight, and remove both weights and tare. Weigh the flask filled with distilled water to the mark by the method of substitution as before. The difference in weights on the left-hand pan will give the weight of the water.
the buoyancy correction (compare Section II, 7) only slightly and can be neglected for most purposes.

If the error, calculated with the aid of Table IX, falls within the limits of tolerance of "Class A" apparatus (see following paragraph), the flask may be taken as accurate for all ordinary quantitative work. If, however, the error is large, the simplest procedure is either to affix a small paraffined label to the flask bearing the true capacity and the date of calibration, or to calibrate another flask. The process of regraduating the flask is best left to the manufacturers.

**Standardised flasks.** Measuring flasks which have been verified at the National Physical Laboratory can be purchased. The N.P.L. recognises one type of volumetric glassware, i.e., apparatus which has passed "Class A" tests (marked N.A.). Apparatus which has passed the "Class A" test can also be supplied with a certificate giving the exact volume; these may be employed in work demanding the highest accuracy. Full details concerning the construction and design of volumetric glassware are given in the pamphlet issued by the N.P.L. in January 1946.* Only the tolerances or permissible errors for flasks "to contain" will be given here.

<table>
<thead>
<tr>
<th>Capacity, ml.</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>250</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tolerance, ±ml., &quot;Class A&quot;</td>
<td>0.03</td>
<td>0.04</td>
<td>0.06</td>
<td>0.1</td>
<td>0.15</td>
<td>0.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**II, 21. Pipettes.**—Pipettes are of two kinds: (i) those which have one mark and deliver a small, constant volume of liquid under certain specified conditions (transfer pipettes); (ii) those in which the stems are graduated and are employed to deliver various small volumes at discretion (graduated or measuring pipettes). They are shown in Fig. II, 21, 1 as a and c; type b is a useful form which is employed for measuring out corrosive liquids, the bulb preventing the entrance of liquid into the mouth. Graduated pipettes are useful for measuring out volumes of liquids approximately; they are not employed in exact work.

Transfer pipettes are constructed with capacities of 1, 2, 5, 10, 20, 25, and 50 ml.; those of 10, 25, and 50 ml. capacity are most frequently employed. In using such pipettes, they are first rinsed with the liquid, then filled by suction to about 1–2 cm. above the mark, and the upper end of the pipette is closed with the tip of the dry index finger; any adhering liquid is wiped from the outside of the lower stem. The liquid is allowed to run out slowly by slightly relaxing the pressure of the finger and by carefully rotating the pipette until the bottom of the meniscus just reaches the graduation mark; the pipette must be held vertically so that the mark is at the same level as the eye. Any

* The U.S. Bureau of Standards issue a similar pamphlet (Circular No. 9 for 1910). The tolerances are similar to those allowed by the N.P.L.
Quantitative Inorganic Analysis

drops adhering to the tip are removed by stroking against a glass surface. The liquid is then allowed to run into the receiving vessel, the tip of the pipette touching the wall of the vessel. When the continuous discharge has ceased, the jet is held in contact with the side of the vessel for 15 seconds (draining time). At the end of the draining time, the receiving vessel is removed from contact with the jet of the pipette, thus removing any drop adhering to the outside of the pipette. The liquid remaining in the jet of the pipette must not be removed either by blowing or by other means; blowing may introduce grease from the mouth. The above standard procedure for filling and emptying a pipette is that recommended by the National Physical Laboratory, and will be employed in its calibration.

A pipette will not deliver constant volumes of liquid if discharged too rapidly. The orifice must be of such size that the time of outflow is about 20 seconds for a 10-ml pipette, 30 seconds for a 25-ml pipette, and 35 seconds for a 50-ml pipette.

Calibration. The pipette is cleaned by filling it with dichromate-sulphuric acid cleaning mixture and allowing it to stand, preferably overnight. Filling is effected by attaching the pipette in a vertical position with the tip dipping into a beaker of "cleaning mixture" and attaching the upper end to a safety flask (Fig. II, 21, 2; the supporting clamps are not shown). The "cleaning mixture" is drawn into the pipette until the level is within 2 cms. of the top, and the rubber connecting tubing is closed with a pinch-cock. The solution is allowed to stand for 5-10 minutes, the pipette is raised, the rubber tubing disconnected, the pipette is allowed to drain, washed thoroughly with tap water, and finally with distilled water. The pipette is then filled with distilled water, which has been standing in the balance room for at least an hour, to a short distance above the mark. Water is run out until the meniscus is exactly on the mark, and the outflow is then stopped. The drop adhering to the jet is removed by bringing the surface of some water contained in a beaker in contact with the jet, and then removing it without jerking. The pipette is then allowed to discharge into a clean, weighed stoppered flask (or a large weighing bottle) and held so that the jet of the pipette is in contact with the side of the vessel (it will be necessary to incline slightly either the pipette or the vessel). The pipette is allowed to drain for 15 seconds after the outflow has ceased, the jet still being in contact with the side of the vessel. At the end of the draining time the receiving vessel is removed from contact with the tip of the pipette, thus removing any drop adhering to the outside of the pipette and ensuring that the drop remaining in the end is always of the same size. To determine the instant at which the
outflow ceases, the motion of the water surface down the delivery tube of the pipette is observed, and the delivery time is considered to be complete when the meniscus comes to rest slightly above the end of the delivery tube. The draining time of 15 seconds is counted from this moment. The receiving vessel is weighed, and the temperature of the water noted. The capacity of the pipette is then calculated with the aid of Table IX. At least two determinations should be made. If the error is within "Class A" tolerance (see below), the pipette may be accepted at its nominal value. If the error is larger, a small paraffined label indicating the error may be attached to the pipette (this is the simpler procedure), or a new graduation may be made as follows. A thin strip of gummed paper is attached to the pipette and a mark made where it is thought that the graduation should be; a rough guide is provided by noting how far the water falls in the narrow tube when one drop (roughly 0.05 ml.) is run out of the pipette. The new graduation is then tested as before. If this is not quite correct, the exact position can now be readily determined. The final mark can be made permanent by etching a ring into the glass with hydrofluoric acid.

Standardised pipettes. Pipettes which have been tested at the National Physical Laboratory may be purchased. The times of outflow and the tolerances for the "Class A" tests are tabulated below.

<table>
<thead>
<tr>
<th>Capacity, ml.</th>
<th>2</th>
<th>20</th>
<th>50</th>
<th>100</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time of outflow, secs.</td>
<td>7–15</td>
<td>20–35</td>
<td>25–40</td>
<td>30–50</td>
<td>50–75</td>
</tr>
<tr>
<td>Tolerance, ±ml.</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.08</td>
</tr>
</tbody>
</table>

For capacities not given in the above table, the delivery times and tolerances corresponding to the next larger tabulated capacity should be taken. "Class A" pipettes are marked with reference to delivery (D), time of outflow, and of drainage (15 seconds). A typical inscription for a 50-ml. pipette would be:

50 ml.
D. 20° C.
(30 ± 15) Sec.

Burettes.—Burettes are long cylindrical tubes of uniform bore throughout the graduated length; they are closed at the bottom by means of a glass stopcock, or with a short piece of india-rubber tubing carrying a glass jet (Fig. II, 22, 1, A and B). The rubber tubing is closed either by means of a pinchcock or by means of a glass bead; by firmly squeezing the rubber surrounding the bead between the thumb and the forefinger a narrow channel is opened, through which the liquid escapes, the rate of flow being readily controlled. Type C (Fig. II, 22, 1) burettes are generally employed for titrating hot solutions; the heat will not reach the bulk of the solution in the burette and thus will not affect its volume. Burettes are usually of 50-ml. capacity graduated to tenths of a ml.; capacities of 10 ml. and 25 ml. are also available. **Burettes are employed to deliver variable volumes of liquid.**

A simple and inexpensive burette holder, designed by the writer,*

Quantitative Inorganic Analysis

is illustrated in Fig. II, 22, 1; burettes A and B are held in position by the double clamp; a single burette holder D, which can be fixed on a retort stand, is also marketed. The burette holder is provided with a white rubber backing, no parts of the holder obscure graduations, and the burette is held firmly in a truly vertical position.

The Fischer double burette holder * (Fig. II, 22, 2) is probably the best burette holder marketed, but is of necessity expensive: both burettes are locked in place by a self-locking mechanism; either burette is easily released and brought to any desired height by merely pressing the gripping mechanism; it is constructed of Castalloy, a rustless alloy. The Fisher double burette holder, students' model

(Fig. II, 22, 3), is inexpensive: each burette is held in place by means of three arms, the centre one under spring tension; a burette is removed by pressing the central lever in front of the holder; it is made largely of steel and is finished in baked black enamel.

The mode of use is as follows. The clean, empty burette is fixed into a suitable stand and clamped vertically. About 10 ml. of the solution to be employed is poured into it so as to wet the whole internal surface, and is then run completely out; this rinsing is repeated. The burette is then filled to a little above the highest graduation; if a short funnel is used it must be removed immediately after the filling. The liquid is then allowed to flow out until the lowest point of the meniscus just touches this graduation; the jet must of course be completely full of liquid. To read the position of the meniscus, the eye must be at the

* Manufactured by Fisher Scientific Co., 717 Forbes Street, Pittsburgh, Pa., U.S.A.
same level as the meniscus, in order to avoid errors due to parallax. In
the best type of burette, the graduations are carried completely round
the tube for each ml. and half-way round for the other graduation
marks: parallax is thus easily avoided. To aid the eye in reading the

![Diagram](image1)

**Fig. II, 22, 2.**

position of the meniscus a piece of white paper or cardboard, the lower
half of which is blackened either by painting with dull black paint or
by pasting a piece of dull black paper upon it, is employed. When
this is placed so that the sharp dividing line is 1–2 mm. below the menis-
cus, the bottom of the meniscus appears to be darkened and is sharply

![Diagram](image2)

**Fig. II, 22, 3.**

outlined against the white background (Fig. II, 22, 4);* the level of
the liquid can then be accurately read. For all ordinary purposes
readings are made to 0.05 ml.; for precision work readings to 0.01–0.2
ml. (by estimation with the aid of a lens) should be made.

* A celluloid black and white disc, which can be slipped over the burette is available
commercially (e.g., "Fisher" burette meniscus holder, "Baird and Tatlock" burette
reader, etc.).
The so-called Schellbach burette, which contains a white enamelled band, with central blue ribbon, fused vertically at the back of the burette tube, was originally intended to improve the ease of reading the level of the liquid and also to eliminate parallax. Its use in practice is not, however, very satisfactory, and hence cannot be recommended.

As a general rule, it is advisable to use the zero mark each time. It has been established that practically no after-drainage takes place in a burette if the rate of outflow does not exceed a certain speed. If the speed is exceeded, owing to the jet being too large, then drainage takes place for several minutes. The limits for the time of outflow with the tap fully open and the jet not in contact with the receiving vessel are given in connexion with the N.P.L. “Class A” tests in a subsequent paragraph. A burette should be selected which conforms to these limits. The drop adhering to the jet after the liquid has been discharged is removed by bringing the side of the receiving vessel into contact with the jet. When not in use, burettes should be well rinsed with distilled water and covered with a short inverted test-tube to keep out dust, or they may be inverted in the burette stand, jet uppermost.

Burettes fitted with rubber and a pinchcock are used for alkaline solutions and as cheap substitutes for glass stopcock burettes; they cannot be employed for such solutions as potassium permanganate and iodine, which attack rubber. The use of any form of burette other than that fitted with a glass stopcock is not recommended, for the following reasons: (i) some of the liquid may attack the rubber, and (ii) it is impossible to see whether the air has been completely displaced in the rubber tube. Alkaline solutions, including those of caustic alkalis, may be used with glass taps, but the burettes must be emptied and washed immediately after use, otherwise the taps are liable to stick. Where the use of alkaline solutions in a burette is a routine process, it is best to utilise a nickel or silver stopcock.

**Lubricants (or greases) for glass stopcocks.** The simplest lubricant is either pure vaseline or a mixture of pure vaseline and resin cerate.

A "soft" grease may be prepared by thoroughly mixing, by melting and stirring, 1 part of beeswax and 3 parts of pure vaseline. A "hard" grease is obtained by adding 1 part of soft black rubber in small pieces to the latter mixture, heating to 140–150° C., and stirring continuously until thoroughly incorporated.

An excellent lubricant (Shepherd, 1931), which is particularly suitable for gas-analysis apparatus, is obtained from 6 parts of rubber (pale crêpe, freshly milled, and free from dirt and lint), 7 parts of white vaseline, and 1 part of paraffin wax, m.p. 40–45° C. The vaseline and paraffin wax are melted in a large porcelain casserole, and the rubber is added in several portions. The mixture is placed in a thermostated oven or in an air-bath (Section II, 12F; first paragraph) and stirred continuously for 190 hours at 155–165° C. It is then transferred to 2-oz. ointment jars and chilled in ice immediately, care being taken to prevent condensation of water on the grease.
Excellent lubricants may be purchased.* The Dow-Corning "silicone" lubricant has many desirable properties and may be strongly recommended.

The objects of adequate lubrication of the stopcock are to prevent sticking or "freezing." The plug of the stopcock is removed from the barrel, and the lubricant is applied lightly to the narrow portion of the barrel of the tap and to the wide portion of the plug, taking care that it does not reach the bore. Upon inserting the plug and turning it in the barrel several times, a uniform film of grease will be distributed in the ground joint. The stopper may be held in position by a rubber band or other suitable device. The use of a stopper tie (Fisher), which prevents loss or interchange of the plug, is recommended.

Calibration of a glass-stoppered burette. The burette is filled with dichromate-sulphuric acid cleaning mixture and a beaker placed beneath the burette. The burette is allowed to stand for one hour, but preferably overnight. The solution is run out, and the burette rinsed five or six times with distilled water. The stopcock and the inside of the ground joint are then wiped dry; the stopcock is then smeared lightly with a suitable lubricant as described in the preceding paragraph and replaced into position. The burette is then clamped vertically and filled with distilled water; the latter should have been standing for at least an hour prior to use so as to be certain that it has acquired the room temperature. The temperature of the water is noted. The air in the jet is expelled by running out water from the burette. Two methods are available for the actual calibration. The first is based upon that employed at the National Physical Laboratory. The second is due to Ostwald; it is very convenient to use, but is not accepted by the N.P.L.

Method I. The burette is filled with water to a short distance above the zero mark, and water is slowly run out until the meniscus is exactly on the zero mark. The drop of water adhering to the jet is removed by bringing the jet into contact with the side of the beaker. For reading the position of the meniscus to 0·01 ml., the device shown in Fig. II, 22, 4 coupled, preferably, with a lens, may be employed. In the better-quality burette in which the calibrations are carried completely round for the 1-ml. divisions and half-round for fractions of a ml., errors due to parallax may be avoided by placing the eye so that the front and back of the graduation at the meniscus appear to coincide. The burette is allowed to deliver freely, i.e., with the stopcock fully open, into a clean, weighed Erlenmeyer (conical) flask of 100–150 ml. capacity. When the meniscus of the water is approximately 1 cm. from the line to be tested, the rate of outflow is reduced so that the motion of the water surface is brought under complete control; the meniscus is adjusted exactly on the mark.† No period of waiting for drainage should be allowed. The drop adhering to the jet after the setting has been made is removed by bringing the side of the flask into contact with the jet. The flask is then stoppered and weighed to the nearest 0·01 g. This procedure is followed for each of the graduations to be tested, e.g., at 5-ml. intervals, 5, 10, 15, 20, etc., or at 10-ml.

† If this has been missed by a small amount, the volume is read to the nearest 0·01 ml.
The zero mark is always taken as the starting-point, since a very small drainage error might take place between the readings and affect the accuracy of the intermediate determinations. The whole process should be repeated; the duplicate determinations should agree within 2 centigrams. The volume actually delivered is calculated from the weight of the water, and the volume of 1 g. of water at the temperature of the calibration given in Table IX. The results should be tabulated as follows:

**Calibration of a Burette. (Temperature = \( -0^\circ \text{C.} \))**

<table>
<thead>
<tr>
<th>Burette Readings (ml.)</th>
<th>Weight of Water Delivered (Mean) (g.)</th>
<th>True Volume at 20^\circ \text{C.} (ml.)</th>
<th>Correction (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·00-5·00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0·00-10·00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0·00-15·00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0·00-20·00, etc.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The results may also be plotted graphically with burette readings (1 ml. = 2 mm.) as abscissae and corrections (0·01 ml. = 2 mm.) as ordinates.

**Method 2.** The so-called burette-calibrator is employed. This consists of a small pipette (usually of 2-ml. capacity) with a mark on the upper and lower limbs, and a tap and side tube fused to the lower end. It is first thoroughly cleaned and then attached by means of a short piece of stout rubber tubing ("pressure tubing") to the jet of the burette (Fig. 11, 22, 5); both burette and pipette are clamped vertically. The tap of the pipette is closed, and distilled water is run in from the burette until its level is about 2 cm. above the upper mark. If all air bubbles have not thus been removed from the pipette and its jet, more water is run in and the adjustment repeated. The drop of water adhering to the jet is removed by bringing it into contact with the inside wall of a beaker. The jet is then placed against the side of a tared weighing-bottle or a small stoppered flask, and water is allowed to flow slowly from the burette-calibrator until the meniscus reaches the lower mark; the bottle or flask is stoppered reweighed. This process is repeated at least six times, and the mean weight of the water delivered is obtained. The exact volume of the pipette can then be calculated from the known temperature of the water and Table IX.

The burette is now filled, adjusted exactly to the zero mark by connexion with the pipette, and the latter, in turn, adjusted to its lower mark. The pipette is then filled to the upper mark from the burette, and the reading of the latter taken. The pipette is emptied to the lower mark, and the process repeated so that successive readings are taken at ca. 2-, 4-, 6-, 8-, . . . 50-ml. marks on the burette. From the known volume of the burette-calibrator (say, 1·9962 ml.), the correct volumes at the successive readings of the burette can be computed and the corrections thus evaluated. The final values may be collected in the form of a table or plotted graphically as described under Method 1.
Technique of Quantitative Analysis

Attention is directed to the fact that only Method 1 is adopted by the N.P.L.; Method 2 is a useful exercise for students.

**Standardised burettes.** The National Physical Laboratory recognises one type of test for burettes, viz., for "Class A." Only burettes with glass taps are admitted; if a filling-tube is sealed in between the lowest graduation mark and the tap, a stopcock must be present in the filling-tube. Various details as to the construction of burettes are to be found in the pamphlet *Tests on Volumetric Glassware* (N.P.L., January 1946), but the tolerances and times of outflow (the latter are important in connexion with the drainage error) are tabulated below.

<table>
<thead>
<tr>
<th>Total capacity, ml.</th>
<th>2</th>
<th>10</th>
<th>30</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum error, ±ml., “Class A”</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.06</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The tolerances apply to the whole of the graduated portion and to any portion of it; the differences in errors between any two points must not exceed these values.

<table>
<thead>
<tr>
<th>Length graduated, ml.</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time of outflow limits, seconds, “Class A”</td>
<td>40–75</td>
<td>60–105</td>
<td>80–135</td>
<td>100–165</td>
<td>120–195</td>
<td>140–225</td>
</tr>
</tbody>
</table>

The N.P.L. will, on payment of a certain fee, give a certificate showing the exact volume delivered at various graduations on “Class A” burettes.

**II, 23. Weight burettes.**—For work demanding the highest possible accuracy in transferring various quantities of liquids, weight burettes are employed. As their name implies, they are weighed before and after a transfer of liquid. A very useful form is shown diagrammatically in Fig. II, 23, 1, a. There are two ground-glass caps, the lower one is closed, whilst the upper one is provided with a capillary opening; the loss by evaporation is accordingly negligible. For hygroscopic liquids, a small ground-glass cap is fitted to the top of the capillary tube. The burette is roughly graduated in 5-ml. intervals.

The Lunge-Rey pipette is shown in Fig. II, 23, 1, b. There is a small central bulb (5–10 ml. capacity) closed by two stopcocks 1 and 2; the pipette 3 below the stopcock has a capacity of about 2 ml., and is fitted with a ground-on test-tube 4. This pipette is of particular value for the weighing out of corrosive and fuming liquids (see Section III, 13).

**II, 24. Graduated cylinders.**—These are graduated vessels of thick

* Also known as measuring-cylinders.
glass (Fig. II, 24, 1), and are available in capacities from 2 to 2000 ml. Since the area of the upper surface of the liquid is much greater than in a measuring flask, the accuracy is not very high. Graduated cylinders cannot therefore be employed for work demanding even a moderate degree of accuracy. They are, however, useful where only rough measurements are required. Two kinds are generally employed: the wide-mouthed, open type with spout (Fig. II, 24, 1, A), and the stoppered type (Fig. II, 24, 1, B). They may be calibrated, if desired, by measuring into them definite volumes of water from calibrated burettes or pipettes.

II, 26. Storage and preservation of solutions in volumetric analysis.—Solutions which are comparatively stable and unaffected by exposure to air may be stored in whole or half Winchester quart bottles; for work requiring the highest accuracy Pyrex, or other resistance glass, bottles fitted with ground-glass stoppers should be employed, the solvent action of the solution being thus considerably reduced. The bottle should be clean and dry: a little of the stock solution is introduced, the bottle well rinsed with this solution, drained, and the remainder of the solution poured in and the bottle immediately stoppered. If the bottle is not dry, but has recently been thoroughly rinsed with distilled water, it may be rinsed successively with three small portions of the solution and drained well after each rinsing; this procedure is, however, less satisfactory than that employing the clean and dry vessel. Immediately after the solution has been transferred to the stock bottle, it should be labelled with: (1) the name of the solution, (2) its concentration, (3) the date of preparation, and (4) the initials of the person who prepared the solution, together with any other relevant data. Unless the bottle is completely filled, internal evaporation and condensation will cause drops of water to form on the upper part of the inside of the vessel. For this reason, the bottle must be thoroughly shaken before removing the stopper.

Solutions which are liable to alter their strength by access of air (e.g., alkali hydroxides, ferrous ammonium sulphate, titanous chloride or sulphate) may be kept in the apparatus shown diagrammatically in Fig. II, 25, 1, a. The burette has a three-way tap which enables it either to be filled from the stock bottle or to be emptied. If such a burette is not available, one with a side-tube and stopcock (Fig. II, 25, 1, b) will serve equally well. The
Technique of Quantitative Analysis 205

Tube $T$ is permanently connected with a source of hydrogen (e.g., from a Kipp’s apparatus) if the solution is oxidised upon exposure to air (e.g., ferrous sulphate, ferrous ammonium sulphate, titanous chloride or sulphate), or to a soda-lime guard tube, if it contains caustic alkali. In the latter case, particularly if ordinary glass vessels are used, the solution may become contaminated with silicates owing to the attack of the alkali on the glass; it is better to employ a resistance glass storage vessel, or the inside of the vessel may be coated with a thin layer of paraffin wax or with “thermoprene.”

An apparatus for the storage of large volumes of solutions which alter their strength upon exposure to air, e.g., ferrous sulphate solution, and which permits of the automatic filling of the burette is shown in

![Diagram](Fig. II, 25, 2)

![Diagram](Fig. II, 25, 3)

Fig. II, 25, 2. $A$ is a large storage bottle of 10–15 litres capacity. $B$ is a 50-ml burette provided with an automatic filling device at $G$ (the point of the drawn-out tube is adjusted to be exactly at the zero mark of the burette), $D$ is the burette-bottle clamp, $E$ is a two-holed rubber stopper, $F$ is a ground-glass tension joint, $G$ is a rubber tube connected to a source of hydrogen (for example, a Kipp’s apparatus), $H$ is a Bunsen valve, and $J$ is hydrogen. The burette is filled by closing tap $K$ and passing hydrogen through the rubber tube attached to tap $L$; tap $L$ is then closed, tap $K$ opened, and the excess of liquid allowed to siphon back.

Two other apparatus $\dagger$ for the storage of standard solutions are shown in Figs. II, 25, 3 and II, 25, 4. These are adaptations of micro-apparatus to the macro scale. Fig. II, 25, 3 is self-explanatory. The solution is contained in the storage bottle $A$, and the 50-ml burette is fitted into this by means of a ground-glass joint $B$. To fill the burette, tap $C$ is opened and the liquid pumped into the burette by means of the small bellows $E$. $F$ is a small guard tube; this is filled with soda-lime or “solfolite” when caustic alkali is contained in the storage

---

* This is a rubber paint made by the B. F. Goodrich Company, Akron, Ohio, U.S.A.

$\dagger$ These are sometimes termed “automatic burettes with glass reservoirs.”
bottle. Bottles with a capacity up to 2 litres are provided with standard ground-glass joints; large bottles, up to 15 litres capacity, can also be obtained. Fig. II, 25, 4, a and b portrays similar apparatus, but with an automatic filling device. The solution is pumped into the burette and enters it through a glass tube which terminates in a capillary exactly at the zero mark; immediately the pressure is released, the solution above the zero mark is automatically siphoned back into the storage bottle.

**Figure II, 25, 4.**

**Technique of Gravimetric Analysis**

The apparatus and operations common both to volumetric and gravimetric analysis have been discussed in the preceding Sections, as has also the general theory underlying gravimetric analysis. The experimental technique peculiar to analysis by weight will be considered in the following pages.

The operations of gravimetric analysis may be summarised under the headings: (a) precipitation; (b) filtration; (c) the washing of the precipitate; and (d) the drying, ignition, and weighing of the precipitate.

**II. 26. Precipitation.**—The conditions for precipitation are given in Section I, 59. Precipitations are usually carried out in resistance-glass beakers, and the solution of the precipitant is added slowly (for example, by means of a pipette, burette, or tap funnel) and with efficient stirring of the suitably diluted solution. The addition must always be made without splashing; this is best achieved by allowing the solution of the reagent to flow down the side of the beaker or precipitating vessel. Only a moderate excess of the reagent is generally required; a very large excess may lead to increasing solubility (compared Section I, 10) or contamination of the precipitate. After the precipitate has settled,
a few drops of the precipitant should always be added to determine whether further precipitation occurs. As a general rule, precipitates are not filtered off immediately after they have been formed; most precipitates, with the exception of those which are definitely colloidal, such as ferric hydroxide, require more or less digestion (Section I, 58) to complete the precipitation and make all particles of filterable size. In some cases digestion is carried out by setting the beaker aside and leaving the precipitate in contact with the mother liquor at room temperature for 12–24 hours; in others, where a higher temperature is permissible, digestion is usually effected near the boiling point of the solution. Hot plates, water-baths, or even a low flame if no bumping occurs, are employed for the latter purpose; in all cases the beaker should be covered with a clock glass with the convex side turned down or, if available, with a Fisher "speedy-vap" beaker cover. If the solubility of the precipitate is appreciable, it may be necessary to allow the solution to attain room temperature before filtration.

II, 27. Filtration.—This operation is the separation of the precipitate from the mother liquor, the object being to get the precipitate and the filtering medium quantitatively free from the solution. The media employed for filtration are: (1) filter-paper; (2) filter-mats of purified asbestos (Gooch crucibles) or of platinum (Munroe crucibles); (3) porous fritted plates of resistance glass, e.g., Pyrex (sintered-glass filtering crucibles), of silica (Vitreosil filtering crucibles), or of porcelain (porous porcelain filtering crucibles). The choice of the filtering medium will be controlled by the nature of the precipitate (filter-paper is especially suitable for gelatinous precipitates and for those which must be heated to a very high temperature before weighing) and also by the question of cost. The latter is of great importance in laboratories where the number of students is large and departmental grants small. The limitations of the various filtering media are given in the account which follows.

II, 28. Filter-papers.—Quantitative filter-papers must have a very small ash content; this is achieved during manufacture by washing with hydrochloric and hydrofluoric acids. The sizes generally used are circles of 7·0, 9·0, 11·0, and 12·5 cm. diameter, those of 9·0 and 11·0 cm. being most widely employed. The ash of a 11-cm. circle should not exceed 0·0001 g.; if the ash exceeds this value, it should be deducted from the weight of the ignited residue. Manufacturers give values for the average ash per paper: the value may also be determined, if desired, by igniting several filter-papers in a crucible. Quantitative filter-paper is made of various degrees of porosity. The filter-paper used must be of such texture as to retain the smallest particles of precipitate and yet permit of rapid filtration. Three textures are generally made, one for very fine precipitates, a second for the average precipitate which contains medium-sized particles, and a third for gelatinous precipitates and coarse particles. The speed of filtration is slow for the first, fast for the third, and medium for the second. Hardened filter-papers are made by treating quantitative filter-papers with nitric acid; these have an extremely small ash, a much greater mechanical strength when wet, and are more resistant to acids and alkalis. They are strongly recommended for use in all quantitative work.

The author has found "Whatman" filter-papers very satisfactory in practice; the characteristics of the chief varieties suitable for quanti-
tative work are collected in the following table;* the ashes for the two most frequently used sizes, 9 and 11 cm., are included.

### Table X.—“Whatman” Quantitative Filter-Papers

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Single acid (HCl) washed</td>
<td>3 cm. 0·00020 g.</td>
<td>No. 31</td>
<td>No. 30 0·00021 g.</td>
</tr>
<tr>
<td></td>
<td>11 cm. 0·00030 g.</td>
<td></td>
<td>0·00031 g.</td>
</tr>
<tr>
<td>Ash (mean)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 cm. 0·00013 g.</td>
<td>No. 331</td>
<td>No. 330</td>
<td>No. 332</td>
</tr>
<tr>
<td>11 cm. 0·00019 g.</td>
<td></td>
<td>0·00014 g.</td>
<td>0·00021 g.</td>
</tr>
<tr>
<td>Hardened single acid washed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash (mean)</td>
<td>3 cm. 0·00009 g.</td>
<td>No. 41</td>
<td>No. 40 0·00009 g.</td>
</tr>
<tr>
<td></td>
<td>11 cm. 0·00014 g.</td>
<td></td>
<td>0·00014 g.</td>
</tr>
<tr>
<td>Double acid (HCl, HF) washed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash (mean)</td>
<td>3 cm. 0·00004 g.</td>
<td>No. 431</td>
<td>No. 430 0·00004 g.</td>
</tr>
<tr>
<td></td>
<td>11 cm. 0·00006 g.</td>
<td></td>
<td>0·00007 g.</td>
</tr>
</tbody>
</table>

The filter-papers Nos. 30–32 and 530–531 are comparatively cheap, and may be used for elementary students. For precise quantitative work, Nos. 40–42 or, preferably, the hardened variety Nos. 540–542, which have a greater mechanical strength and a greater resistance to acids and alkalis, should be employed. Nos. 41 and 541 are used for gelatinous and flocculent precipitates, and Nos. 40 and 540 for most other precipitates encountered in quantitative analysis. Nos. 42 and 542 are intended for the finest precipitates, but are very slow filtering; for the latter reason they do not find wide application in routine quantitative analysis. The rough average diameters (in microns) of the pores of the various filter-papers are: 30, 2·2; 31, 4·7; 32, 1·1; 40, 2·4; 41, 4·1; 42, 1·1; 540, 1·6; 541, 4·8; and 542, 0·5.

The size of the filter-paper selected for a particular operation is determined by the bulk of the precipitate, and not by the volume of the liquid to be filtered. The entire precipitate should occupy about a third of the capacity of the filter at the end of the filtration. As already pointed out, filter-papers of 9 and 11 cm. diameter find the most frequent use. The funnel should match the filter-paper in size. The folded paper should extend to within 1–2 cm. of the top of the funnel, but never closer than 1 cm.

A funnel with an angle as nearly 60° as possible should be employed; the stem should have a length of about 15 cm. in order to promote rapid filtration. The filter-paper must be carefully fitted into the funnel so that the upper portion beds tightly against the glass. Some analysts recommend that the filter-paper should rest completely against the wall of the funnel; this is really unnecessary, since a filter-paper which adheres snugly to the funnel over the upper half will

* Compiled from the pamphlet issued by the manufacturers, W. and R. Balston, Ltd., Maidstone, England.
permit of more rapid filtration. To prepare the filter-paper for use, the dry paper is usually folded exactly in half and exactly again in quarters. The folded paper is then opened so that a 60°-angle cone is formed with three thicknesses of paper on the one side and a single thickness on the other; the paper is then adjusted to fit the funnel. The paper is placed in the funnel, moistened thoroughly with water, pressed down tightly to the sides of the funnel either with the clean forefinger or with a flattened glass rod, and then filled with water. If the paper fits properly, the stem of the funnel will remain filled with liquid during the filtration. Another method of folding the filter, which is preferable to that just described, consists in folding the paper across a diameter and then once again so that the two halves of the first crease do not quite coincide (the two extreme edges should enclose an angle of 3-4° for a 60° funnel); the corner of the fold should be torn off to a depth of about one-third of the radius of the paper (Fig. II, 28, 1). When this filter is opened and placed in the funnel, it should fit the walls tightly at the upper half; if it does not fit properly, the angle of the second fold must be adjusted until it does. Here also, the ultimate test of a proper fit is that the stem of the funnel remains filled with liquid throughout the filtration. It must be emphasised that a funnel of proper size must be used: the top of the filter-paper when set in the funnel should be about 1 cm. below the rim of the latter.

To carry out a filtration, the funnel containing the properly fitted paper is placed in a funnel stand (or is supported vertically in some other way) and a clean beaker placed so that the stem of the funnel just touches the side; this will prevent splashing. The liquid to be filtered is then poured down a glass rod into the filter, directing the liquid against the side of the filter and not in the apex (Fig. II, 28, 2): the lower end of the stirring-rod should be very close to, but should not quite touch, the filter-paper on the side having three thicknesses of paper. The paper is never filled completely with the solution; the level of the liquid should not rise closer than to within 5-10 mm. from the top of the paper. Any precipitate which adheres firmly to the side of the beaker or to the stirring-rod may be removed with a rubber-tipped rod or "policeman" (Section II, 10L).

Filtration may be appreciably accelerated by the use of resistance glass (e.g., Phoenix *) analytical funnels or the similar Pyrex 60° funnels. These funnels have an exact angle of 60°, possess a stem about 150 mm. long, and are usually specially grooved to permit of rapid filtration. Filtration by suction with a filter-paper (for apparatus see Section II, 31) is rarely necessary: with gelatinous and some finely divided precipitates, the suction will draw the particles into the pores of the paper, and the speed of filtration will actually be reduced rather than increased. If suction is used with filter-paper, it is necessary to

* Supplied by Townson and Mercer, Ltd., Croydon, England.
support the paper in a perforated cone made of platinum ("filter cone") or in a Whatman filter cone (hardened, No. 51).

II, 29. Macerated filter-paper.—Dittrich (1904) first recommended the use of filter-paper pulp as an aid in the filtration and washing of gelatinous or slimy precipitates, which tend to clog the pores of ordinary filter-paper. The macerated paper may be prepared by vigorously shaking an ordinary quantitative filter-paper, torn into small pieces, with hot distilled water in a stoppered conical flask until it is disintegrated to a pulp. This is unnecessary, as macerated filter-paper tablets may be purchased ready for use. Two types are available; the first, known as Whatman "accelerators," is in the form of oblong pieces \((1 \times \frac{3}{4} \times \frac{1}{4} \text{ in.})\), each weighing about 0·33 g. and giving an ash of about 0·00035 g.; the second, known as Whatman "ashless tablets," is in the form of tablets \((4·25 \times 4·25 \text{ cm.} \text{ and about } 4 \text{ mm. thickness})\), each weighing about 2·28 g. and giving an ash of about 0·00025 g. Either one or two accelerators or a quarter of a tablet is used in the average precipitation; these disintegrate readily when placed in water. The bulk of the macerated filter-paper should be approximately equal to that of the gelatinous precipitate. The macerated filter-paper is added after the precipitate has formed, and immediately before filtration. When the bulk of the precipitate and paper is large, it is usually advisable to support the filter-paper on a Whatman filter cone (hardened No. 51), and drain well on the pump upon completion of the washing. It is best not to dry the filter and precipitate completely, as a hard mass may be formed, which is difficult to insert in the crucible in the subsequent ignition. While still slightly moist it should be transferred to the crucible, and the drying completed in the crucible by heating over a very small luminous flame. Alternatively, the wet mass may be ignited in a silica crucible, preferably of the Main Smith form (see Section II, 36B).

Macerated filter-paper is also useful when it is desired to clarify a solution containing a finely divided precipitate that is difficult to coagulate.

II, 30. Filter-mats. Gooch crucibles.—F. A. Gooch (1878) first employed a filter-mat of purified asbestos; this was supported inside a tall-form platinum crucible, the bottom of which was perforated with numerous small holes. Subsequently the idea was extended to porcelain crucibles, and later to silica crucibles. All crucibles of this type are now termed Gooch crucibles. The porcelain type is the most widely used for student and routine work. When the term Gooch crucible is employed in this book, the porcelain variety must be understood; crucibles of platinum and of silica will be called platinum Gooch crucibles and silica Gooch crucibles respectively. The asbestos must be carefully selected and prepared: the long-fibred, amphibole asbestos is the most suitable. Gooch specified "white, silky, anhydrous asbestos." The tedious process of preparing the asbestos by boiling with hydrochloric acid, etc., is now usually carried out by chemical manufacturers. "Asbestos for Gooch crucibles" may be purchased at a reasonable price from any firm of repute, and used with confidence. When such asbestos is shaken with water, it should separate into very small fibres; no undisintegrated asbestos should be present. All Gooch crucibles are used under suction, and require holders and receivers that are strong enough to withstand a partial vacuum. These are described in the following paragraph.
II, 31. Preparation of a Gooch crucible.—The Gooch crucible (Fig. II, 31, 1, A) is usually supported in a special holder, known as a Gooch funnel, by means of a wide rubber tube (Fig. II, 31, 1, B); the bottom of the crucible should be quite free from the side of the funnel and from the rubber gasket, the latter in order to be quite sure that the filtrate does not come into contact with the rubber. The Gooch funnel passes through a one-holed rubber bung into a large filter-flask of about 750 ml. capacity. The tip of the funnel must project below the side arm of the filter-flask so that any risk that the liquid may be sucked out of the filter-flask may be avoided. The filter-flask should be coupled with another flask of similar capacity, and the latter connected with a water filter-pump; if the water in the pump should “suck back,” it will first enter the empty flask and the filtrate will not be contaminated. It is advisable also to have some sort of pressure regulator to limit the maximum pressure under which filtration is conducted. A simple method is to insert a glass tap in the second

![Diagram](A) ![Diagram](B) ![Diagram](C)

Fig. II, 31, 1.

filter flask, as in Fig. II, 31, 1, B; alternatively, a glass T-piece may be introduced between the receiver and the pump, and one arm closed either by a glass tap or by a piece of heavy rubber tubing (“pressure” tubing) carrying a screw clip. For some work it is convenient to collect the filtrate directly in a beaker: this may be done by means of the apparatus shown in Fig. II, 31, 2. It consists of a bell jar resting upon a ground-glass plate and provided with tubulures at the top and side; a three-way tap is attached to the side tubulure so that suction is easily applied or stopped. Here also it is advisable to provide a trap to protect the filtrate from the back flow from the pump.

The rubber sleeve for fitting the Gooch crucible into the Gooch funnel may be replaced with advantage by either of the devices shown in Fig. II, 31, 3:

(a) consists of a solid rubber ring, shaped as in the figure,* which fits into a 3-in. funnel;
(b) is a solid rubber washer; the wide part of the washer merely rests on top of the Gooch funnel, and the inside part conforms to the shape of and supports the crucible.


The Fisher Scientific Company of Pittsburgh, Pa., supply: (i) a Bailey crucible holder, similar to (b), which fits the top of a 2-in. funnel and accommodates crucibles of 25-ml and 35-ml capacity, and (ii) a Sargent crucible holder consisting of a tapered rubber washer which fits in an ordinary funnel and has an opening to hold the crucible.
Upon applying suction, an air-tight joint is formed between the upper edge of the funnel and the Gooch washer.

The Gooch crucible should be of suitable size. One about 4 cm. in height, with a capacity of 25 ml. and perforations about 0.5-0.8 mm. in diameter, will be found serviceable for most purposes. The crucible is first placed in the suction-filtering apparatus, and then half to two-thirds filled with the suspension of asbestos in water. The whole is allowed to stand for 2-3 minutes in order to allow the larger particles to settle to the bottom, and then suction is applied gently. When the water has passed through, the pump is turned on full, and the mat sucked down tight. The final uniform pad of asbestos should have a thickness of 2-3 mm. (see Fig. 58, A); it is possible to tell approximately when the mat has the correct thickness by holding the crucible up to the light and looking through it, when the outline of the holes should be barely visible. If the pad is too thin, more asbestos must be added and the process repeated. The asbestos pad is now thoroughly washed with distilled water under the maximum suction of the pump until no fine fibres pass into the filtrate. It should be mentioned that some analysts prefer to place a perforated porcelain plate ("Witt" plate, Fig. II, 31, 1, O) upon the asbestos mat to prevent its dislodgement: a little more of the suspension is poured in to furnish enough asbestos to barely cover the plate and to hold it in place. This procedure is unnecessary if it be remembered that no liquid may be poured into the crucible unless suction is being applied. Liquids should be poured gently on to the centre of the mat down a stirring-rod: a jet of water from a wash bottle should never be directed into the prepared crucible. If these precautions are taken there is little danger that the mat will become torn and allow the precipitate to pass through.

The crucible is placed on a small ignition dish or saucer or upon a shallow-form Vitreosil capsule and dried to constant weight at the same temperature as that which will be subsequently used in drying the precipitate. For temperatures up to about 250° C, a thermostatically controlled electric oven should be used. For higher temperatures, the crucible may be heated in an electrically heated muffle furnace. If the latter is not available, it may be placed inside a larger nickel crucible fitted with an asbestos ring (as in Fig. II, 31, 4), and the larger crucible heated directly with a flame. In all cases the crucible is allowed to cool in a desiccator (Section II, 10N) before weighing. The
Technique of Quantitative Analysis

asbestos normally used for Gooch crucibles tends to lose weight above 283° C. (C. Duval, 1948), hence it is recommended that precipitates which require heating above 280° C. should not be collected in Gooch crucibles. Porous filtering crucibles (see below) may be employed.

II. 32. Munroe crucibles.—A platinum Gooch crucible, containing a platinum mat, was devised by C. E. Munroe in 1888. The platinum mat is prepared by igniting a layer of ammonium chloroplatinate, moistened with alcohol, in the crucible. The chief features of such crucibles are: resistance to chemical attack, rapidity of filtration, retention of the finest precipitates, and possibility of heating to very high temperatures. The platinum mat lasts almost indefinitely, for the residues can be removed by any solution treatment which does not dissolve platinum. On account of the high price of platinum, Munroe crucibles are rarely employed in routine analysis; they find some application for most exacting work, as in atomic-weight determinations.

II. 38. Crucibles fitted with permanent porous plates.—These possess an advantage over Gooch crucibles in so far that no preparation of a filter-mat is necessary. The best known are the sintered-glass crucibles.

They are made of resistance glass, for example, Pyrex, and have a porous disc of sintered, ground glass fused into the body of the crucible (Fig. II, 33, 1). The fused-in fritted filter-disc can be obtained in various degrees of porosity. Thus the average diameter of the pores for plates numbered 1, 2, 3, and 4 are 100–120 microns, 40–50 microns, 20–30 microns, and 5–10 microns respectively. No. 4 is suitable for very fine precipitates (such as barium sulphate), and No. 3 for precipitates of medium particle size. Two types of crucible find wide application in quantitative analysis, the tall form and the low, wide form. A crucible with a capacity of 30 ml. is satisfactory for most work.

The advantages of sintered-glass crucibles are: (i) they are made entirely of glass, which is resistant to most chemical reagents with the exception of hydrofluoric acid and hot, concentrated alkalis; (ii) they can be dried to constant weight at 100–150° C.; and (iii) they are readily cleaned. These crucibles can be heated to a temperature not exceeding about 400° C. (Pyrex glass softens at about 610° C. and permanent strain may be introduced at temperatures above 430° C.) If heating above 150–200° C. is required, they should be placed in a cold electric oven or furnace, heated to the appropriate temperature, and allowed to cool to about 200° C. (in the furnace) before being removed to a desiccator.

For temperatures above 200° C. Vitreosil filtering-crucibles * may be

employed. These are similar to the sintered-glass crucibles, are available in porosities 1, 2, 3, and 4, but are made of Vitreosil pure fused silica. They can be used up to 1000° C. and there is no danger of cracking owing to sudden change of temperature. These crucibles are attacked by phosphates, strong alkalis, and hydrofluoric acid, but are otherwise very resistant to chemical reagents.

Another variety of crucible, which possesses many advantages over the Gooch crucible, is the porous-porcelain filter-crucible. It consists of a porcelain crucible, glazed inside and outside, with a porous porcelain bottom. The Worcester Royal Porcelain Co.* manufactures one type of crucible (Gooch form) in various sizes and an average pore diameter of 5–10 microns; this meets most of the requirements of quantitative inorganic analysis. It may be mentioned that crucibles with an average pore diameter of 10–15 microns are also obtainable from this firm. It is claimed that these filter-crucibles may be heated to temperatures as high (1000° C.) as those possible for porcelain crucibles, but the temperature must be raised slowly, as the joint between the porous disc and the porcelain to which it is sealed may develop strain if heated suddenly. A direct flame should be avoided: special ignition saucers are marketed for heating the filter-crucibles up to a temperature of 1000° C. The Selas Corporation of America † offer a wide range of porous filtering-crucibles in porosities designated as XF, XFP, 10 and 01 corresponding to average pore radii of 25, 10, 2.2, and 1.5 microns respectively and to maximum pore radii of 50, 20, 4.4, and 3.0 microns respectively. The crucibles graded as 10 and 01 find the widest application in analytical work. Selas crucibles are chemically inert, and are resistant to all solutions which do not attack silica: they are attacked by hydrofluoric acid, soluble fluorides, and strong alkalis. They possess a high degree of heat resistance, and are therefore capable of withstanding abnormal heat shock. These crucibles may be heated to well over 1000° C., and indeed will withstand direct heating by a powerful burner; in view, however, of the possible action of the products of combustion upon the precipitate, it is recommended that direct heating with a flame be carried out in the special ignition dishes provided by the Selas Corporation. Porous porcelain filter-crucibles may also be heated in a larger nickel crucible (Fig. II, 31, 4) or in a muffle furnace. These crucibles are inexpensive, and therefore merit wide application in instructional courses of quantitative analysis; they are used exactly as already described for Gooch crucibles (Fig. II, 31, 3, a illustrates an excellent support in a 3-in. funnel) except, of course, that they require no preparation.

Crucibles fitted with permanent porous plates are cleaned by shaking out as much of the solid as possible, and then dissolving out the remainder of the solid with a suitable solvent. An alternative method is to suck water or some other liquid through from the reverse side. The process will be evident upon reference to Fig. II, 33, 2; the crucible is placed inside the wide glass tube and over the tube leading to the filter-flask maintained under diminished pressure. Crucibles with permanent porous plates must not be cleaned by fusion with potassium or sodium bisulphates; if this procedure is undertaken the crystallisation of the salt in the pores of the filter disc will crack the crucible on cooling.

† Selas Corporation of America, Erie Avenue and D Street, Philadelphia 34, Pa., U.S.A.
A hot 0·1111 solution of the tetrasodium salt of ethylenediamine tetra-acetic acid (see Section III, 148) is an excellent solvent for many of the precipitates (except metallic sulphides and ferricyanides) encountered in analysis. These include barium sulphate, calcium oxalate, calcium phosphate, calcium oxide, lead carbonate, lead iodate, lead oxalate, and magnesium ammonium phosphate.

The crucible may either be completely immersed in the hot reagent or the latter may be drawn by suction through the crucible.

**II, 34. Washing of precipitates.**—Most precipitates are produced in the presence of one or more soluble compounds. Since the latter are frequently not volatile at the temperature at which the precipitate is ultimately dried, it is necessary to wash the precipitate to remove such material as completely as possible. The minimum volume of the washing liquid required to remove the objectionable matter should be used, since no precipitate is absolutely insoluble. Qualitative tests for the removal of the impurities should be made on small volumes of the filtered washing solution. Furthermore, it is better to wash with a number of small portions of the washing liquid, which are well drained between each washing, than with one or two large portions, or by adding fresh portions of the washing liquid whilst solution still remains on the filter (see Section I, 60). The precipitate should never more than one-third to one-half fill the filter-paper, and the liquid should be kept from 5–10 mm. below the edge.

The ideal washing liquid should comply as far as possible with the following conditions:

1. It should have no solvent action upon the precipitate, and dissolve foreign substances easily;
2. It should have no dispersive action on the precipitate;
3. It should form no volatile or insoluble product with the precipitate;
4. It should be easily volatile at the temperature of drying of the precipitate;
5. It should contain no substance which is likely to interfere with subsequent determinations in the filtrate.

In general, water should not be used unless it is certain that it will not dissolve appreciable amounts of the precipitate or peptise it. If the precipitate is appreciably soluble in water, a common ion is usually added, since any electrolyte is less soluble in a dilute solution containing one of its ions than it is in pure water (Section I, 9); as an example the washing of calcium oxalate with dilute ammonium oxalate solution may be cited. If the precipitate tends to become colloidal and pass through the filter-paper (this is frequently observed with gelatinous or flocculent precipitates), a wash solution containing an electrolyte must be employed (compare Section I, 56). The nature of the electrolyte is immaterial, provided it has no action upon the precipitate during washing and is volatilised during the final heating. Ammonium salts are usually selected for this purpose: thus ammonium nitrate solution is employed for washing ferric hydroxide. In some cases it is possible to select a solution which will both reduce the solubility of the precipi-
Quantitative Inorganic Analysis

tate and prevent peptisation, for example, the use of dilute nitric acid with silver chloride. Some precipitates tend to oxidise during washing; in such instances the precipitate cannot be allowed to run dry, and a special washing solution which re-converts the oxidised compounds into the original condition must be employed, e.g., acidulated hydrogen sulphide water for copper sulphide. Gelatinous precipitates, like aluminium hydroxide, require more washing than crystalline ones, such as calcium oxalate. With gelatinous precipitates there is also a danger of channel formation if the wash liquid is allowed to drain completely; these precipitates should be washed as far as possible by decantation.

The reader may have observed that full details of the technique of filtration have not so far been given. This is because the filtration of a precipitate is so closely associated with the washing process that a consideration of the former is logically deferred until the latter has been discussed, at least in outline.

II, 35. Technique of filtration.—When the proper filtering medium (filter-paper, Gooch crucible, etc.) has been prepared, as much as possible of the supernatant liquid is poured off without disturbing the precipitate by directing the stream of liquid against a glass rod held against the lip of the beaker (compare Fig. II, 28, 2). The precautions already mentioned against filling a filter-paper too full must be taken. In most cases, particularly if the precipitate settles rapidly or is gelatinous, washing by decantation may be employed. Twenty to fifty ml. of a suitable wash liquid is added to the residue in the beaker, the solid stirred up and allowed to settle. If the solubility of the precipitate allows, the solution should be heated, since, inter alia, the rate of filtration will thus be increased. When the supernatant liquid is clear, as much as possible of the clear liquid is decanted through the filtering medium. This process is repeated three to five times (or as many times as is necessary) before the precipitate is transferred to the filter. The main bulk of the precipitate is first transferred by mixing with the wash solution and pouring off the suspension, the process being repeated until most of the solid has been removed from the beaker. The precipitate adhering to the sides and the bottom of the beaker is removed as follows. The beaker is grasped in the left hand, and the stirring-rod is held firmly against the top of the beaker with the index finger and should project 2–3 cm. beyond the lip; the wash bottle is controlled by the right hand. The beaker is inclined and a stream of water (or wash liquid) is directed against the precipitate to dislodge it and wash it against the rod into the filter. The process is shown diagrammatically for a filter-paper in Fig. II, 35, 1. For some precipitates, where washing by decantation is inadmissible because of solubility influences, the whole of the precipitate must be transferred to the filter in this way. After the above treatment there will generally be small amounts of the precipitate adhering to the walls of the beaker. These are removed by rubbing with a "policeman" (Section II, 10L); when all the particles have been dislodged, the "policeman" is rinsed with the wash liquid, and the remaining precipitate transferred to the filter.
Where the precipitate is washed on the filter, in the last stages the washing solution is directed along the rim and then gradually towards the apex of the cone. In all cases, tests for the completeness of washing must be made by collecting a small sample of the washing solution after it is estimated that most of the impurities have been removed, and applying an appropriate qualitative test. Where filtration is carried out under suction, a small test-tube may be attached to the bottom of the Gooch funnel by means of a wire.

II, 36. Drying and ignition of precipitates.—After a precipitate has been filtered and washed, it must be brought to a constant composition before it can be weighed. The further treatment will depend both upon the nature of the precipitate and upon that of the filtering medium. This treatment consists in drying or igniting the precipitate. Which of the latter two terms is employed depends upon the temperature at which the precipitate is heated. There is, however, no definite temperature below or above which the precipitate is said to be dried or ignited respectively. The meaning will be adequately conveyed for our purpose if we designate drying when the temperature is below 250°C (the maximum temperature which is readily reached in the usual thermostatically controlled, electric drying-oven), and ignition above 250°C up to, say, 1200°C. Precipitates that are to be dried should be collected on filter-paper, Gooch, sintered glass, or porous porcelain filter-crucibles. Precipitates that are to be ignited are collected on filter-paper, porous-porcelain filter-crucibles, Vitreosil filter-crucibles, or, less commonly, in platinum Gooch or Munroe crucibles. Ignition is simply effected by placing in a special ignition dish or in a larger nickel or platinum crucible, as in Fig. II, 31, 4, and heating with the appropriate burner (Section II, 10A); alternatively, these crucibles (and, indeed, any type of crucible) may be placed in an electrically heated muffle furnace, which is equipped with a pyrometer and a means for controlling the temperature.

Many of the precipitates which are subsequently to be ignited are filtered through filter-paper, and it is therefore necessary to describe the method to be adopted in such cases. The exact technique will depend upon whether the precipitate may be safely ignited in contact with the filter-paper or not. It must be remembered that some precipitates, such as barium sulphate, may be reduced or changed in contact with filter-paper or its decomposition products.

A. Incineration of the filter-paper in the presence of the precipitate. On account of cheapness, porcelain crucibles are usually employed for this operation, particularly in instructional courses. Silica crucibles, although somewhat more expensive, are to be preferred because of their greater resistance to thermal shock. The crucible is first ignited to constant weight (i.e., to within 0.0002 g.) at the same temperature as that to which the precipitate is ultimately heated. The well-drained filter-paper and precipitate are carefully detached from the funnel; the filter-paper is folded so as to completely enclose the precipitate, care being taken not to tear the paper.* The packet is then placed point down in the weighed crucible, which is supported on a pipe-clay or, better, a silica triangle resting on a ring stand as in

* For bulky precipitates, such as those containing macerated filter-paper, it is advisable to remove most of the moisture by a preliminary drying in the steam oven, or at 100–105°C.
The crucible is slightly inclined, as shown in the diagram, and partially covered with the lid, which should rest partly on the triangle. A very small flame is then placed under the crucible lid; drying thus proceeds quickly and without undue risk. When the moisture has been expelled, the flame is increased slightly so as to slowly carbonise the paper. The paper should not be allowed to inflame, as this may cause a mechanical expulsion of fine particles of the precipitate owing to the rapid escape of the products of combustion; if, by chance, it does catch fire, the flame should be extinguished by momentarily placing the cover on the mouth of the crucible with the aid of a pair of crucible tongs. When the paper has completely carbonised and vapours are no longer evolved, the flame is moved to the back (bottom) of the crucible and the carbon slowly burned off whilst the flame is gradually increased. After all the carbon has been burned away, the crucible is covered completely (if desired, the crucible may be placed in a vertical position for this purpose) and heated to the required temperature by means of a Bunsen, Meker, or Fisher flame. Usually it takes about 20 minutes to char the paper, and 30–60 minutes to complete the ignition.

When the ignition is ended, the flame is removed and, after 1–2 minutes, the crucible and lid are placed in a desiccator containing a suitable desiccant (Section II, 10N), and allowed to cool for 25–30 minutes. The crucible and lid are then weighed. The crucible and contents are then ignited at the same temperature for 10–20 minutes, allowed to cool in a desiccator as before, and weighed again. The ignition is repeated until constant weight is attained. Crucibles should always be handled with clean crucible tongs.

**B. Use of crucible with interior-fitting serrated lid.** J. D. Main Smith (1925) has designed an improved form of crucible lid. This is an interior-fitting lid of which the vertical flange is serrated around the edge; it fits into a squat-shaped crucible, the upper surface of the lid being about 1 cm. from the top of the crucible (Fig. II, 36, 2). The advantages are: (i) gases or vapours, which are disengaged in the operation, can escape freely; (ii) loss by creeping, spattering, and decrepitation are prevented; (iii) the contents of the crucible can be easily inspected, since the lid easily swivels up by pressing on one side lightly with the clean crucible tongs (this is, of course, unnecessary if the lid is of transparent silica); (iv) liquids can easily be added simply by pouring on to the lid, the serrations providing ingress into the crucible. Vitreosil crucibles of 15, 25, 40, and 50 ml. capacity with serrated lids are commercially available, and are comparatively inexpensive. Lids of transparent silica can also be obtained.

* It is preferable to attach the triangle to the ring of a retort stand by bending the wire ends of the triangle round it rather than to support it on a tripod. In the former case, the crucible is more readily accessible and also the height of the crucible above the burner can be easily adjusted.

† If the carbon on the lid is oxidised only slowly, the cover may be heated separately in a flame. It is, of course, held in clean crucible tongs.
The ignition of a precipitate in a wet filter-paper is readily effected by placing the precipitate and filter-paper into a previously ignited and weighed crucible and lid, and conducting the initial heating exactly as described under A. Care must be taken that a sufficiently large crucible is used (usually of 40 ml. capacity); an over-large crucible is no disadvantage. After the paper has been carbonised and vapours are no longer evolved, the lid is removed and laid aside upside-down on a clock glass, and the combustion of the carbon completed at a red heat in the usual manner. If the lid has been blackened by the preliminary heating, it should be held by the ring upside-down by means of clean crucible tongs, and carefully ignited over the open crucible by means of a small flame until all the carbon has been burned off; the clean lid is then replaced in the crucible, care being taken that any fragments of residue present fall into the crucible. The crucible and lid are then ignited at the appropriate temperature to constant weight.

C. Incineration of the filter-paper apart from the precipitate. This method is employed in all those cases where the ignited substance is reduced by the burning paper, for example, barium sulphate, lead sulphate, bismuth oxide, copper oxide, etc. The funnel containing the precipitate is covered by a piece of qualitative filter-paper upon which is written the formula of the precipitate and the name of the owner; the paper is made secure by crumpling its edges over the rim of the funnel so that they will engage the outer conical portion of the funnel. The funnel is placed in the steam oven, or in a drying-oven maintained at 100–105° C., for 1–2 hours or until completely dry. A sheet of glazed paper about 25 cm. square (white or black, to contrast with the colour of the precipitate) is placed on the bench away from all draughts. The dried filter is removed from the funnel, and as much as possible of the precipitate is removed from the paper and allowed to drop on a clock glass resting upon the glazed paper. This is readily done by very gently rubbing the sides of the filter-paper together, when the bulk of the precipitate becomes detached and drops upon the clock glass. Any small particles of the precipitate which may have fallen upon the glazed paper are brushed into the crucible with a small camel-hair brush. The clock glass containing the precipitate is then covered with a larger clock glass or with a beaker. The filter-paper is now carefully folded and placed inside a weighed porcelain or silica crucible. The crucible is placed on a triangle and the filter-paper incinerated as detailed in the first paragraph of this Section. The crucible is allowed to cool, and the filter ash subjected to a suitable chemical treatment in order to convert any reduced or changed material into the form finally desired. The cold crucible is then placed upon the glazed paper and the main part of the precipitate carefully transferred from the clock glass to the crucible. A small camel-hair brush will assist in the transfer. Finally, the precipitate is brought to constant weight by heating to the necessary temperature.

Here also the Main Smith crucible may be used. The dried filter-paper, from which most of the precipitate has been detached as described above, is first ignited exactly as already detailed. The crucible and lid are allowed to cool, a small quantity of the liquid chemical required to convert any reduced or changed material to the form finally desired is poured on to the lid, and the whole slowly heated to the correct temperature. The crucible is then allowed to cool, placed upon a
sheet of glazed paper, the main part of the precipitate added, and the whole ignited to constant weight at the appropriate temperature.

II, 37. The care and use of platinum vessels.—Platinum has a very high melting point (1770° C.). The pure metal is, however, too soft for general use, and is therefore always hardened with small quantities of rhodium, iridium, or gold. These alloys are slightly volatile at temperatures above 1100° C., but retain most of the advantageous properties of pure platinum, such as resistance to most chemical reagents, including molten alkali carbonates and hydrofluoric acid (the exceptions are dealt with below), excellent conductivity of heat, and extremely small adsorption of water vapour. A 25-ml. platinum crucible has an area of 80–100 sq. cm. and, in consequence, the error due to volatility may be appreciable if the crucible is made of an alloy high in iridium content. The magnitude of this loss will be evident from the following table, which gives the approximate loss in weight of crucibles expressed in mg./100 sq. cm./hour at the temperature indicated:

<table>
<thead>
<tr>
<th>Temp. (° C.)</th>
<th>Pure Pt</th>
<th>99% Pt — 1% Ir.</th>
<th>97-5% Pt — 2-5% Ir.</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>0-00</td>
<td>0-00</td>
<td>0-00</td>
</tr>
<tr>
<td>1000</td>
<td>0-08</td>
<td>0-30</td>
<td>0-67</td>
</tr>
<tr>
<td>1200</td>
<td>0-81</td>
<td>1-2</td>
<td>2-5</td>
</tr>
</tbody>
</table>

Not all crucibles will change in weight (much will depend upon the exact composition), but this possibility should be borne in mind. If the financial resources of the laboratory are limited, at least two crucibles of 25-ml. capacity, provided with covers, should be purchased; these will meet most ordinary requirements. It is useful, if finances permit, to have crucibles of 10-ml. capacity and platinum dishes of 100, 300, and 500-ml. capacity.

Platinum crucibles should be supported when heated upon a platinum triangle. If the latter is not available, a silica triangle may be used. Nichrome and other metal triangles should be avoided; pipe-clay triangles may contain enough iron to damage the platinum. Hot platinum crucibles must always be handled with platinum-tipped crucible tongs, or with ordinary tongs which are covered with platinum foil, securely attached by platinum wire. Unprotected brass or iron tongs produce stains on the crucible. Vessels of platinum must not be exposed to a luminous flame, nor may they be allowed to come into contact with the inner cone of a gas flame (see Fig. II, 37, 1); this may result in the disintegration of the surface of the metal, causing it to become brittle, owing, probably, to the formation of a carbide of platinum.
It will be appreciated that at high temperatures platinum permits the flame gases to diffuse through it, and this may cause the reduction of some substances not otherwise affected. Hence if a covered crucible is heated by a gas flame there is a reducing atmosphere in the crucible: in an open crucible diffusion into the air is so rapid that this effect is not appreciable. If ferric oxide is thus heated in a covered crucible, it is partly reduced to metallic iron, which alloys with the platinum; sodium sulphate is similarly partly reduced to the sulphide. It is, advisable, therefore, in the ignition of iron compounds or sulphates to place the crucible in a slanting position with free access of air.

Platinum apparatus may be used without sensible loss for:

1. Fusions with (a) sodium carbonate or fusion mixture, (b) borax, (c) alkali bifluorides, and (d) alkali bisulphates (slight attack in the last case above 700° C., which is diminished by the addition of ammonium sulphate).

2. Evaporations with (a) hydrofluoric acid, (b) hydrochloric acid in the absence of oxidising agents which yield nascent chlorine, and (c) concentrated sulphuric acid (a slight attack may occur).

3. Ignition of (a) barium sulphate and sulphates of metals which are not readily reducible, (b) alkaline-earth carbonates, oxalates, etc., and (c) oxides which are not readily reducible, e.g., CaO, SrO, BaO, Al₂O₃, Cr₂O₃, Mn₃O₄, TiO₂, ZrO₂, ThO₂, MoO₃, and WO₃.

Platinum is attacked under the following conditions, and such operations must not be conducted in platinum vessels:

1. Heating with the following liquids: (a) aqua regia, (b) hydrochloric acid and oxidising agents, (c) liquid mixtures which evolve bromine or iodine, (d) concentrated sulphuric acid (slight action, which is, however, negligible for most purposes), and (e) concentrated phosphoric acid (slight, but appreciable action after prolonged heating).

2. Heating with the following solids, their fusions, or vapours: (a) oxides, peroxides, hydroxides, nitrates, nitrites, sulphides, cyanides, ferricyanides, and ferrocyanides of the alkali and alkaline-earth metals; (b) molten lead, silver, copper, bismuth, tin, or gold, or mixtures which form these metals upon reduction; (c) phosphorus, arsenic, or antimony, or mixtures which form these elements on reduction, particularly phosphates in the presence of reducing agents; (d) sulphur (slight action), selenium, and tellurium; (e) volatile halides (including ferric chloride), especially those which decompose readily; (f) all sulphides or mixtures containing sulphur and a carbonate or hydroxide; and (g) substances of unknown composition.

Cleaning and preservation of platinum ware. All platinum apparatus (crucibles, dishes, etc.) should be kept clean, polished, and in proper shape. If, say, a platinum crucible becomes stained, it should be fused with a little sodium carbonate, the molten solid poured out on to a dry stone or iron slab, the residual solid dissolved out with water, and the vessel then digested with concentrated hydrochloric acid: this treatment may be repeated, if necessary. If fusion with sodium carbonate is without effect, potassium hydrogen sulphate may be substituted; a slight attack of the platinum will occur. In some cases, the use of hydrofluoric acid or potassium hydrogen fluoride may be

* Extracted from the booklet entitled *Platinum Laboratory Apparatus* issued by Johnson Matthey and Co., Ltd., Hatton Garden, London, E.C.1, England. Further details will be found in this booklet.
necessary. Iron stains may be removed by heating the covered crucible with a gram or two of A.R. ammonium chloride and applying the full heat of a burner for 2–3 minutes.

If the surface exhibits signs of becoming dull, the vessel must be polished with fine silver sand, say of 75 to 100 mesh. Care must be taken that the sand consists of rounded grains (examine under microscope) and that it is free from angular pieces and grit, which would scratch the metal. The sand should be moistened and applied with the finger or a soft cloth.

All platinum vessels must be handled with care to prevent deformation and denting. Platinum crucibles must on no account be squeezed with the object of loosening the solidified cake after a fusion. Boxwood formers can be purchased for crucibles and dishes; these are invaluable for re-shaping dented or deformed platinum ware.

II, 38. Perforated screens for crucibles.—It is often important to exclude flame gases from the interior of a crucible during an ignition, e.g., in the ignition of ferric oxide. For this purpose we may employ a vitreosil plate, about 10 cm. square, in which a round opening is cut large enough to admit the crucible to two-thirds of its depth. The plate is held at an angle of about 30° from the horizontal by means of a clamp; alternatively, but less satisfactorily, it may be suspended on a tripod. Asbestos board may also be employed, but this has the disadvantage that fibres may adhere to the crucible: this difficulty is less likely to occur with "uralite." To obtain the maximum temperature, the following device may be used. An asbestos, "uralite," or vitreosil sheet is provided with a comparatively large hole, say 5 cm. in diameter; upon this is placed a thin sheet of platinum with an opening just large enough to support the crucible.

MISCELLANEOUS OPERATIONS

II, 39. Reduction with Metals

A. The Jones reductor. A glass tube filled with a column of amalgamated zinc constitutes what is known as a Jones reductor. If hydrochloric or sulphuric acid solutions of reducible elements, such as Fe(III), Mo(VI), Ti(IV), or Cr(III), are passed through such a tube, quantitative reduction (to Fe(II), Mo(III), Ti(II), Cr(II)) takes place. The reduced compounds can then be determined by titration with a solution of an appropriate oxidising agent. For some elements, e.g., titanium and chromium, it is necessary to collect and keep the reduced solution in an oxygen-free atmosphere.

Full details of the applications of the Jones reductor are given in Section III, 51B. The disadvantages of the Jones reductor are: (i) the large volumes of solutions which are normally required during its use, (ii) a long length of amalgamated zinc column is employed, and (iii) the difficulty of securing iron-free zinc and the consequent necessity of carrying out a blank determination. For these reasons the cadmium reductor is often preferred for elements other than iron.

B. The cadmium reductor. This acts similarly to the Jones reductor. A shorter column (ca. 10 cm. against 30–40 cm.) suffices, and no suction is required. A simple apparatus is shown in Fig. II, 39, 1.
The tube charged with the cadmium is 10 cm. long, and has a diameter of 18 mm.; the upper bulb is of 75-ml. capacity, and the tube below the stopcock is about 25 cm. long. The titration flask, of 750-ml. capacity, is provided with a sealed-in tube (or an equivalent device) for the introduction of an inert gas, and is covered with a watch glass with a central hole.

The cadmium powder may be prepared electrolytically. Two platinum discs of 4.5 cm. diameter are placed 5 cm. apart in a cylindrical glass vessel of 7 cm. diameter: the lower disc is the cathode, and the upper one is the anode. The electrolyte consists of a concentrated solution of cadmium sulphate faintly acidified with dilute sulphuric acid. The current density employed is 30 amps./sq. dm. With a current of 5 amps., 5 g. of cadmium as a fine crystalline powder are precipitated in about an hour. When the cadmium-ion concentration is so far reduced that hydrogen is evolved at the cathode, more cadmium sulphate must be added if the formation of spongy cadmium is to be avoided. Cadmium granules, suitable for the reductor, may also be obtained from E. Merck; these must be digested with 2N-sulphuric acid to remove surface oxide.

The technique for the reduction of a TiIV compound will now be discussed as illustrative of the manipulation of a reduction product (TiIII) which is sensitive to oxygen. The reductor is filled with boiled-out water and the cadmium added so as to occupy a length of about 10 cm. in the column; care must be taken that all air bubbles are removed. Air-free solutions and reagents (attained, e.g., by boiling) are used throughout. The titration flask is first filled with air-free carbon dioxide (or nitrogen); traces of oxygen in the gas are removed by passage through chromous chloride solution. The reductor is rinsed several times with 2N-sulphuric acid, and the washings are discarded: at each washing the liquid level is not allowed to fall below the surface of the cadmium granules, i.e., the metal is always covered with liquid. The reductor is then introduced into the titration flask, and the titanium solution (which may be 1-2N in sulphuric or hydrochloric acid) allowed to flow through the column. The rate of flow is controlled by the glass stopcock at 50-75 ml. per minute. The cadmium is washed with 100 ml. of 1-2N-sulphuric or hydrochloric acid, added in portions of 20 ml. The reductor is removed, a burette inserted into the hole in the watch glass, and the titanous solution titrated. It is usual to have excess of ferric ammonium sulphate present in the titration flask and to titrate the ferrous salt produced, for example, with ceric sulphate solution and ferroin as indicator.

It is recommended that the titanium (or other) solution be first partially reduced in a beaker with a little cadmium powder: this renders it air-free. The wash solutions are most simply made air-free by boiling under reduced pressure at the laboratory temperature; finally, a little sodium bicarbonate is added. When the reductor is no longer required, the cadmium should be covered with ca. 0.5N-sulphuric acid; it should be washed with 100-150 ml.
of 2N-sulphuric acid before use. The cadmium powder tends to pack down rather tightly after considerable use; it should therefore be removed from the tube occasionally and the tube refilled.

C. The silver reductor. The silver reductor has a relatively low oxidation potential (the Ag/AgCl electrode potential in N-hydrochloric acid is 0.2245 volt), and consequently it is not able to effect many of the reductions which can be made with amalgamated zinc or with cadmium. The silver reductor is preferably used with hydrochloric acid solutions, and this is frequently an advantage. The various reductions which can be effected with the silver, amalgamated zinc, and cadmium reductors are summarised in the following table:

<table>
<thead>
<tr>
<th>Silver Reductor.</th>
<th>Amalgamated Zinc (Jones) or the Cadmium Reductor.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric Acid Solution.</td>
<td>Sulphuric Acid Solution.</td>
</tr>
<tr>
<td>Fe³⁺ → Fe²⁺</td>
<td>Fe³⁺ → Fe²⁺</td>
</tr>
<tr>
<td>Ti⁴⁺ not reduced</td>
<td>Ti⁺</td>
</tr>
<tr>
<td>Mo⁶⁺ → Mo⁵⁺ (2N-HCl; 60–80° C.)</td>
<td>Mo⁶⁺ → Mo⁵⁺</td>
</tr>
<tr>
<td>Cr⁶⁺ not reduced</td>
<td>Cr⁺</td>
</tr>
<tr>
<td>UO₂⁺ → U⁴⁺ (4N-HCl; 80–90° C.)</td>
<td>UO₂⁺ → U⁴⁺</td>
</tr>
<tr>
<td>V⁶⁺ → V⁴⁺</td>
<td>V⁺</td>
</tr>
<tr>
<td>Cu²⁺ → Cu⁺ (2N-HCl)</td>
<td>Cu²⁺ → Cu⁰</td>
</tr>
</tbody>
</table>

The construction of the silver reductor is similar to the cadmium reductor (Fig. II, 39, 1): a tube 12 cm. long and 2 cm. internal diameter, together with a reservoir bulb of 50–75-ml. capacity, is satisfactory. It is not always necessary to use suction (compare Fig. III, 51, 1). The silver is conveniently prepared as follows on a large scale; for preparations on a smaller scale the procedure must be appropriately adapted.* A solution of 500 g. of silver nitrate in 2500 ml. of water, slightly acidified with dilute nitric acid, is placed in a 4-litre beaker. The cathodes consist of two heavy-gauge platinum plates, each 10 cm. square, and suspended in the electrolyte by the use of a heavy copper bus-bar connexion to a source of current. The anode consists of either a silver rod 200 mm. long and 10–25 mm. in diameter or a similar weight of silver as a heavy-gauge rectangular sheet; it is suspended in the centre of the electrolyte with the platinum cathodes placed at the outer edges of the deposition cell. Silver is deposited as granular crystals with high ratio of surface to mass by a current of 60–70 amps. at 5–6 volts. These crystals, obtained in excellent yield, are deposited on the four outside edges of the cathodes, are dislodged by gentle tapping, and are washed by decantation with dilute sulphuric acid. About 30 g. of silver in this form occupy a volume of 40–50 ml.—sufficient to fill one reductor tube.

The necessary quantity of silver is introduced into a reductor above

* The process originally employed consisted in dissolving 29 g. of silver nitrate in 400 ml. of water and adding a few drops of nitric acid. A sheet of electrolytic copper, about 10 cm. square, is suspended in the boiling solution and the mixture stirred mechanically. The displacement reaction is allowed to proceed until a test indicated the absence of silver ions in the solution. The precipitated silver is washed with dilute sulphuric acid until all copper is removed. This silver is in a finely-divided state and suction is sometimes required when used in the reductor. The flow is further retarded by the decomposition of silver chloride. Regeneration is difficult, but may be accomplished by filling the column with about 0.2N-sulphuric acid and inserting a zinc rod into the reductor so that it touches the silver; the reduction proceeds rapidly and, after washing, the column may be used again.
Technique of Quantitative Analysis

225

a small plug of glass wool: it is compressed with a glass rod flattened at one end to as great an extent as necessary without restricting the free flow of solution through the column. The reductor is rinsed with 100 ml. of N-hydrochloric acid, added in five equal portions, each consecutive portion being allowed to pass through the reductor to just above the level of the silver.

The dark silver chloride coating which covers the silver of the upper part of the reductor when hydrochloric acid solutions are employed moves farther down the column in use, and when it extends to about three-quarters of the length of the column, the reductor must be regenerated by the following method. The reductor is rinsed with water and filled completely with 1:3-ammonia solution. The silver chloride dissolves; after 10 minutes, the solution is rinsed out of the reductor tube with water, followed by N-hydrochloric acid and is then ready for re-use. As a precautionary measure the ammoniacal solution of silver chloride should be immediately acidified.

D. Amalgamated zinc wire spirals. The use of amalgamated zinc spirals for reduction is somewhat more convenient than the Jones reductor in that no special glass apparatus is required: furthermore, little attention is necessary, and consequently a large number of determinations may be carried out simultaneously. Very pure zinc wire must be used: this has a tendency to crystallise when bent, and it is advisable to anneal it at 125°C, for several hours before amalgamation. A wire 80–100 cm. long and of about 3 mm. diameter is wound round a glass tube or borer of about 20 mm. diameter to form a spiral: a length of 15–20 cm. is left to serve as a handle to insert and withdraw the coil when employed for reductions.* The spiral is amalgamated by immersion during 10 minutes in a 10 per cent solution of mercuric nitrate acidified with 5 per cent by volume of concentrated nitric acid contained in a 300- or 350-ml. conical flask; the solution is shaken at frequent intervals. The increase in weight, due to amalgamation, is usually of the order of 1–2 per cent.

The method of use will be apparent from the following experimental details for the reduction of a ferric salt. Place a solution (200 ml.) of ferric iron (0.01–0.03N) in 5–10 per cent sulphuric acid in a 300- or 350-ml. conical flask, insert an amalgamated zinc spiral, and cover the flask with an inverted crucible cover. Heat the solution just to the boiling point and maintain the gentle ebullition until the colour of the ferric salt has disappeared. Continue the gentle boiling for a further 10–15 minutes: do not allow the solution to evaporate to any appreciable extent. Cool the flask and solution rapidly under the tap to room temperature; remove and rinse off the cover; then lift out the spiral from the flask, wash it with a generous stream of water from a wash bottle and allow the washings from the spiral to return to the flask. Treat the solution with a few ml. of syrupy phosphoric acid and titrate with standard potassium permanganate solution.

A cadmium wire spiral may replace the cadmium reductor (see B), but the cadmium must be of high purity.

E. Reduction by means of amalgams. This subject is discussed in Section III, 90, et seq.

* Zinc wire of 99.99 per cent purity supplied by Charles Clifford and Son Ltd., Dog Pool Mills, Birmingham 30, England. Amalgamated zinc spirals may be purchased from the G. Frederick Smith Chemical Co., of Columbus, Ohio, U.S.A.
SELECTED BIBLIOGRAPHY ON TECHNIQUE OF QUANTITATIVE ANALYSIS


CHAPTER III

VOLUMETRIC ANALYSIS

ACIDIMETRY AND ALKALIMETRY

III, 1. Preparation of a standard acid. Discussion.—Two acids, namely hydrochloric acid and sulphuric acid, are widely employed in the preparation of standard solutions of acids. Both of these are commercially available as concentrated solutions; concentrated hydrochloric acid is about 10.5-12N, and concentrated sulphuric acid is about 36N. By suitable dilution, solutions of any desired approximate strength may be readily prepared. Hydrochloric acid is generally more convenient, since most chlorides are soluble in water. Sulphuric acid forms insoluble salts with lime and baryta; for titration of hot liquids or for determinations which require boiling for some time with excess of acid, standard sulphuric acid is, however, preferable. Nitric acid is rarely employed, because it almost invariably contains a little nitrous acid, which has a destructive action upon many indicators.

For the present, we shall confine our attention to the preparation of standard solutions of hydrochloric acid. Two methods are available. The first utilises the experimental fact that aqueous solutions of hydrochloric acid lose either hydrogen chloride or water upon boiling, according as to whether they are stronger or weaker, until they attain a practically constant composition (constant-boiling-point mixture), which depends upon the prevailing pressure. The composition of this constant-boiling mixture and its dependence upon pressure have been determined with great accuracy by Hulett and Bonner (1909) and by Foulk and Hollingsworth (1923). The relevant data are collected in Table I.

The constant-boiling-point acid is neither hygroscopic nor appreciably volatile, and its concentration remains unchanged if kept in a well-stoppered vessel out of direct sunlight. This acid may be employed directly in the preparation of a solution of hydrochloric acid of known concentration.

In the second method a solution of the approximate strength required is prepared, and this is standardised against some standard alkaline substance, such as borax or anhydrous sodium carbonate; other

 TABLE I.—COMPOSITION OF CONSTANT-BOILING-POINT HYDROCHLORIC ACID

<table>
<thead>
<tr>
<th>Pressure (mm. of Hg.)</th>
<th>Per cent HCl in Acid (vac. wt.)</th>
<th>Grams of Acid, weighed in air, containing 36.47 g. of HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>790</td>
<td>20.173</td>
<td>180.621</td>
</tr>
<tr>
<td>770</td>
<td>20.197</td>
<td>180.407</td>
</tr>
<tr>
<td>760</td>
<td>20.221</td>
<td>180.183</td>
</tr>
<tr>
<td>750</td>
<td>20.245</td>
<td>179.979</td>
</tr>
<tr>
<td>740</td>
<td>20.269</td>
<td>179.766</td>
</tr>
<tr>
<td>730</td>
<td>20.293</td>
<td>179.565</td>
</tr>
</tbody>
</table>
suitable substances are given in Section III, 7. Both methods will be described. If a solution of an exact normality is required, a solution of an approximate strength somewhat greater than that desired is first prepared; this is suitably diluted with water after standardisation (for a typical calculation, see Section I, 24, Example 15).

The student should read the following theoretical sections before embarking upon the experimental work:

Sections I, 27–29—theory of acidimetry and alkalimetry;
Section I, 23—equivalent weights, normal solutions.

III. 2. Preparation of constant-boiling-point hydrochloric acid.—
Method A. Mix 500 ml. of pure concentrated hydrochloric acid (sp. gr. 1·19), preferably of analytical-reagent quality, with 500 ml. of distilled water;* the resultant acid should have a specific gravity of 1·10 (test with a hydrometer). Fit up an apparatus consisting of a 1·5-litre Pyrex distilling-flask surmounted with a splash bulb but no trap (which might set up a back pressure), and connected to a Liebig's condenser having a 75-cm. water-jacket and an inner tube of 6–10 mm. bore. Insert the end of the condenser inside the neck of a Pyrex Erlenmeyer (conical) flask. Make all connections with new rubber stoppers, and arrange that the glass tubing projects at least 2 cm. beyond the rubber. Place the diluted acid in the flask. To prevent superheating, allow the flask to rest on a sheet of asbestos in which a hole is cut for the flame; insulate the upper part of the flask against heat radiation by means of asbestos paper or cloth. Conduct the distillation continuously at a rate not exceeding 8–10 ml. per minute. Do not immerse the condenser in the distillate, but allow the condensate to flow freely into the flask. Set aside the first 75 per cent of the volume of the original distillate for ordinary laboratory use, and retain the next 10–15 per cent as constant-boiling-point acid. Discard the residue in the flask (about 100 ml.). Read the barometric pressure to the nearest mm. at the beginning of the distillation, again after 75 per cent has passed over, and finally at the end of the distillation. The mean of the last two readings is calculated and the concentration of the acid interpolated from Table I.

Method B. Mix 400 ml. of pure concentrated hydrochloric acid with 260–400 ml. of distilled water so that the specific gravity of the resultant acid is 1·10 (test with a hydrometer). Insert a thermometer in the neck of a 1-litre Pyrex distilling-flask so that the bulb is just opposite the side tube, and attach a Liebig's condenser to the side tube; use new rubber bungs. Place 500 ml. of the diluted acid in the flask, and distil the liquid at a rate not exceeding 8–10 ml. per minute (3–4 ml. per minute is a convenient rate), and collect the distillate in a small Pyrex flask. From time to time pour off the distillate into a 500-ml. measuring-cylinder. When 375 ml. has been collected and transferred to the measuring-cylinder, collect a further 50 ml. in the small Pyrex flask; watch the thermometer to see that the temperature remains constant. Remove the receiver and cork it. This contains the pure, constant-boiling-point acid. Note the barometric pressure to the nearest mm. during the distillation and at the end, and take the mean value. Interpolate the concentration of the acid from Table I.

* If the concentrated acid has a specific gravity of 1·16, as is often the case, 300 ml. of water are required for 500 ml. of acid.
III, 3. Direct preparation of 0·1N-hydrochloric acid from the constant-boiling-point acid.—Clean and dry a small, stoppered conical flask; a glass-stoppered flask is preferable. After weighing, do not handle the flask directly with the fingers, handle it with the aid of a strip of paper or of linen cloth. Add the calculated quantity of constant-boiling-point acid required for the preparation of 1 litre of 0·1N-acid (see Table I) with the aid of a pipette; make the final adjustment with a small piece of glass capillary, to one end of which a piece of rubber tubing is attached. By this method it should be possible to weigh the acid to the nearest centigram. Re-weigh the flask to 0·001 g. after replacing the stopper. Add an equal volume of water to prevent loss of acid, and transfer the contents to a litre volumetric flask. Wash out the weighing-flask several times with distilled water and add the washings to the original solution. Make up to the mark with distilled water. Insert the stopper and mix the solution thoroughly by shaking and inverting the flask repeatedly.

Note.—Unless a solution of exact normality is required, it is not necessary to weigh out the exact quantity of constant-boiling acid. The exact normality may be calculated from the weight of acid used. Thus, if 18·305 g. of acid, prepared at 760 mm., was diluted to 1 litre, its normality would be 18·305/180·193 = 0·10118N.

Solutions of other concentrations are similarly prepared.

III, 4. Preparation of 0·1N-hydrochloric acid and standardisation.—
Measure out by means of a graduated cylinder or a burette 90 ml. of pure concentrated hydrochloric acid; pour the acid into a litre volumetric flask or into a litre measuring-cylinder (Fig. II, 24, 1, B) containing about 500 ml. of distilled water. Make up to the litre mark with distilled water and thoroughly mix by shaking. This will give a solution approximately 0·1N (1).

Note. 1. If 1N-hydrochloric acid is required, use 90 ml. of the concentrated acid. If 0·01N-acid is required, dilute two 50-ml. portions of the approximately 0·1N-acid, removed with a 50-ml. pipette, in a volumetric flask to 1 litre.

Approximately 0·1N-sulphuric acid is similarly prepared from 3 ml. of pure concentrated sulphuric acid.

Two excellent methods are available for standardisation. The first has been widely employed, but the second, of more recent date, is more convenient, less time-consuming, and equally accurate.

A. Standardisation with anhydrous sodium carbonate. Pure sodium carbonate. Analytical-reagent-quality * sodium carbonate of 99·9 per cent purity is obtainable commercially. This contains a little moisture and must be dehydrated by heating at 260–270° C. for half an hour and allowed to cool in a desiccator before use. Alternatively, pure sodium carbonate may be prepared by heating A.R. sodium bicarbonate to 260–270° C. for 60–90 minutes; the temperature must not be allowed to exceed 270° C., for above this temperature the sodium carbonate may lose carbon dioxide. A small quantity (5–10 g.) of A.R. sodium bicarbonate is placed in a porcelain, nickel or, best, a platinum crucible, and pressed against the walls of

* Analytical reagent will be abbreviated to A.R.
the crucible so as to form a uniformly thick layer. The crucible is
heated by any of the following methods:

(i) Embed the crucible in a sand-bath, immerse the bulb of a 360°C.
thermometer in the sand adjacent to the crucible, and heat the sand-
bath with a free flame; maintain the temperature at 260–270°C for
one hour.

(ii) Use an air-bath as in Fig. II, 12, 1, or Fig. II, 31, 4.

(iii) Heat in a thermostatically controlled electric oven maintained
at 265°C. (A Pyrex or silica weighing-bottle may also be used.)

It is advisable to stir the mass occasionally. In all cases the crucible
is allowed to cool in a desiccator, and, before it is quite cold, the solid
is transferred to a warm, dry, glass-stoppered tube or bottle, out of
which, when cold, it may be weighed rapidly as required. It is im-
portant to remember that anhydrous sodium carbonate is hygroscopic
and exhibits a tendency to pass into the monohydrate.

Procedure. Weigh out accurately from a weighing-bottle about 0.2
g. of the pure sodium carbonate into a 250-ml. conical flask (1), dissolve
it in 50–75 ml. of water, and add 2 drops of methyl orange indicator
(2) or preferably of methyl orange–indigo carmine indicator (Section
I, 29), which gives a very much more satisfactory end point.* Rinse a
clean burette three times with 5-ml. portions of the acid; fill the burette
to a point 2–3 cm. above the zero mark and open the stopcock momen-
tarily in order to fill the jet with liquid. Examine the jet to see that no
air bubbles are enclosed. If there are, more liquid must be run out
until the jet is completely filled. Re-fill, if necessary, to bring the
level above the zero mark; then slowly run out the liquid until the
level is between the 0.0 and 0.5-ml. marks. Read the position of the
meniscus to 0.01 ml. (Section II, 22). Place the conical flask containing
the sodium carbonate solution upon a piece of unglazed white paper
beneath the burette, and run in the acid slowly from the burette.
During the addition of the acid, the flask must be constantly rotated
with one hand whilst the other hand controls the stopcock. Continue
the addition until the methyl orange becomes a very faint yellow or the
green colour commences to become paler, when the methyl orange–
indigo carmine indicator is used. Wash the walls of the flask down with
a little distilled water from a wash bottle, and continue the titration
very carefully by adding the acid dropwise until the colour of the
methyl orange becomes orange or a faint pink, or the colour of the mixed
indicator is a neutral grey; if the end point is overstepped with the
latter indicator, the colour is magenta. This marks the end point of
the titration, and the burette-reading should be taken and recorded in
a note-book. The procedure is repeated with two or three other
portions of sodium carbonate. The first (or preliminary) titration
will indicate the location of the true end point within 0.5 ml. With
experience and care, subsequent titrations can be carried out very
accurately, and should yield concordant results. From the weights
of sodium carbonate and the volumes of hydrochloric acid employed,
the strength of the acid may be computed for each titration. The
arithmetical mean is taken as the strength of the solution.

* This indicator is prepared by dissolving 1 g. of methyl orange and 2.5 g. of purified
indigo carmine in 1 litre of distilled water, and filtering the solution. The colour change
on passing from alkaline to acid solution is from green to magenta with a neutral-grey
colour at pH of about 4.
Notes.—1. For elementary students, an approximately 0·1\(N\) solution of sodium carbonate may be prepared by weighing out accurately about 1·3 g. of pure sodium carbonate in a weighing-bottle or in a small beaker, transferring it to a 250-ml. volumetric flask, dissolving it in water (Section II, 6A (iii)), and making up to the mark. The flask is well shaken. Twenty-five-ml. portions are withdrawn with a pipette and titrated with the acid as described above. Individual titrations should not differ by more than 0·1 ml.

2. Alternatively, bromo-phenol blue or methyl yellow may be used as indicators. With the former a few drops of indicator solution impart a blue colour to the solution, which becomes purplish-green at the end point; with the latter the colour changes are similar to those for methyl orange, but are more readily perceived.

**Calculation of normality.** The normality may be computed from the equation:

\[ \text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} \]

but the best method is to derive the normality entirely in terms of the primary standard substance, here, sodium carbonate. The equivalent weight (Section I, 23) of sodium carbonate is 52·997 or 53·00. If the weight of the sodium carbonate is divided by the number of ml. of hydrochloric acid to which it is equivalent, as found by titration, we have the weight of primary standard equivalent to 1 ml. of the acid. Thus if 0·2500 g. of sodium carbonate is required for the neutralisation of 45·00 ml. of hydrochloric acid, 1 ml. of the acid would be equivalent to 0·2500/45·00 = 0·005556 g. of sodium carbonate. The milli-equivalent weight or the weight in 1 ml. of N-sodium carbonate solution is 0·005556 g. Hence the normality of the acid is 0·005556/0·06300 = 0·1048\(N\).

Another method is the following. 0·2500 G. of sodium carbonate requires 45·00 ml. of acid, hence 1 litre of acid is equivalent to 1000 \times 0·2500/45·00 = 5·556 g. of sodium carbonate. But a litre of N-acid is equivalent to 53·00 g. of sodium carbonate, hence the acid is 5·556/53·00 = 0·1048\(N\).

In the method described in Note 1 above, the normality of the sodium carbonate is first computed from the weight of sodium carbonate used. The mode of calculation described in Section I, 24 is employed. If \(V_A\) is the volume in ml. of the standard solution of normality \(n_A\) required to react completely with \(V_A\) ml. of the unknown solution of normality \(n_B\), then:

\[ V_A \times n_A = V_B \times n_B \]

from which the value of \(n_A\) is readily deduced. Thus if 1·3890 g. of anhydrous sodium carbonate is dissolved in 250 ml. of water, the normality of the sodium carbonate solution is 1·3890 \times 4/53·00 = 0·1048\(N\). If 25 ml. of the sodium carbonate solution exactly neutralise 25·45 ml. of the hydrochloric acid, then:

\[ 25·00 \times 0·1048 = 25·45 \times n_B \]

or the acid is 0·1030\(N\).

**B. Standardisation against borax.** The advantages of sodium tetra-borate decahydrate are: (i) it has a large equivalent weight, 190·72 (that of anhydrous sodium carbonate is 53·00); (ii) it is easily and economically purified by recrystallisation; (iii) heating to constant weight is not required; (iv) it is practically non-hygroscopic; and (v)
a sharp end point can be obtained with methyl red at room temperatures, since this indicator has no effect upon the very weak boric acid.

\[
\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O} + 2\text{HCl} = 2\text{NaCl} + 4\text{H}_3\text{BO}_3 + 5\text{H}_2\text{O}
\]

**Pure borax.** A.R. Borax is recrystallised from distilled water; 50 ml. of water is used for every 15 g. of borax. Care must be taken that the crystallisation does not take place above 55° C.; above this temperature there is a possibility of the formation of the pentahydrate, since the transition temperature, decahydrate \(\rightleftharpoons\) pentahydrate, is 61° C. The crystals are filtered at the pump (Section II, 12), washed twice with water, then twice with portions of 95 per cent alcohol, followed by two portions of ether. Five-ml. portions of water, alcohol, or ether are used for 10 g. of borax crystals. Each washing must be followed by suction to remove the wash liquid. After washing with alcohol and ether, the borax is spread in a thin layer on a watch or clock glass and allowed to stand at room temperature for 12-18 hours. The borax is then dry, and may be kept in a well-stoppered tube for three to four weeks without appreciable change. An alternative method of drying is to place the recrystallised product (after having been washed twice with water) in a desiccator over a solution saturated with respect to sugar (sucrose) and sodium chloride. The borax is dry after about three days, and may be kept indefinitely in the desiccator without change. The latter method is more time-consuming; the product is identical with that obtained by the alcohol-ether process.

**Procedure.** Weigh out accurately from a weighing-bottle 0·4-0·5 g. of pure borax into a 250-ml. conical flask (1), dissolve it in about 50 ml. of water and add a few drops of methyl red (2). Titrate with the hydrochloric acid contained in a burette (for details, see under A) until the colour changes to pink (3). Repeat the titration with two other portions of borax. Calculate the strength of the hydrochloric acid from the weight of borax and the volume of acid used. The average deviation of these results should not exceed 1-2 parts per thousand. If it is greater, further titrations must be performed until the average deviation is within these limits. The arithmetical mean is taken as the concentration of the solution.

**Notes.**—1. For elementary students, an approximately 0·1N solution of borax may be prepared by weighing out accurately 4·7-4·8 g. of A.R. borax on a watch glass or in a small beaker, transferring it to a 250-ml. volumetric flask, dissolving it in water (Section II, 6A (iii)), and making up to the mark. The contents of the flask are well mixed by shaking. Twenty-five-ml. portions are withdrawn with a pipette and titrated with the acid as detailed under Method A. Individual titrations should not differ by more than 0·1 ml.

2. Methyl orange, methyl orange–indigo carmine or bromocresol green may also be used as indicators (compare Note 2 in Method A). If the comparison solution procedure is adopted (see Note 3), the mixed indicator should not be used.

3. For work of the highest precision a comparison solution or colour standard may be prepared for detecting the equivalence point. For 0·1N solutions, this is made by adding 5 drops of methyl red to a solution containing 1·0 g. of sodium chloride and 2·2 g. of boric acid in 500 ml. of water; the solution must be boiled to remove any carbon dioxide which may be present in the water. It is assumed that 20 ml. of wash water are used in the titration.
Calculation of the normality. This is carried out as described in Method A. The equivalent weight of borax is 190.72.

C. Standardisation by an iodometric method. The experimental details are given in Section III, 100.

III, 5. Preparation of standard alkali.—Discussion. The hydroxides of sodium, potassium, and barium are generally employed for the preparation of solutions of standard alkalis. They are strong bases and are readily soluble in water. Solutions made from ammonium hydroxide are undesirable, because they tend to lose ammonia, especially if the concentration exceeds 0.5N; moreover, it is a weak base, and difficulties arise in titrations with weak acids (compare Section I, 36). Sodium hydroxide is most commonly used because of its cheapness. None of these solid hydroxides can be obtained pure, so that a standard solution cannot be prepared by dissolving a known weight in a definite volume of water. Both sodium and potassium hydroxides are extremely hygroscopic; a certain amount of alkali carbonate and water are always present. Exact results cannot be obtained in the presence of carbonate with some indicators, and it is therefore necessary to discuss methods for the preparation of carbonate-free alkali solutions. For many purposes the A.R. sodium hydroxide (which contains 1–2 per cent of sodium carbonate) or the commercially available sodium hydroxide prepared from metallic sodium (sodium carbonate content <1 per cent) is sufficiently pure.

To prepare carbonate-free sodium hydroxide solution one of several methods may be used:

(i) Rinse the sticks of A.R. quality, or those prepared from metallic sodium, rapidly with water; this removes the carbonate from the surface. A solution prepared from the washed sticks is satisfactory for most purposes.

(ii) If a concentrated solution of sodium hydroxide (equal weights of solid and water) is prepared, covered, and allowed to stand, the carbonate remains insoluble; the clear supernatant liquid may be poured or siphoned off, and suitably diluted. (Potassium carbonate is too soluble in the concentrated alkali for this method to be applicable.)

(iii) Carbonate may be removed by the addition of a slight excess of a concentrated solution of barium chloride or of barium hydroxide, shaking well, and allowing the precipitate to settle. The amount of Ba(OH)$_2$,8H$_2$O or of BaCl$_2$·2H$_2$O required is 10 or 8 g. respectively for 100 g. of A.R. sodium hydroxide.

(iv) The best method, which yields a product completely free from carbonate ions, consists in the electrolysis of a saturated solution of A.R. sodium chloride with a mercury cathode and a platinum anode in the apparatus shown in Fig. III, 5, 1. About 20–30 ml. of re-distilled mercury are placed in a 250-ml. pear-shaped Pyrex separating-funnel, over which is poured about 100–125 ml. of an almost saturated solution of A.R. sodium chloride. Two short lengths of platinum wire are sealed into Pyrex glass tubing; one of these dips into the mercury (cathode), and the other into the salt solution (anode). A little mercury is placed in the glass tubes, and electrical contact is made by means of amalgamated copper wires dipping into the mercury in the tubes.
Electrolysis is carried out using 6–8 volts and 0·5–1 amp. for several hours; the funnel is shaken at intervals in order to break up the amalgam crystals that form on the surface of the mercury. The weight of the sodium dissolved in the amalgam may be roughly computed from the total current passed; the current efficiency is 75–80 per cent. When sufficient amalgam has formed, the mercury is run into a Pyrex or, preferably, a Jena flask containing about 100 ml. of boiled-out distilled water and closed with a rubber bung carrying a soda-lime guard tube. Decomposition of the amalgam is complete after several days: after 12–18 hours about 75 per cent of the amalgam is decomposed. Dilute solutions of sodium hydroxide are prepared by transferring the concentrated solution to the appropriate quantity of boiled-out (or conductivity) water, an atmosphere of nitrogen being maintained throughout. This method is rather time-consuming, and need only be used for work demanding the highest precision.

Attention must be directed to the fact that alkaline solutions, particularly if concentrated, attack glass. They may be preserved, if required, in either a paraffined bottle * or a bottle in which the inside is coated with a rubber paint, such as “Thermoprene” (compare Section II, 23). Furthermore, solutions of the strong bases absorb carbon dioxide from the air. If such solutions are exposed to the atmosphere for any appreciable time they become contaminated with carbonate. This may be prevented by the use of a storage vessel such as is shown in Fig. II, 25, 1; the guard tube should be filled with soda-lime or “solfelite.” A short exposure of an alkali hydroxide solution to the air will not, however, introduce any serious error. If such solutions are quickly transferred to a burette and the latter fitted with a soda-lime guard tube, the error due to contamination by carbon dioxide may be neglected.

The solution of alkali hydroxide prepared by any of the above methods must be standardised. Alkaline solutions that are subsequently to be used in the presence of carbon dioxide or with strong acids are best standardised against solutions prepared from constant-boiling-point hydrochloric acid or potassium bi-iodate or sulphamic acid, or against hydrochloric acid which has been standardised by means of borax or sodium carbonate. If the alkali solution is to be used in the titration of weak acids, it is best standardised against organic acids or acid salts of organic dibasic acids, such as benzoic acid or potassium hydrogen phthalate, respectively. The last two are commercially available in a purity exceeding 99·9 per cent. Potassium hydrogen phthalate is preferable, since it is more soluble in water and has a greater molecular weight.

Procedure A. Weigh out rapidly about 4·2 g. of A.R. sodium hydroxide on a watch glass or into a small beaker, dissolve it in water, make up to 1 litre with boiled-out distilled water, mix thoroughly by shaking, and pour the resultant solution into the stock bottle, which should be closed by a rubber stopper.

Procedure B (carbonate-free sodium hydroxide). Dissolve 50 g. of sodium hydroxide in 50 ml. of distilled water in a Pyrex or Jena flask,
Volumetric Analysis

transfer to a 75-mI. test-tube of Jena or Pyrex glass, and insert a well-fitting stopper covered with tinfoil. Allow it to stand in a vertical position until the supernatant liquid is clear. For a 0.1N-sodium hydroxide solution carefully withdraw 6.5 mI. of the concentrated clear solution through a graduated pipette (Fig. II, 21, 10) into a litre bottle or flask, and dilute quickly with 1 litre of recently boiled-out water.

A clear solution can be obtained more quickly, and incidentally the transfer can be made more satisfactorily, by rapidly filtering the solution through a sintered-glass funnel with exclusion of carbon dioxide with the aid of the apparatus shown in Fig. III, 5, 2. It is advisable to roughly calibrate the test-tube in 5-mI. intervals and to put the graduations on a thin slip of paper gummed to the outside of the tube.

Procedure C (carbonate-free sodium hydroxide). Weigh out about 5 g. of dry sodium hydroxide sticks or pellets on a watch glass on the rough balance, transfer to a 500-m1. Pyrex beaker, and dissolve in about 300 ml. of water. Warm and add slowly a solution (20-25 ml.) prepared from 2-2.5 g. of solid crystallised barium hydroxide or barium chloride. Allow the barium carbonate to settle, and decant the clear solution into a litre bottle or flask; dilute to about 1 litre with carbon dioxide-free water and shake well. Allow the solution to settle again: siphon or filter off the solution into a clean bottle fitted with a rubber stopper. Alternatively, the solution may be stored in an apparatus similar to that shown in Fig. II, 25, 1; a soda-lime guard tube should be provided.

III. 6. Standardisation of the approximately 0.1N-sodium hydroxide.—If the solution contains carbonate (Procedure A), methyl orange, methyl orange–indigo carmine, or bromphenol blue must be used in standardisation against hydrochloric acid of known normality. Phenolphthalein or indicators with a similar pH range, which are affected by carbon dioxide, cannot be used at the ordinary temperature (compare Section I, 27). With carbonate-free sodium hydroxide (Procedure B) phenolphthalein or thymol blue (Section I, 33) may be employed, and standardisation may be effected against hydrochloric acid, potassium bi-iodate, potassium hydrogen phthalate, benzoic acid, or other organic acids (Section III, 7).

Procedure A. With standard hydrochloric acid. Place the 0.1N hydrochloric acid, prepared from the constant-boiling-point acid or which has been standardised by means of sodium carbonate or borax, in the burette. Transfer 25 ml. of the sodium hydroxide solution into
a 250-ml. conical flask with the aid of a pipette (1), dilute with a little water, add 1–2 drops of methyl orange or 3–4 drops of methyl orange–indigo carmine indicator, and titrate with the previously standardised hydrochloric acid. Repeat the titrations until duplicate determinations agree within 0·05 ml. of each other.

Note. 1. If another burette is available, the alkali solution may be placed in it, and definite volumes transferred from the burette to the conical flask for titrations. This method has the advantage that volumes of the order of 40 ml. of solution can be conveniently titrated, thus reducing the experimental error; also, back titration may be effected if the end point is overstepped.

Calculation of the normality. The normality is readily computed from the simple relationship:

\[ V_A \times n_A = V_B \times n_B \]

where \( V_A \) and \( n_A \) refer to the volume and known normality of the acid respectively, \( V_B \) is the volume of alkali solution required for the neutralisation, and \( n_B \) is its (unknown) normality.

Procedure B. With potassium hydrogen phthalate. The A.R. potassium hydrogen phthalate has a purity of at least 99·9 per cent; it is almost non-hygroscopic, but, unless a product of guaranteed purity is purchased, it is advisable to dry it at 120° C. for 2 hours, and allow it to cool in a desiccator. Weigh out three 0·6–0·7-g. portions of the salt into 250-ml. Pyrex or Rysil conical flasks (1), add 75 ml. of boiled-out water to each portion, stopper each flask and shake gently until the solid has dissolved. Titrate each solution with the sodium hydroxide solution contained in a burette, using phenolphthalein or thymol blue as indicator.

Calculation of normality. This is similar to that described in Section III, 4. The equivalent weight of potassium hydrogen phthalate is 204·22. The mean deviation should not exceed 0·1–0·2 per cent.

\[ \text{HK\cdotC}_4\text{H}_4\text{O}_4 + \text{NaOH} = \text{NaK\cdotC}_4\text{H}_4\text{O}_4 + \text{H}_2\text{O} \]

Note. 1. For elementary students, an approximately 0·1N solution is prepared by weighing out accurately about 5·1 g. of the ordinary A.R. product, dissolving it in water, and making it up to 250 ml. in a volumetric flask. Twenty-five-ml. portions are employed in the titrations with the sodium hydroxide solution. Individual titrations should not differ by more than 0·1 ml. The normality is calculated in a similar manner to that given in Section III, 4; the equivalent weight is 204·22.

III, 7. Other standard substances for acidimetry and alkalimetry.—In addition to the standard substances already detailed for use in standardising acids and alkalis, numerous others have been proposed. A number of these will be briefly described.

A. Sodium oxalate (\( \text{Na}_2\text{C}_2\text{O}_4 \); equiv. wt. = 134·02). The A.R. product has a purity of 99·9 per cent or better. It is recommended that the salt be dried for 2 hours at 120° C. before use in order to remove hygroscopic moisture. Upon strong heating the salt largely decomposes with the formation of sodium carbonate:

\[ \text{Na}_2\text{C}_2\text{O}_4 = \text{Na}_2\text{CO}_3 + \text{CO} \]

If a little carbon dioxide is lost by the decomposition of the sodium carbonate, no error is introduced because the total alkalinity is un-
affected. Some of the salt (0.25–0.3 g. for a 0.1N solution) is carefully weighed into a platinum crucible, which is then covered with the lid. The crucible and lid are heated, while supported in a hole in a sheet of asbestos, over a small flame for 15–30 minutes until the sodium carbonate formed just begins to fuse. Towards the end of the operation the lid is moved aside to bring about the complete combustion of any carbon formed. The resultant carbonate is transferred to a conical flask or beaker, dissolved in water, and titrated with the acid solution, using methyl orange or methyl orange–indigo carmine as indicator. The disadvantages of the method are the possibility of mechanical loss during the evolution of carbon monoxide and its tedious nature.

**B. Mercuric oxide (HgO; equiv. wt. = 108.31).** Mercuric oxide can be readily obtained pure and dry, and has a comparatively high equivalent weight. It dissolves in potassium bromide solution with the production of potassium mercuric bromide and an equivalent quantity of potassium hydroxide:

\[ HgO + 4KBr + H_2O = K_2[HgBr_4] + 2KOH \]

A 0.1N solution of potassium hydroxide is obtained by dissolving 10.83 g. of A.R. mercuric oxide in a solution of 200 g. of A.R. potassium bromide in 300 ml. of water, and diluting to 1 litre. This solution may be titrated against acids with *inter alia* phenolphthalein or methyl orange as indicators.

**C. Benzoic acid (H·C_7H_5O_2; equiv. wt. = 122.12).** The A.R. product has a purity of at least 99.9 per cent. For work demanding the highest accuracy, the acid should be dried before use by careful fusion in a platinum crucible at about 130°C, and then powdered in an agate mortar. Benzoic acid is sparingly soluble in water (which is a disadvantage) and must therefore be dissolved in 95 per cent alcohol. The mode of use is similar to that already described for potassium hydrogen phthalate (Section **III, 6B**). For a 0.1N solution, of, say, sodium hydroxide, weigh out accurately 0.4-g. portions of the acid into a 250-ml. conical flask, add 10–20 ml. of alcohol, shake until dissolved, and then titrate the solution with the strong alkali using phenolphthalein as indicator. A blank test should be made with the same volume of alcohol and the indicator: deduct, if necessary, the volume of the alkali solution consumed in the blank test.

**D. Succinic acid (H_2C_4H_4O_4; equiv. wt. = 59.045).** The A.R. product or a pure commercial product should be recrystallised from pure acetone and dried in a vacuum desiccator. The purity is checked by means of a melting-point determination (185–185.5°C). The acid is fairly soluble in water; phenolphthalein is a suitable indicator.

**E. Furoic acid (H·C_5H_5Os; equiv. wt. = 112.08).** The purified commercial acid, m.p. 131–132°C, is crystallised once from chloroform and dried at 120°C for 2 hours. The technical product is purified by one recrystallisation from hot water with the aid of a little animal charcoal (2 g. of animal charcoal for 20 g. of acid), dried at 120°C for 2 hours, and then re-crystallised from chloroform as above. The resultant solid is pure. The acid is only moderately soluble in cold water, and is best dissolved in alcohol as detailed under C for benzoic acid. Phenolphthalein or an indicator of similar pH range must be used in the titration with a strong base.
Quantitative Inorganic Analysis

F. Adipic acid (H₂C₆H₅O₄; equiv. wt. = 73-07). The commercial acid is crystallised once from hot water with the addition of a little animal charcoal, dried at 120° C. for 2 hours, then recrystallised from acetone and again dried at 120° C. for 2 hours. The pure acid has a melting point of 152° C. The acid is slightly soluble in cold water, but, like furoic acid, it dissolves readily in hot water and can be titrated in hot solution with an indicator of the phenolphthalein type. It is best, however, to dissolve it in rectified spirit (compare benzoic acid above). This is an excellent and inexpensive standard.

G. Potassium bi-iodate (KH(IO₃)₂; equiv. wt. = 389-95). Unlike the other solid standards already described, this is a strong acid and thus permits the use of any indicator having a pH range between 4-5 and 9-5 for titration with strong bases (compare Section I, 38). It may be employed for the standardisation of bases which are subsequently to be used with strong acids; an indicator, such as methyl red, must then be used. The salt is moderately soluble in water (1·33 g./100 ml. at 16°), is anhydrous and non-hygrosopic, and its aqueous solution is stable for long periods; the equivalent weight is high. The only disadvantage is that the pure substance is expensive. A 0-01N solution of potassium bi-iodate contains 3·8995 g. per litre.

Preparation of pure potassium bi-iodate. Dissolve 27 g. of A.R. potassium iodate in 125 ml. of boiling water, and add a solution of 22 g. of A.R. iodic acid in 45 ml. of warm water acidified with 6 drops of concentrated hydrochloric acid. Potassium bi-iodate separates on cooling. Filter on a sintered-glass funnel, and wash with cold water. Recrystallise three times from hot water: use 3 parts of water for 1 part of the salt and stir continuously during each cooling. Dry the crystals at 100° C. for several hours. The purity exceeds 99·95 per cent.

H. Oxalic acid dihydrate (H₂C₂O₄·2H₂O; equiv. wt. = 63-034). The A.R. acid has been widely used as a standard, but in view of the possible uncertainty of the water content this is not recommended except for elementary students. The latter objection may be surmounted if the acid is preserved in a desiccator over deliquescent sodium bromide.

I. Potassium tetroxalate (KHC₂O₄·H₂C₂O₄·2H₂O; equiv. wt. = 84-732). This is suitable only for elementary or approximate work owing to the possible uncertainty of the water content.

J. Potassium bi-tartrate (KHC₄H₄O₆; equiv. wt. = 188·18). The A.R. product has a purity of 99·9 per cent. The substance is sparingly soluble in cold water, and must be titrated in hot solution, in which it is more soluble.

Phenolphthalein or thymol blue must be used as indicators for H, I, and J.

K. Sulphamic acid (NH₂SO₂OH; equiv. = 97-09). A product of comparatively high purity is commercially available. It is prepared by the action of fuming sulphuric acid upon urea:

\[ \text{CO(NH}_2)_2 + \text{H}_2\text{SO}_4 + \text{SO}_3 = 2\text{NH}_2\text{SO}_2\text{OH} + \text{CO}_2 \]

It is purified by crystallisation from hot water (see below). The acid is moderately soluble in water (21·3 and 47·1 g. in 100 g. of water at 20° and 80° C. respectively), appreciably soluble in methanol and ethanol, slightly soluble in acetone, and practically insoluble in ether;
it is a colourless, crystalline, non-hygroscopic solid melting with decomposition at 205° C. Sulphamic acid is largely dissociated in aqueous solution (it is similar to hydrochloric acid in this respect), so that any indicator with a pH range of 4–9 may be employed with the 0·1N solution; the best indicator for use with strong bases is bromo-thymol blue. The aqueous solution is, however, not stable, as hydrolysis slowly occurs at room temperature with the formation of ammonium bisulphate:

$$\text{NH}_2\text{SO}_2\text{OH} + \text{H}_2\text{O} = \text{NH}_4\text{HSO}_4$$

**Purification of sulphamic acid.** Dissolve 125 g. of the commercial product in 300 ml. of water preheated to 70° C. Filter the hot solution three times and discard each time the material crystallising from solution (altogether about 25 g.); there will, of necessity, be a lowering of temperature during this process. Cool the final filtrate in a mixture of ice and salt for 20 minutes, filter on a sintered-glass funnel, and wash successively with a small quantity of ice water, twice with cold ethyl alcohol, and finally with anhydrous ether. Dry the recrystallised solid in the air for 1 hour, grind it in an agate or glass mortar, and preserve in a desiccator. The resultant sulphamic acid is 99·95 per cent pure. The substance may also be dried at 105° C.; decomposition commences at about 135° C.

**III, 8. Standard barium hydroxide (baryta) solution.**—This solution is widely employed, particularly for the titration of organic acids. Barium carbonate is insoluble, so that a clear solution is a carbonate-free strong alkali. The equivalent weight of Ba(OH)$_2$$\cdot$8H$_2$O is 157·75, but a standard solution cannot be prepared by direct weighing owing to the uncertainty of the hydration and the possible presence of carbonate. To prepare an approximately 0·1N solution, dissolve 18 g. of A.R. crystallised baryta (or 20 g. of the commercial substance) in about 1 litre of water in a large flask. Stopper the flask and shake until all the crystals have disappeared. Allow the solution to stand for 2 days or until all the barium carbonate has completely settled out. Decant or siphon off the clear solution into a storage-bottle of the type depicted in Fig. II, 25, 1. A soda-lime guard tube must be provided to prevent ingress of carbon dioxide. The solution may be standardised against standard 0·1N-hydrochloric acid or potassium hydrogen phthalate; phenolphthalein or thymol blue is employed as indicator.

**ANALYSES INVOLVING THE USE OF STANDARD ACID AND ALKALI**

**III, 9. Determination of the Na$_2$CO$_3$ content of washing soda.**—Procedure. Weigh out accurately about 3·6 g. of the washing-soda crystals, dissolve in water, and make up to 250 ml. in a graduated flask. Mix thoroughly. Titrate 25 ml. of the solution with standard hydrochloric acid of approximately 0·1N concentration using methyl orange, or, better, methyl orange–indigo carmine or bromo-cresol green as indicator (compare Chapter I, Table X). Two consecutive titrations should agree within 0·1 ml.

**Calculation.** The weight of anhydrous sodium carbonate Na$_2$CO$_3$ which has reacted with the standard hydrochloric acid can be readily computed from the equation:

$$\text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

$$106·01 \quad 2 \times 35·46$$
The percentage of Na₂CO₃ can then be calculated from the known weight of washing soda employed.

A simpler and more general procedure is to employ the "normality" method. A normal solution of sodium carbonate contains 53.00 g. of Na₂CO₃ per litre; 1 ml. of a N solution of sodium carbonate contains 0.05300 g. or the milli-equivalent weight. If the volume of hydrochloric acid is multiplied by the normality we obtain the number of ml. of N acid. By multiplying the latter figure by the milli-equivalent weight of sodium carbonate, the weight of Na₂CO₃ in the sample titrated is found: 1 ml. N-HCl = 0.05300 g. of Na₂CO₃. The percentage of Na₂CO₃ can then be readily calculated.

An actual example will make this clear.

Weight of weighing-bottle + substance = 16.7910 g.
Weight of weighing-bottle + residual substance = 13.0110 g.

\[ \text{Weight of sample used} = 3.7800 \text{ g.} \]

This was dissolved in water and made up to 250 ml.

Titration of 25.00 ml. of the carbonate solution against 0.1060N-HCl, with methyl orange-indigo carmine as indicator.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Reading 1.</th>
<th>Reading 2.</th>
<th>Difference.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00 ml.</td>
<td>26.10 ml.</td>
<td>26.10 ml. (preliminary)</td>
</tr>
<tr>
<td>2</td>
<td>0.00 ml.</td>
<td>25.90 ml.</td>
<td>25.90 ml.</td>
</tr>
<tr>
<td>3</td>
<td>0.00 ml.</td>
<td>25.95 ml.</td>
<td>25.95 ml.</td>
</tr>
<tr>
<td>Mean</td>
<td>25.93 ml.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 ml. N-HCl = 0.05300 g. Na₂CO₃

\[ 25.93 \times 0.1060 = 2.749 \text{ ml. N-HCl} \]

\[ 2.749 \times 0.05300 = 0.1457 \text{ g. Na₂CO₃ in portion titrated.} \]

Weight of washing soda in portion titrated

\[ = 3.7800 \times 25.0/250 = 0.3780 \text{ g.} \]

\[ \therefore \text{Percentage of Na₂CO₃ = 0.1457 \times 100/0.3780 = 38.54 per cent.} \]

Alternative method of calculation. 25.0 Ml. of the carbonate solution required 25.93 ml. of 0.1050N-HCl:

\[ \therefore 25.0 \times \text{normality of carbonate solution} = 25.93 \times 0.1060, \text{whence the carbonate solution is 25.93 \times 0.1060/25.0 = 0.1099N.} \]

But \( N \)-Na₂CO₃ contains 106.00/2 = 53.00 g. Na₂CO₃ per litre.

\[ \therefore \text{the given solution contains 0.1099 \times 53.00 = 5.8271 g. Na₂CO₃ per litre, and 250 ml. would contain 5.8271 \times 250/1000 = 1.4568 g.} \]

Thus percentage of Na₂CO₃ = 1.4568 \times 100/3.7800 = 38.54 per cent.

III. 10. Determination of the strength of glacial acetic acid.—Weigh a dry, stoppered 50-ml. flask, introduce about 2 g. of glacial acetic acid and weigh again. Add about 20 ml. of water and transfer the solution quantitatively to a 250-ml. graduated flask. Wash the small flask several times with water and add the washings to the volumetric flask. Make up to the mark with distilled, preferably boiled-out, water. Shake the flask well to ensure thorough mixing. Titrate 25-ml. portions
of the acid with 0·1N standard sodium hydroxide solution, using phenolphthalein or thymol blue as indicator.

\[ \text{NaOH} + \text{H}_2\text{C}_2\text{H}_3\text{O}_2 = \text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \]

1 ml. N-NaOH = 0·06005 g. H-C\text{H}_3\text{O}_2

Calculate the percentage of H-C\text{H}_3\text{O}_2 in the sample of glacial acetic acid.

Note on the determination of the acetic acid content of vinegar. Vinegar usually contains 4-5 per cent of acetic acid. Weigh out about 20 g. of vinegar as described above, and make up to 100 ml. in a graduated flask. Remove 25 ml. with a pipette, dilute with an equal volume of water, add a few drops of phenolphthalein, and titrate with standard 0·1N-sodium hydroxide solution. As a result of the dilution of the vinegar, its natural colour will be so reduced that it will not interfere with the colour change of the indicator. Calculate the acetic acid content of the vinegar, and express your result in g. of acetic acid per 100 ml.

III, 11. Determination of sulphuric acid in the concentrated acid.— Accurately weigh a small, glass-stoppered weighing-bottle, and add from a clean, dry 2-ml. pipette or measuring cylinder 0·7-0·8 ml. of the concentrated acid. Re-stopper the bottle immediately and re-weigh accurately.* Place about 100 ml. of water in a 250-ml. volumetric flask, and insert a short-necked funnel in the mouth of the flask. Pour the weighed acid into the funnel, and, without removing the weighing-bottle, wash it thoroughly both inside and outside with a stream of water from the wash bottle. Rinse the funnel thoroughly and remove it. Dilute nearly to the mark, and after 1-2 hours, when the solution has acquired the laboratory temperature, make up exactly to the mark. Shake and mix thoroughly. Titrate 25-ml. portions against standard 0·1N-sodium hydroxide, using methyl orange or methyl orange-indigo carmine as indicator.

From the results calculate the percentage by weight of H\text{2}SO\text{4} in the original concentrated acid.

1 ml. N-NaOH = 0·04904 g. H\text{2}SO\text{4}

III, 12. Determination of sulphuric acid in the fuming acid (oleum).— Fuming sulphuric acid may be considered as a mixture of sulphur trioxide and sulphuric acid, although it may contain pyrosulphuric acid H\text{2}S\text{4}O\text{7}; if rich in sulphur trioxide, it is solid. The acid must not be exposed to the atmosphere during weighing as it is extremely hygroscopic. The Lunge-Rey pipette (Fig. II, 23, 1, b) is particularly suitable for this determination; the lower part of the pipette is protected by a ground-on test-tube.

Weigh the complete dry pipette (it may be suspended from the balance by means of a thin silver wire). Close tap 2, open tap 1, and produce a slight vacuum in the bulb by applying suction (water-pump, etc.), and then close stopcock 1. Dip the dry point of the pipette into the fuming acid (solid oleum must first be melted by warming gently), and cautiously open the lower stopcock. As soon as the acid

* Alternatively, a weight pipette (Fig. II, 23, 1, a) may be used. See, however, Section III, 12.
has entered the widened part of the pipette below the lower bulb, close tap 2. Replace the test-tube 4, and weigh again. The increase in weight will give the weight of acid taken; this should be about 1 g. Place about 100 ml. of distilled water in a beaker and cautiously dip the point of the pipette in the water; open first tap 1 and then tap 2, and allow the acid to run into the beaker. Wash the pipette thoroughly with distilled water. Transfer the contents of the beaker to a 250-ml volumetric flask, make up to the mark, and shake well. Complete the determination as in Section III, 11.

Calculate the percentage of SO₃ in the sample of oleum.

III, 13. Determination of carbon dioxide in the atmosphere.—Discussion. The method to be described is due to Pettenkofer, as modified by Hesse. The carbon dioxide in a known volume of air is absorbed by excess of standard baryta solution, and the excess of the latter is determined by titration against standard oxalic acid or, better, hydrochloric acid, using phenolphthalein as indicator.

Procedure. The sample of air is collected in a thick-walled, conical flask of 500 or 1000 ml. capacity. The flask is fitted with a two-holed rubber stopper, the holes being closed by glass-rod plugs; a mark is made on the flask at the point where the rubber stopper ends. The capacity of the flask up to the point at which the rubber stopper reaches into the neck is determined by filling with water at a known temperature to this mark.

Fill the flask with air by aspiration with a rubber aspirator, or by filling it with distilled water and then pouring the water out slowly, or by any other convenient method: note the temperature and pressure of the air in the vessel. Add a five-fold excess of standard barium hydroxide solution (Section III, 8) by removing both glass plugs from the stopper and inserting the tip of the baryta solution burette into one of the holes; remove the burette and replace both glass plugs. Shake the vessel gently for about 20 minutes, and allow to stand for 1 hour. Remove both plugs, add a few drops of phenolphthalein, insert the tip of a burette containing standard hydrochloric acid (0·02-0·1N) into one of the holes, and titrate the excess of barium hydroxide present. Repeat the determination with another sample of air.

Compute the volume of standard alkali which has reacted with the carbon dioxide. From this volume and the known volume of the air less the volume of baryta solution added, calculate the percentage of CO₂ in the air.

$$1 \text{ ml. } 0·1N-\text{Ba(OH)}_2 = 1·119 \text{ ml. of } \text{CO}_2 \text{ at N.T.P.}$$

III, 14. Determination of a mixture of carbonate and hydroxide. Analysis of commercial caustic soda.—Discussion. Two methods may be used for this analysis. In the first method the total alkali (carbonate + hydroxide) is determined by titration with standard acid, using methyl orange, methyl orange-indigo carmine, or bromo-phenol blue as indicator. The carbonate is precipitated with a slight excess of barium chloride solution, and, without filtering,* the solution is titrated against standard acid with thymol blue or phenolphthalein as indicator. The latter titration gives the hydroxide content, and by subtracting

* The strong alkalinity of the soluble sodium carbonate due to hydrolysis is replaced by that (pH 8·8) due to a saturated solution of the sparingly soluble barium carbonate; hence phenolphthalein or thymol blue can then be employed as indicators.
Volumetric Analysis

243

this from the first titration, the volume of acid required for the carbonate is obtained.

\[
\begin{align*}
Na_2CO_3 + BaCl_2 &= BaCO_3 \text{ (insoluble)} + 2NaCl \\
BaCl_2 + 2NaOH &= Ba(OH)_2 \text{ (soluble)} + 2NaCl
\end{align*}
\]

The second method utilises two indicators. It has been stated in Section I, 37 that the pH of half-neutralised sodium carbonate, i.e., at the sodium bicarbonate stage, is about 8.3, but the pH changes comparatively slowly in the neighbourhood of the equivalence point (compare Fig. I, 37, 1), consequently the indicator colour-change with phenolphthalein (pH range 8.3–10.0) or thymol blue (pH range (base) 8.0–9.6) is not too sharp. This difficulty may be surmounted by using a comparison solution containing sodium bicarbonate of approximately the same concentration as the unknown and the same volume of indicator. A simpler method is to employ a mixed indicator (Section I, 29) composed of 6 parts of thymol blue and 1 part of cresol red; this mixture is violet at pH 8.4, blue at pH 8.3, and rose at pH 8.2. With this mixed indicator the mixture has a violet colour in alkaline solution and changes to blue in the vicinity of the equivalence point; in making the titration the acid is added slowly until the solution assumes a rose colour. At this stage all the hydroxide and half the carbonate (by conversion into bicarbonate) have been neutralised. Let the volume of standard acid consumed be \(v\) ml.

\[
\begin{align*}
NaOH + HCl &= NaCl + H_2O \\
Na_2CO_3 + HCl &= NaHCO_3 + NaCl
\end{align*}
\]

Another titration is performed with methyl orange or methyl orange-indigo carmine as indicator. Let the volume of acid be \(V\) ml.

\[
\begin{align*}
NaOH + HCl &= NaCl + H_2O \\
Na_2CO_3 + 2HCl &= 2NaCl + H_2O + CO_2
\end{align*}
\]

Then \(V - 2(V-v)\) corresponds to the hydroxide, \(2(V-v)\) to the carbonate, and \(V\) to the total alkali. To obtain satisfactory results by this method the solution titrated must be cold (as near 0°C as is practicable), and loss of carbon dioxide must be prevented as far as possible by keeping the tip of the burette immersed in the liquid.

Procedure A. Weigh out accurately in a glass-stoppered weighing-bottle about 2.5 g. of commercial sodium hydroxide (e.g., in flake form). Transfer quantitatively to a 500-ml. volumetric flask and make up to the mark. Shake the flask well. Titrate 25 or 50 ml. of this solution with standard 0.1N-hydrochloric acid, using methyl yellow, methyl orange, or methyl orange-indigo carmine as indicator. Carry out two or three titrations: these should not differ by more than 0.1 ml. This gives the total alkalinity (hydroxide + carbonate). Warm another 25 or 50 ml. of the solution to 70°C, and add 1 per cent barium chloride solution slowly from a burette or pipette in slight excess, i.e., until no further precipitate is produced. Cool to room temperature, add a few drops of phenolphthalein to the solution, and titrate very slowly and with constant stirring with standard 0.1N-hydrochloric acid; the end point is reached when the colour just changes from pink to colourless. If thymol blue is used as indicator, the colour change is from blue to yellow. The amount of acid used corresponds to the hydroxide present.
This method yields only approximate results because of the precipitation of basic barium carbonate in the presence of hydroxide. More accurate results are obtained by considering the above titration as a preliminary one in order to ascertain the approximate hydroxide content, and then carrying out another titration as follows. Treat 25–50 ml. of the solution with sufficient standard hydrochloric acid to neutralise most of the hydroxide, then heat and precipitate as before. Under these conditions, practically pure barium carbonate is precipitated.

\[ 1 \text{ ml. } N\text{-HCl} = 0.0401 \text{ g. } \text{NaOH} \]
\[ 1 \text{ ml. } N\text{-HCl} = 0.05300 \text{ g. } \text{Na}_2\text{CO}_3 \]

Procedure B. The experimental details for the preparation of the initial solution are similar to those given under Procedure A. Titrate 25 or 50 ml. of the cold solution with standard 0·1N-hydrochloric acid and methyl orange, methyl orange–indigo carmine, or bromo-phenol blue as indicator. Titrate another 25 or 50 ml. of the cold solution, diluted with an equal volume of water, slowly against the standard acid with phenolphthalein or, better, with the thymol blue–oresol red mixed indicator; in the latter case, the colour at the end point is rose.

Calculate the result as described in the Discussion above.

III. 15. Determination of a mixture of carbonate and bicarbonate.

The two methods available for this estimation are modifications of those described in the previous Section for hydroxide–carbonate mixtures. In the first procedure, which is particularly valuable when the sample contains relatively large amounts of carbonate and small amounts of bicarbonate, the total alkali is first determined in one portion of the solution by titration against standard 0·1N-hydrochloric acid with methyl orange, methyl orange–indigo carmine, or bromo-phenol blue as indicator:

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + 2\text{HCl} &= 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \\
\text{NaHCO}_3 + \text{HCl} &= \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 
\end{align*}
\]

Let this volume correspond to \( V \) ml. \( N\text{-HCl} \). To another sample, a measured excess of standard 0·1N-sodium hydroxide (free from carbonate) over that required to transform the bicarbonate to carbonate is added:

\[
\text{NaHCO}_3 + \text{NaOH} = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}
\]

A slight excess of 10 per cent barium chloride solution is added to the hot solution to precipitate the carbonate as barium carbonate, and the excess of sodium hydroxide solution immediately determined without filtering off the precipitate by titration with the same standard acid; phenolphthalein or thymol blue is used as indicator. If the volume of excess of sodium hydroxide solution added be equivalent to \( v \) ml. of \( N\)-sodium hydroxide and \( v' \) ml. \( N\)-acid corresponds to the excess of the latter, then \( v - v' = \text{bicarbonate} \), and \( V - (v - v') = \text{carbonate} \).

In the second procedure a portion of the cold solution is slowly titrated with standard 0·1N-hydrochloric acid, using phenolphthalein or, better, the thymol blue–oresol red mixed indicator. This (say, \( M \) ml.) corresponds to half the carbonate (compare Section III, 14):

\[
\text{Na}_2\text{CO}_3 + \text{HCl} = \text{NaHCO}_3 + \text{NaCl}
\]
Another sample is then titrated against the same standard acid with methyl orange, methyl orange-indigo carmine or bromo-phenol blue as indicator. The volume of acid used (say, m ml.) corresponds to carbonate + bicarbonate. Hence \(2M = \text{carbonate, and } m-2M = \text{bicarbonate.}\)

For practice the student should employ sodium sesquicarbonate \(\text{Na}_2\text{CO}_3, \text{NaHCO}_3, 2\text{H}_2\text{O}\) (approx.), or else should use an artificial mixture prepared from 4 g. of A.R. potassium carbonate and 1 g. of A.R. sodium bicarbonate. The experimental details are similar to those given in Section III, 14.

III, 16. Determination of phosphoric acid in commercial orthophosphoric acid.—Discussion. Phosphoric acid is a tribasic acid; the \(pH\) at the equivalence point in 0·1\(N\) solutions corresponding to the primary, secondary, and tertiary stages of ionisation are approximately 4·6, 9·7, and 12·6 respectively (compare Section I, 37). The \(pH\) changes in the neighbourhood of the equivalence points are not, however, very marked (see Fig. I, 36, 1). For the first stage \((pH 4·6)\) we may employ methyl orange or methyl orange-indigo carmine mixture \((pH\) range 3·1–4·4) or bromo-creosol green \((pH\) range 3·8–5·4), but it is best to use a solution of potassium or sodium dihydrogen phosphate containing the same amount of indicator for comparison. For the second stage \((pH 9·7)\) phenolphthalein \((pH\) range 8·3–10·0) is only approximate, thymolphthalein \((pH\) range 9·3–10·5) is better, but the best indicator is a mixture of phenolphthalein (2 parts) and \(\alpha\)-naphtholphthalein (1 part), which gives a colour change from pale rose through green to violet at \(pH\) 9·6. For the third stage \((pH 12·6)\) no satisfactory indicator is known. If titration be carried out to the second stage, and then calcium chloride solution be added to precipitate the trivalent ion as formed, titration as a tribasic acid is possible with thymolphthalein or the mixed indicator.

Procedure. Weigh out accurately in a ground-stoppered weighing-bottle about 2 g. of commercial syrupy phosphoric acid. Transfer quantitatively to a 250-ml. volumetric flask and make up to the mark. Shake well. Titrate 25-ml. portions with standard carbonate-free sodium hydroxide, using thymolphthalein or, preferably, \(\alpha\)-naphtholphthalein–phenolphthalein as indicator. Carry out two or three titrations; these should not differ by more than 0·1 ml.

\[
\text{H}_3\text{PO}_4 + 2\text{NaOH} = \text{Na}_2\text{HPO}_4 + 2\text{H}_2\text{O}
\]

1 ml. \(N\)-NaOH = 0·04902 g. \(\text{H}_3\text{PO}_4\)

Calculate the percentage of \(\text{H}_3\text{PO}_4\) in the sample.

III, 17. Determination of boric acid and borax.—Discussion. Boric acid acts as a weak monobasic acid \((K_a = 5·8 \times 10^{-10})\); it cannot therefore be titrated accurately with 0·1\(N\) standard alkali (compare Section I, 34). However, by the addition of certain organic polyhydroxy compounds, such as glycerol, mannitol, dextrose, or invert sugar, it is transformed into a relatively strong monobasic acid, probably of the type:

\[
\begin{align*}
\text{C} - \text{OH} + \text{HO} - \text{B} - \text{OH} & \rightarrow \text{C} - \text{O} \rightarrow \text{B} - \text{OH} + 2\text{H}_2\text{O} \\
\text{C} - \text{OH} + \text{HO} & \rightarrow \text{C} - \text{O} \rightarrow \text{B} - \text{OH} + 2\text{H}_2\text{O}
\end{align*}
\]
Glycerol is widely employed; the commercial substance is often acidic, consequently it is necessary to make the diluted glycerol neutral to phenolphthalein by adding sodium hydroxide solution. Mannitol (mannite) is more effective and has the advantage of being a solid and does not materially increase the volume of the solution being titrated; 0·5-0·7 g. of mannitol to 10 ml. of solution is a convenient quantity:

\[
\text{H [boric acid complex]} + \text{NaOH} = \text{Na [boric acid complex]} + \text{H}_2\text{O}
\]

1 ml. N-NaOH = 0·06184 g. H\(_3\)BO\(_3\)

The method may be applied to boric acid of commerce and to borates. The technical boric acid may contain ammonium salts. It is best to dissolve 1 g. in hot water, add a slight excess of sodium carbonate, boil the solution down to half bulk in order to expel ammonia, filter any precipitate which may be formed, and to titrate the filtrate against standard 0·1N-sodium hydroxide with phenolphthalein as indicator.

For practice in the titration the student may employ commercial borax. This may be titrated against standard acid with methyl orange or with methyl orange-indigo carmine mixed indicator (Section I, 37):

\[
\text{Na}_2\text{B}_4\text{O}_7 + 2\text{HCl} + 5\text{H}_2\text{O} = 4\text{H}_3\text{BO}_3 + 2\text{NaCl}
\]

1 ml. N-HCl = 0·10065 g. Na\(_2\)B\(_4\)O\(_7\)

The liberated boric acid may then be titrated against standard alkali in the presence of mannitol with phenolphthalein as indicator. Carbonic acid must be absent, as it leads to high results.

1 ml. N-NaOH = 0·06184 g. H\(_3\)BO\(_3\) = 0·05033 g. Na\(_2\)B\(_4\)O\(_7\)

**Procedure.** Weigh out accurately about 4 g. of commercial borax, transfer it quantitatively to a 250-ml. volumetric flask, and make up to the mark. Shake well. Titrate 25 ml. of this solution with standard 0·1N-hydrochloric acid, using methyl orange or methyl orange-indigo carmine as indicator.

To another 25 ml. of the solution, add the quantity of standard hydrochloric acid determined in the previous titration,* cover the beaker or conical flask with a clock glass or Fisher “speedyvap” beaker-cover, heat to simmering temperature for 10 minutes to expel carbon dioxide (prolonged vigorous boiling may cause loss of boric acid which is volatile in steam), cool the solution to room temperature, and add just sufficient standard sodium hydroxide solution to restore the transition colour of the original indicator. Then introduce about 2 g. of mannitol, and shake until dissolved; add a few drops of phenolphthalein and titrate against standard 0·1N carbonate-free sodium hydroxide to the first permanent faint-pink colour. Add a further 0·5 g. of mannitol; if the solution becomes colourless, add more standard sodium hydroxide until the pink colour reappears. Repeat the process until the addition of mannitol has no effect upon the end point.

Calculate the percentage of Na\(_2\)B\(_4\)O\(_7\) in the sample from the results of both titrations.

**III. 18. Determination of ammonia in an ammonium salt.**—Discussion. Two methods, the direct and indirect, may be used for this determina-

* If carbonate is absent, mannitol may be added at this stage, and the titration completed with standard sodium hydroxide solution in the presence of phenolphthalein.
Volumetric Analysis

In the direct method, a solution of the ammonium salt is treated with a solution of a strong base (e.g., sodium hydroxide) and the mixture distilled. Ammonia is quantitatively expelled, and is absorbed in an excess of standard acid. The excess of acid is back-titrated in the presence of methyl red (or methyl orange, methyl orange-indigo carmine, bromo-phenol blue, or bromo-cresol green). Each ml. of $N$ acid consumed in the reaction is equivalent to 0.017032 g. NH$_3$:

$$\text{NH}_4\text{Cl} + \text{NaOH} = \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O}$$

In the indirect method, the ammonium salt (other than the carbonate or bicarbonate) is boiled with a known excess of standard sodium hydroxide solution. The boiling is continued until no more ammonia escapes with the steam. The excess of sodium hydroxide is titrated with standard acid, using methyl red (or methyl orange-indigo carmine) as indicator.

**Procedure (direct method).** Fit up the apparatus shown in Fig. III, 18, 1. A is a 1-litre Pyrex glass flask provided with a two-holed rubber stopper which carries a tap funnel B and a glass spray trap C. The purpose of the trap is to prevent any droplets of sodium hydroxide solution being driven over in the subsequent distillation. D is a Liebig's condenser attached to the trap by means of a rubber bung, and E is a 350-ml. Pyrex conical flask which serves as a receiver. For practice, weigh out 1.5 g. of A.R. ammonium chloride or of crude sal ammoniac, dissolve it in water, and make up to 250 ml. in a volumetric flask. Shake thoroughly. Transfer 50 ml. of the solution into the distillation flask and dilute with 200 ml. of water; add a few fragments of porous porcelain to promote regular ebullition in the subsequent distillation. Place 100 ml. of standard 0.1N-hydrochloric acid in the receiver and adjust the flask so that the end of the condenser just dips into the acid. Make sure that all the corks are fitting tightly. Place 100 ml. of 10 per cent sodium hydroxide solution in the funnel. Run the sodium hydroxide solution into the flask by opening the tap F; close the tap as soon as all the alkali has entered. Heat the flask so that the contents boil gently. Continue the distillation for 30-40 minutes, by which time all the ammonia should have passed over into the receiver. Open the tap F before removing the flame. Disconnect the trap from the top of the condenser. Lower the receiver and rinse the condenser with a little water. Add a few drops of methyl red * and titrate the excess of acid in the solution with standard 0.1N-sodium hydroxide. Repeat the determination.

Calculate the percentage of NH$_3$ in the solid ammonium salt employed.

**Procedure (indirect method).** Weigh out accurately 0.1-0.2 g. of the ammonium salt into a 350-ml. Pyrex or Jena glass conical flask,

* A sharper colour change is obtained with the mixed indicator methyl red-bromo-cresol green (prepared from 1 part of 0.2 per cent methyl red in alcohol and 3 parts of 0.1 per cent bromo-cresol green in alcohol.
and add 100 ml. of standard 0.1N-sodium hydroxide. Place a small funnel in the neck of the flask in order to prevent mechanical loss, and boil the mixture until a piece of filter-paper moistened with mercurous nitrate solution and held in the escaping steam is no longer turned black. Cool the solution, add a few drops of methyl red, and titrate with standard 0.1N-hydrochloric acid. Repeat the determination. Calculate the percentage of NH₃ in the substance.

III, 19. Determination of nitrates (sodium nitrate in Chile saltpetre).—

Discussion. Nitrates are reduced to ammonia by means of aluminium, zinc or, most conveniently, by Devarda's alloy (50Cu, 45Al, 5Zn) in strongly alkaline solution:

$$3\text{NO}_3^- + 8\text{Al} + 5\text{OH}^- + 2\text{H}_2\text{O} = 8\text{AlO}_2^- + 3\text{NH}_3$$

The ammonia is distilled into excess of standard acid as in Section III, 18.

Nitrites are similarly reduced, and must be allowed for if nitrate alone is to be determined.

Procedure. Weigh out accurately about 1 g. of Chile saltpetre. Dissolve it in water and transfer the solution quantitatively to the distillation flask of Fig. III, 18, 1. Dilute to about 240 ml. Add 3 g. of pure, finely divided Devarda's alloy (it should all pass a 20-mesh sieve). Fit up the apparatus completely (all connexions must be made with rubber bungs), and place 75-100 ml. of standard 0.2N-hydrochloric acid in the receiver (500-ml. Pyrex conical flask). Introduce 10 ml. of 20 per cent sodium hydroxide solution through the funnel, and immediately close the tap. Warm gently to start the reaction, and allow the apparatus to stand for an hour, by which time the evolution of hydrogen should have practically ceased and the reduction of nitrate to ammonia be complete. Then boil the liquid gently and continue the distillation until 40-50 ml. of liquid remain in the distillation flask. Open the tap before removing the flame. Wash the condenser with a little distilled water, and titrate the contents of the receiver and the washings with standard 0.2N-sodium hydroxide, using methyl red as indicator. Repeat the determination. For very accurate work, it is recommended that a blank test be carried out with distilled water.

Calculate the percentage of NaNO₃ in Chile saltpetre.

1 ml. N-HCl = 0.08501 g. NaNO₃

Note. Nitrates can be reduced in neutral solution quantitatively to ammonia with Arndt's alloy (60 per cent Mg; 40 per cent Cu); any slight spurring of the boiling liquid does not vitiate the titration. Here the distillation flask will contain 50 ml. of the above nitrate solution, 150 ml. of water, 2 g. of hydrated magnesium chloride, and 5 g. of the finely divided alloy. The whole is boiled until about two-thirds of the liquid has passed over. The distillate is collected in 50 ml. of 0.1N-hydrochloric acid.

III, 20. Determination of nitrogen by Kjeldahl's method.—Discussion. This process is so widely employed in industrial and research laboratories that an account of it must be included in this book. The principle of the method is the conversion of the nitrogen of the nitrogenous substance into ammonia by boiling with concentrated sulphuric acid, which is fixed by the excess of acid as ammonium sulphate. The latter is determined by adding an excess of caustic alkali to the solution after
digestion with the acid, and distilling off the liberated ammonia into standard acid as detailed in Section III, 18. Simple digestion with concentrated sulphuric acid is, however, a slow process, and various modifications have been suggested to increase the speed of the reaction. These include the addition of potassium sulphate, which raises the boiling point of the acid (Kjeldahl–Gunning process), and of catalysts, such as mercury, mercuric oxide, anhydrous copper sulphate, selenium, or a mixture of equal parts of ferrous sulphate and selenium. The simple process works well for nitrogen determinations in proteins and also in amines and amides, but is not applicable to nitro, azo, hydrazo, and cyano compounds without modification. In the presence of nitrates there is a danger of loss of nitric acid: salicylic acid is then added to the sulphuric acid (proportion: 1 g. to 30 ml.), which fixes the nitric acid as nitro-salicylic acid. Upon the addition of zine dust (1 g.) or of anhydrous sodium thiosulphate (5 g.), the nitro-salicylic acid is reduced to the amino-compound, which can then be estimated by the Kjeldahl process.

Procedure. The determination may be carried out with 1·5–2·0 g. of flour or with acetanilide. Weigh out accurately about 0·1 g. of acetamidide into a dry Pyrex Kjeldahl flask—a round-bottomed flask with a long narrow neck. Add 10 g. of A.R. potassium sulphate, 0·2 g. of selenium or 0·5 g. of anhydrous copper sulphate or 0·5 g. of equal parts of ferrous sulphate and selenium, and pour 25 ml. of concentrated sulphuric acid into the flask in such a way as to wash down any solid adhering to the neck. Support the flask on a hole (4·5 cm. in diameter) in a piece of asbestos board, and incline the neck at an angle of about 60°. Close the flask with a loosely fitting glass stopper elongated to a point and having a balloon-shaped top: a small funnel or a flat reagent bottle stopper will serve the same purpose. Heat the flask in a fume cupboard with a small flame. When frothing has ceased, increase the flame until the mixture boils gently. Continue the heating for 30 minutes after the solution has become colourless or clear (usually 90–120 minutes), and then allow the solution to cool. When cold, add about 200 ml. of water carefully and with frequent shaking. Transfer completely to the ammonia-distillation apparatus (Fig. III, 18, 1), add a few fragments of porous porcelain, followed by excess of sodium hydroxide solution. Distil off the ammonia into excess of standard acid exactly as described in Section III, 18. Carry out a blank determination exactly as above, but with the nitrogen-containing sample omitted, subtract the “blank,” if any.

Calculate the percentage of nitrogen in the solid.

Note. If mercury (0·7 g.) or mercuric oxide (1 g.) is employed as catalyst, it is necessary to add 25 ml. of a solution containing 8 g. of sodium thiosulphate or 4 g. of potassium sulphide per 100 ml. before distilling in order to decompose the mercouri-ammonium compounds formed.
III, 21. General discussion.—The reader should be familiar with the theory of precipitation and complex formation processes given in Sections I, 40–42. With this theoretical groundwork, he should experience little difficulty in carrying out the following determinations in an intelligent manner, and also be able to modify them when occasion demands.

The standard solutions employed include those of silver nitrate, sodium chloride, potassium or ammonium thiocyanate, and potassium cyanide.

III, 22. Preparation of 0.1N–silver nitrate.—Discussion. Very pure silver can be obtained commercially, and a standard solution can be prepared by dissolving a known weight (say, 10.788 g.) in pure dilute nitric acid in a conical flask having a funnel in the neck to prevent mechanical loss, and making up to a known volume (say, 1 litre for a 0.1N solution). The presence of acid must, however, be avoided in such determinations as that of Mohr (Section I, 41A) with potassium chromate as indicator or in determinations employing adsorption indicators (Section I, 41C). It is therefore preferable to employ a neutral solution by dissolving silver nitrate (equivalent weight, 169.89) in water.

A.R. Silver nitrate has a purity of at least 99.9 per cent, so that a standard solution can be prepared by direct weighing. If, however, the commercial recrystallised silver nitrate be employed, or if an additional check of the normality of the silver nitrate solution is required, standardisation may be effected with pure sodium chloride:

\[ \text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3 \]

A.R. Sodium chloride has a purity of 99.9–100.0 per cent; the substance is therefore an excellent primary standard. Sodium chloride is very slightly hygroscopic, and for accurate work it is best to dry the finely powdered solid in an electric oven at 250–350° C. for 1–2 hours, and allow it to cool in a desiccator.*

Procedure A. From A.R. silver nitrate. Dry some finely powdered A.R. silver nitrate at 150° C. for 2 hours and allow it to cool in a desiccator. Weigh out accurately 8.496 g.,† dissolve it in water and make up to 500 ml. in a volumetric flask. This gives a 0.1000N solution. Alternatively, about 8.5 g. of the pure, dry silver nitrate may be weighed out accurately, dissolved in 500 ml. of water in a graduated flask, and the exact normality computed from the weight of silver nitrate employed.

Procedure B. From recrystallised silver nitrate. Weigh out about 8.5 g. of the silver nitrate, dissolve it in water, and make up to 500 ml. in a volumetric flask. Shake well.

* For the most precise work, the powdered solid should be dried in an electric muffle furnace at 500–600° C. and then allowed to cool in a desiccator. This high temperature is unnecessary for work of ordinary accuracy (within 0.1 per cent).
† This weight should be multiplied by the purity factor of the A.R. silver nitrate, e.g., by 1/0.999.
Solutions of silver nitrate should be protected from light; they are best stored in amber-coloured glass bottles.

III. 23. Standardisation of the silver nitrate solution.—Sodium chloride has an equivalent weight of 58·46. A 0·1000 N solution is prepared by weighing out 2·923 g. of the pure dry salt (e.g., A.R., but see Discussion in Section III, 22) and dissolving it in 500 ml. of water in a volumetric flask. Alternatively about 2·9 g. of the pure salt is accurately weighed out, dissolved in 500 ml. of water in a graduated flask, and the exact normality calculated from the weight of sodium chloride employed.

A. With potassium chromate as indicator. The Mohr titration. The student is referred to Section I, 41B for the detailed theory of the titration. Prepare the indicator solution by dissolving 5 g. of A.R. potassium chromate in 100 ml. of water. The final volume of the solution in the titration is 50–100 ml., and 1 ml. of the indicator solution is used, so that the indicator concentration in the actual titration is 0·005–0·0025 M.

Pipette 25 ml. of the standard 0·1N-sodium chloride into a 250-ml. conical flask resting upon a white tile (1), and add 1 ml. of the indicator solution (preferably with a 1-ml. pipette). Add the silver nitrate solution slowly from a burette, swirling the liquid constantly, until the red colour formed by the addition of each drop begins to disappear more slowly: this is an indication that most of the chloride has been precipitated. Continue the addition dropwise until a faint but distinct change in colour occurs. This faint reddish-brown colour should persist after brisk shaking. If the end point is overstepped (production of a deep reddish-brown colour), add more of the chloride solution and titrate again. Determine the indicator blank correction by adding 1 ml. of the indicator to a volume of water equal to the final volume in the titration (2), and then silver nitrate solution until the colour of the blank matches that of the solution titrated. The indicator blank correction, which should not amount to more than 0·03–0·10 ml. silver nitrate, is deducted from the volume of silver nitrate used in the titration. Repeat the titration with two further 25-ml. portions of the sodium chloride solution (3). The various titrations should agree within 0·1 ml.

Calculate the normality of the silver nitrate solution (see Section III, 4A).

Notes. 1. The end point is very readily detected in a large porcelain basin or in a casserole. The solution is stirred with a short glass stirring-rod.
2. A better blank is obtained by adding about 0·5 g. of A.R. calcium carbonate before determining the correction. This gives an inert white precipitate similar to that obtained in the titration of chlorides and materially assists in matching the colour tints.
3. See Note 1 to Procedure A in Section III, 6.

B. With an adsorption indicator. Discussion.—The detailed theory of the process is given in Section I, 41C. Both fluorescein and dichlorofluorescein are suitable for the titration of chlorides. In both cases the end point is reached when the white precipitate in the greenish-yellow solution suddenly assumes a pronounced reddish tint. The change is reversible upon the addition of chloride. With fluorescein the solution must be neutral or only faintly acidic with acetic acid;
acid solutions should be treated with a slight excess of sodium acetate. The chloride solution should be diluted to about 0.01-0.05N, for if it is more concentrated the precipitate coagulates too soon and interferes. Fluorescein cannot be used in solutions more dilute than 0.005N. With more dilute solutions resort must be made to dichlorofluorescein, which possesses other advantages over fluorescein. Dichlorofluorescein gives good results in very dilute solutions (e.g., for drinking-water) and is applicable in the presence of acetic acid and in weakly acid solutions. For this reason the chlorides of copper, nickel, manganese, zinc, aluminium, and magnesium, which cannot be titrated according to the method of Mohr, can be determined by a direct titration when dichlorofluorescein is used as indicator.

For the reverse titration (chloride into silver nitrate), tartrazine (4 drops of a 0.2 per cent solution per 100 ml.) is a good indicator. At the end point, the almost colourless liquid assumes a blue colour (see Section I, 410.)

The indicator solutions are prepared as follows:

Fluorescein. Dissolve 0.1 g. of fluorescein in 100 ml. of 70 per cent alcohol, or dissolve 0.1 g. of sodium fluoresceinate in 100 ml. of water.

Dichlorofluorescein. Dissolve 0.1 g. of dichlorofluorescein in 100 ml of 60-70 per cent alcohol, or dissolve 0.1 g. of sodium dichlorofluoresceinate in 100 ml. of water.

Procedure. Pipette 25 ml. of the standard 0.1N-sodium chloride into a 250-ml. conical flask. Add 10 drops of either fluorescein or dichlorofluorescein indicator, and titrate with the silver nitrate solution in a diffuse light, while rotating the flask constantly. As the end point is approached, the silver chloride coagulates appreciably, and the local development of a pink colour upon the addition of a drop of the silver nitrate solution becomes more and more pronounced. Continue the addition of the silver nitrate solution until the precipitate suddenly assumes a pronounced pink or red colour. Repeat the titration with two other 25-ml. portions of the chloride solution. Individual titrations should agree within 0.1 ml.

Calculate the normality of the silver nitrate solution.

III, 24. Determination of chlorides.—Either the Mohr titration or the adsorption-indicator method may be used for the estimation of chlorides in neutral solution by titration with standard 0.1N-silver nitrate. If the solution is acid, neutralisation may be effected with chloride-free calcium carbonate, sodium bicarbonate, or borax; the A.R. substances are suitable. Mineral acid may also be removed by neutralising most of the acid with ammonia solution and then adding an excess of A.R. ammonium acetate. Titration of the neutral solution prepared with calcium carbonate by the adsorption indicator method is rendered more facile by the addition of 5 ml. of 2 per cent dextrin solution; this offsets the coagulating effect of the calcium ion. If the solution is basic, it may be neutralised with chloride-free nitric acid, using phenolphthalein as indicator.

III, 25. Determination of bromides.—Discussion. The Mohr titration may be applied to the determination of bromides. The most suitable adsorption indicator is eosin, although fluorescein may be used but is subject to the limitations detailed under Chlorides in Section III, 23B. Eosin is serviceable in dilute solutions and even in the presence of
0.1N-nitric acid, but in general, however, acetic acid solutions are to be preferred.

The eosin indicator is prepared by dissolving 0.1 g. of eosin in 100 ml. of 70 per cent alcohol, or by dissolving 0.1 g. of the sodium salt in 100 ml. of water.

For the reverse titration (bromide into silver nitrate), rhodamine 6G (10 drops of a 0.05 per cent aqueous solution) is an excellent indicator (see Section I, 41O). The solution is best rendered 0.5N with respect to silver. The precipitate acquires a violet colour at the end point.

For practice in the use of eosin, the student may determine the purity of potassium bromide, preferably of A.R. quality.

Procedure. Weigh out accurately about 3 g. of the potassium bromide, dissolve it in water, and make up to 250 ml. in a graduated flask. Pipette 25 ml. of the well-mixed solution into a 250-ml. conical flask, add 75 ml. of water, a few ml. of 6N-acetic acid and 10 drops of eosin solution. Titrate against the standard 0.1N-silver nitrate, with constant agitation, in a diffuse light. The silver bromide flocculates approximately 1 per cent before the equivalence point, and the local development of red colour becomes more and more pronounced upon the addition of silver nitrate solution. Continue the addition dropwise with vigorous swirling of the liquid until the precipitate suddenly assumes a pronounced magenta colour. Repeat the titration with two other 25-ml. portions of the bromide solution.

Calculate the purity of the sample.

1 ml. N-AgNO₃ = 0.07992 g. Br = 0.1190 g. KBr

Another method for the volumetric determination of bromides, which utilises an adsorption indicator (bromo-phenol blue), involves titration with mercuric nitrate solution. The solid reagent is deliquescent, and cannot therefore be obtained in a state of appropriate purity for accurate weighing: the A.R. product Hg(NO₃)₂·H₂O has a purity of not less than 95 per cent. Thirty grams of A.R. mercurous nitrate are dissolved in water containing a little nitric acid, and made up to 1 litre in a volumetric flask. The reagent is first standardised against 0.1N-potassium bromide, prepared by dissolving 11.902 g. of dry A.R. potassium bromide in 1 litre of water. Twenty-five ml. of the bromide solution is diluted with an equal volume of water and treated with a few drops of a 0.1 per cent solution of bromo-phenol blue. Titration is then carried out with the mercurous nitrate solution until the yellowish tint on the precipitate suddenly changes to lilac. A similar titration is then carried out with the unknown bromide solution.

III, 26. Determination of chlorides and bromides with standard mercurous perchlorate solution.—Discussion. Mercurous perchlorate, with bromo-phenol blue as adsorption indicator, may be used for the determination of chlorides and bromides. It can be applied in acid solution; its solutions are stable for long periods when kept in the dark, they are easy to prepare, are free from interfering mercuric ions (compare mercurous nitrate solution, Section III, 25), and give sharp end points which coincide almost exactly with the equivalence points. The colour change at the end point is from creamy white to lilac; the best results are obtained if the addition of the indicator is delayed until near the end point.
Nitric, perchloric, and acetic acids have no effect if the total acid concentration does not exceed 0.04N; higher concentrations of acid inhibit the colour change. Sulphuric acid and sulphates cause a high titre; this error is completely eliminated by adding an excess of lead nitrate to the boiling solution; the lead sulphate need not be filtered off before titration. The only cations which interfere are those of silver and mercuric mercury; the latter reduces the titre by an amount proportional to their concentration, due presumably to the removal of some of the halide ions as undissociated mercuric halide.

Procedure.

A. Preparation of approximately 0.1N-mercurous perchlorate.
Shake the following materials vigorously together at intervals over a period of 1 hour: 22 g. of A.R. red mercuric oxide,* 45 g. of perchloric acid (d 1.5; 60 per cent), 50 ml. of water, and 30 g. of pure mercury. From time to time withdraw a few drops of the liquid, dilute, treat with sodium chloride solution, and filter; the preparation is complete when the filtrate from the test portion gives no precipitate with hydrogen sulphide. Decant or filter the liquid from the excess of mercury, and dilute to 2 litres. Keep the solution in the dark; if it is exposed to light, decomposition into mercury and mercuric perchlorate occurs.

B. Standardisation. Deci-normal sodium chloride (Section III, 23) or potassium bromide (Section III, 25) may be employed. Twenty-five ml. of either solution is diluted to 100 ml. in a conical flask, 0.5 ml. of bromo-phenol blue (0.05 per cent solution in water) added, and the mercurous perchlorate solution run in from a burette until the colour of the precipitate changes from creamy white to lilac. It is best to add the indicator near the end point.

C. Use in determination of chlorides and bromides. Dilute the solution of the halide to 100 ml. If sulphates are present, boil, add 10–20 ml. of 5 per cent lead nitrate solution, and cool. Add 1 drop of bromo-phenol blue, then ammonia or sodium carbonate solution until the indicator turns faintly blue, and titrate with the 0.1N (or 0.05N)-mercurous perchlorate. Just before the end point is attained, add 0.5 ml. of bromo-phenol blue, and continue the titration until the colour of the precipitate changes to lilac.

For practice, the student may determine the percentage of chlorine in A.R. crystallised barium chloride.

III, 27. Determination of iodides.—Discussion. The Mohr method cannot be applied to the titration of iodides (or of thiocyanates), because of adsorption phenomena and the difficulty of distinguishing the colour change of the potassium chromate. Eosin is a suitable adsorption indicator, but di-iododimethylfluorescein is better. Eosin is employed as described under bromides (Section III, 25).

The di-iododimethylfluorescein indicator is prepared by dissolving 1.0 g. in 100 ml. of 70 per cent alcohol. The colour change is from an orange-red to a blue-red on the precipitate.

For practice, the student may determine the purity of potassium iodide, preferably of A.R. quality.

* If the mercuric oxide reacts slowly, it should be prepared as follows. Add a slight excess of sodium hydroxide solution to a hot solution of mercuric chloride (prepared from the A.R. solid), filter on a sintered-glass funnel, wash well with water, and dry at 100–120°C.
**Procedure.** Weigh out accurately about 4 g. of the potassium iodide, dissolve it in water and make up to 250 ml. in a volumetric flask. Pipette 25 ml. of the well-mixed solution into a 250-ml. conical flask, add 75 ml. of water and 1 ml. of di-iododimethylfluorescein indicator. Titrate against the standard 0·1N-silver nitrate as detailed under Chlorides (Section III, 23B). Flocculation of the silver iodide occurs about 1 per cent before the end point, and the colour change at the end point is from orange-red to blue-red. Repeat with two other 25-ml. portions of the solution.

Calculate the purity of the sample.

\[ 1 \text{ ml. } N \text{-AgNO}_3 = 0.1269 \text{ g. I} = 0.1660 \text{ g. KI} \]

**III, 28. Determination of thiocyanates.**—These may be estimated with adsorption indicators exactly as for chlorides and bromides. Further experimental details are therefore superfluous. For another method, see Section III, 43.

**III, 29. Determination of mixtures of halides with adsorption indicators.**—A. Chloride and iodide in admixture. These two ions differ considerably in the ease with which they are adsorbed on the corresponding silver halide. This makes it possible to select adsorption indicators which will permit of the estimation of chloride and iodide in the presence of one another. Thus the iodide may be determined with di-iododimethylfluorescein (Section III, 27) by titration with standard 0·1N-silver nitrate, and the iodide + chloride by a similar titration with fluorescein. Chloride is obtained by difference. If a large excess of chloride is present the result for iodide may be as much as 1 per cent high. If however, Rose Bengal (dichlorotetraiodofluorescein) is used as indicator (colour change, carmine red to blue-red) in the presence of ammonium carbonate, the iodide titration is exact.

B. Bromide and iodide in admixture. The total halide (bromide + iodide) is determined by titration with standard 0·1N-silver nitrate with eosin or fluorescein as indicator. The iodide is estimated by titration with 0·01-0·2N-silver nitrate, using di-iododimethylfluorescein as indicator. Bromide is obtained by difference.

Numerous adsorption indicators have been suggested for various purposes, but a full treatment is outside the scope of this work.*

**III, 30. Determination of mixtures of halides by an indirect method.**—**Discussion.** The method is applicable to the determination of a mixture of two salts having the same anion (e.g., sodium and potassium chlorides) or the same cation (e.g., potassium chloride and potassium bromide). Let us first suppose that it is desired to estimate the amount of sodium and potassium chlorides in a mixture of the two salts. A known weight \(w_1\) g. of the solid mixture is taken, and the total chloride is determined with standard 0·1N-silver nitrate, using Mohr's method or an adsorption indicator. Let \(w_2\) g. of silver nitrate be required for the complete precipitation of \(w_1\) g. of the mixture, which contains \(x\) g. of NaCl and \(y\) g. of KCl. Then:

\[
x + y = w_1 \\
\frac{169.89x}{58.46} + \frac{169.89y}{74.56} = w_2
\]

Upon solving these two simultaneous equations, the values for \( x \) and \( y \) are deduced.

Let us now suppose that the estimation of potassium chloride and potassium bromide in admixture is desired. The total halide is determined by Mohr's method or with an adsorption indicator. Let the weight of the mixture be \( w_3 \) g., \( w_4 \) g. be the weight of silver nitrate required for complete precipitation, \( p \) g. be the weight of the potassium chloride, and \( q \) g. be the weight of the potassium bromide. Then:

\[
\begin{align*}
p + q &= w_3 \\
\frac{169\cdot98p}{74\cdot56} + \frac{169\cdot89q}{119\cdot02} &= w_4
\end{align*}
\]

The values of \( p \) and \( q \) can be obtained by solving the simultaneous equations.

It can be shown* that the method depends upon the difference between the equivalent weights of the two components of the mixture and that inter alia it is most satisfactory when the two constituents are present in approximately equal proportions.

For practice, the student may prepare for himself, or obtain from the teacher, a mixture of equal weights of potassium and sodium chlorides or of potassium chloride and bromide, and determine the proportions of each by titration with standard 0·1N-silver nitrate. The experimental details for the titrations have been given in previous Sections.

III, 31. Preparation and use of 0·1N-ammonium or potassium thiocyanate. Titrations according to Volhard's method.—Discussion. Volhard's original method (1874, 1878) for the determination of silver in dilute nitric acid solution by titration with standard thiocyanate solution in the presence of a ferric salt as indicator has proved of great value not only for silver estimations, but also in numerous indirect analyses. The theory of the Volhard process has been given in Section I, 41B. In this connexion it must be pointed out that the concentration of the nitric acid should be from 1 to 10 per cent by volume (strong nitric acid retards the formation of the "ferric thiocyanate") and at a temperature not exceeding 25° C. (higher temperatures tend to bleach the colour of the indicator). The solutions must be free from nitrous acid, which gives a red colour with thiocyanic acid, and may be mistaken for "ferric thiocyanate." Pure nitric acid is prepared by diluting the usual pure (e.g., A.R.) acid with about one-fourth of its volume of water and boiling until perfectly colourless; this eliminates any lower oxides of nitrogen which may be present.

The method may be applied to those anions (e.g., chloride, bromide, and iodide) which are completely precipitated by silver and are sparingly soluble in dilute nitric acid. Excess of standard silver nitrate solution is added to the solution containing free nitric acid, and the residual silver nitrate solution is titrated with standard thiocyanate solution. This is sometimes termed the residual process. Anions whose silver salts are slightly soluble in water, but which are soluble in nitric acid, such as phosphate, arsenate, chromate, sulphide, and oxalate, may be precipitated in neutral solution with an excess of standard silver nitrate solution. The precipitate is filtered off, thoroughly washed, dissolved

in dilute nitric acid, and the silver titrated with thiocyanate solution. Alternatively, the residual silver nitrate in the filtrate from the precipitation may be determined with thiocyanate solution after acidification with dilute nitric acid.

Both ammonium and potassium thiocyanates are usually available as deliquescent solids; the A.R. products are, however, free from chlorides and other interfering substances. An approximately 0·1N solution is therefore first prepared, and this is standardised by titration against standard 0·1N-silver nitrate.

Procedure. Weigh out about 9 g. of A.R. ammonium thiocyanate, or 11 g. of A.R. potassium thiocyanate, and dissolve it in 1 litre of water in a volumetric flask. Shake well.

Standardisation. Use 0·1N-silver nitrate, which has been prepared and standardised as described in Section III, 23.

The ferric indicator solution consists of a cold, saturated solution of A.R. ferric ammonium sulphate in water (about 40 per cent) to which a little 6N-nitric acid has been added. One ml. of this solution is employed for each titration.

Pipette 25 ml. of the standard 0·1N-silver nitrate into a 250 ml. conical flask, add 5 ml. of 6N-nitric acid and 1 ml. of the ferric indicator solution. Run in the potassium or ammonium thiocyanate solution from a burette. At first a white precipitate is produced, rendering the liquid of a milky appearance, and as each drop of thiocyanate falls in, it produces a reddish-brown cloud, which quickly disappears on shaking. As the end point approaches, the precipitate becomes flocculent and settles easily; finally one drop of the thiocyanate solution produces a faint brown colour, which no longer disappears upon shaking. This is the end point. The indicator blank amounts to 0·01 ml. of 0·1N-silver nitrate. It is essential to shake vigorously during the titration in order to obtain correct results. Repeat the titration with two other 25-ml. portions of the silver nitrate solution. Individual titrations should agree within 0·1 ml.

Calculate the normality of the thiocyanate solution from the known normality of the silver nitrate solution (for details of calculation, see Sections I, 24 and III, 4A). It will be found that the thiocyanate solution is a little stronger than 0·1N. The volume of water that must be added to make the solution exactly 0·1000N is computed as described in Example 15 (Section I, 24).

The standard solution thus prepared remains of the same strength for a very long period if evaporation is prevented.

Use of tartrazine as indicator. Satisfactory results may be obtained by the use of tartrazine as indicator. Proceed as above, but add 4 drops of tartrazine (0·5 per cent aqueous solution) in lieu of the ferric indicator. The precipitate will appear pale yellow during the titration, but the supernatant liquid (best viewed by placing the eye at the level of the liquid and looking through it) is colourless. At the end point, the supernatant liquid assumes a bright lemon-yellow colour. The titration is sharp to one drop of 0·1N-thiocyanate solution.

III, 32. Determination of silver in a silver alloy.—A silver threepenny piece (or any other small silver coin) is suitable for this determination. Clean the coin with emery cloth and weigh it accurately. Place
Quantitative Inorganic Analysis

it in a 250-ml. conical flask, add 5 ml. of water and 10 ml. of concentrated nitric acid; place a funnel in the mouth of the flask to avoid mechanical loss. Warm the flask gently until the coin has dissolved. Add a little water and boil for 5 minutes in order to expel oxides of nitrogen. Transfer the cold solution quantitatively to a 100-ml. standard flask and make up to the mark with distilled water. Titrate 25-ml. portions of the solution with standard 0·IN-thiocyanate as described in Section III, 31.

Calculate the percentage of silver in the alloy.

\[
1 \text{ ml. } N \text{-KCNS or NH}_4\text{CNS} = 0\cdot10788 \text{ g. Ag}
\]

Note. The presence of metals whose salts are colourless does not influence the accuracy of the determination, except that mercury and palladium must be absent since their thiocyanates are insoluble. Salts of metals (e.g., nickel and cobalt) which are coloured must not be present to any considerable extent. Copper does not interfere, provided it does not form more than about 40 per cent of the alloy.

III, 33. Determination of chlorides (Volhard's method).—Discussion.
The chloride solution is treated with an excess of standard silver nitrate solution, and the residual silver nitrate determined by titration with standard thiocyanate solution. Now silver chloride is more soluble than silver thiocyanate, and would react with the thiocyanate thus:

\[
\text{AgCl} + \text{CNS}^- \rightleftharpoons \text{AgCNS} + \text{Cl}^-
\]

(the theory of this process is given in Section I, 41B). It is therefore necessary to remove the silver chloride by filtration. The filtration may be avoided by the addition of a little nitrobenzene (about 1 ml. for each 0·05 g. of chloride); the silver chloride is probably surrounded by a film of nitrobenzene. Another method, applicable to chlorides (A. J. Berry, 1948), in which filtration of the silver chloride is unnecessary, is to employ tartrazine as indicator (Section III, 31).

For practice in this estimation, the student may determine the HCl content of concentrated hydrochloric acid.

Procedure A (HCl content of concentrated hydrochloric acid). Ordinary concentrated hydrochloric acid is usually 10–11N, and must be diluted first. Measure out accurately 10 ml. of the concentrated acid from a burette into a 1-litre volumetric flask and make up to the mark with distilled water. Shake well. Pipette 25 ml. into a 250-ml. conical flask, add 5 ml. of 6N-nitric acid and then add 30 ml. of standard 0·1N-silver nitrate (or sufficient to give 2–5 ml. excess). Shake to coagulate the precipitate, filter through a quantitative filter-paper (or through a porous porcelain or sintered-glass crucible), and wash thoroughly with very dilute nitric acid. Add 1 ml. of the saturated ferric alum solution to the combined filtrate and washings, and titrate the residual silver nitrate with standard 0·1N-thiocyanate. Repeat the titration with two other 25-ml. portions of the chloride solution.

Calculate the volume of standard 0·1N-silver nitrate that has reacted with the hydrochloric acid, and therefrom the percentage of HCl in the sample employed.

Procedure B. Pipette 25 ml. of the diluted solution into a 250-ml. conical flask containing 5 ml. of 6N-nitric acid. Add a slight excess
(2–5 ml.) of standard 0·1N-silver nitrate (about 30 ml.) from a burette. Then add 2–3 ml. of pure (e.g., A.R.) nitrobenzene and 1 ml. of the ferric alum indicator, and shake vigorously to coagulate the precipitate. Titrate the residual silver nitrate with standard 0·1N-thio-cyanate until a permanent faint reddish-brown coloration appears. Repeat the titration with two other 25-ml. portions of the solution.

From the volume of silver nitrate solution added, subtract the volume of silver nitrate solution that is equivalent to the volume of standard thiocyanate required. Then calculate the percentage of HOI in the sample.

\[
1 \text{ ml. } N\text{-AgNO}_3 = 0.03546 \text{ g. Cl. } = 0.03647 \text{ g. HCl}
\]

**Procedure C.** Pipette 25 ml. of the diluted solution into a 250-ml. conical flask containing 5 ml. of 6N-nitric acid, add a slight excess of 0·1N-silver nitrate (30–35 ml.) from a burette, and 4 drops of tartrazine indicator (0·5 per cent aqueous solution). Shake the suspension for about a minute in order to ensure that the indicator is adsorbed on the precipitate as far as possible. Titrate the residual silver nitrate with standard 0·1N-ammonium or potassium thiocyanate with swirling of the suspension until the very pale yellow supernatant liquid (viewed with the eye at the level of the liquid) assumes a rich lemon-yellow colour. At the end point, the dye is removed from the precipitate and colours the supernatant liquid. Repeat the titration with two other portions of the solution.

**III, 34. Determination of bromides (Volhard’s method).**—Silver bromide is less soluble than silver thiocyanate so that it is not necessary to filter off the silver bromide (compare previous Section). The bromide solution is acidified with dilute nitric acid, an excess of standard 0·1N-silver nitrate added, the mixture thoroughly shaken, and the residual silver nitrate determined with standard 0·1N-ammonium or potassium thiocyanate, using ferric alum as indicator.

\[
1 \text{ ml. } N\text{-AgNO}_3 = 0.07992 \text{ g. Br. } = 0.08093 \text{ g. HBr}
\]

For practice, the student may determine the percentage of HBr in the constant b.p. hydrobromic acid, or of bromine in potassium bromide, preferably of A.R. quality (compare Section III, 28).

**III, 35. Determination of iodides (Volhard’s method).**—Here also there is no need to filter off the silver halide, since silver iodide is very much less soluble than silver thiocyanate. In this determination the iodide solution must be very dilute in order to reduce adsorption effects. The dilute iodide solution (ca. 300 ml.), acidified with dilute nitric acid, is treated very slowly and with vigorous stirring or shaking with standard 0·1N-silver nitrate until the yellow precipitate coagulates and the supernatant liquid appears colourless. Silver nitrate is then present in excess. One ml. of saturated iron alum solution is added, and the residual silver nitrate is titrated against standard 0·1N-ammonium or potassium thiocyanate.

\[
1 \text{ ml. } N\text{-AgNO}_3 = 0.12869 \text{ g. I. } = 0.1279 \text{ g. HI}
\]

For practice, the student may determine the percentage of HI in the constant-boiling-point hydriodic acid or of iodide in potassium iodide, preferably of A.R. quality (compare Section III, 27).
III, 36. Determination of hyposulphites.*—Discussion. The method depends upon the reduction of ammoniacal silver nitrate solution by the hyposulphite to metallic silver; the silver is dissolved in nitric acid and titrated with standard thiocyanate solution, using ferric alum as indicator.

\[
\text{Na}_2\text{S}_2\text{O}_4 + 2\text{AgNO}_3 + 2\text{H}_2\text{O} = 2\text{Ag} + 2\text{NaHSO}_3 + 2\text{HNO}_3
\]

The procedure has the advantage that the solid is weighed directly into the reagent, and thus avoids the rapid atmospheric oxidation of the solution.

Procedure (hyposulphite content of commercial "hydras"). Weigh out accurately about 0·4 g. of powdered "hydras" (sodium hyposulphite, usually \(\text{Na}_2\text{S}_2\text{O}_4\cdot\text{H}_2\text{O}\)) from a stoppered weighing-bottle into a dry beaker, and cover it with at least a two-fold excess of ammoniacal silver nitrate solution (prepared by the addition of dilute ammonia solution in excess of that required to re-dissolve the silver hydroxide first formed). As the salt dissolves, it is at once oxidised, and metallic silver is precipitated. It is essential not to warm the solution. When dissolution of the salt is complete, filter the precipitated silver on asbestos in a Gooch crucible (or through a sintered-glass or porous-porcelain crucible), and wash it with dilute ammonia solution containing a little ammonium nitrate to prevent peptisation of the finely divided metal. Transfer the crucible and contents to the beaker in which precipitation took place, dissolve the metal in nitric acid, and boil the solution to remove nitrous fumes. Filter the resultant solution through a sintered-glass crucible, dilute the filtrate, add 1 mI. of saturated ferric alum solution, and titrate with standard 0·1 N-thiocyanate.

Calculate the percentage of \(\text{Na}_2\text{S}_2\text{O}_4\) in the sample.

\[1 \text{ mI. } \text{N-NH}_4\text{CNS (or KCNS)} = 0·08706 \text{ g. } \text{Na}_2\text{S}_2\text{O}_4\]

III, 37. Determination of cobalt.—Discussion. This method is based upon the formation of the compound \(\text{[Co(C}_6\text{H}_5\text{N})_4](\text{CNS})_2\) (Sections I, 62K and IV, 330). Excess of a standard solution of ammonium thiocyanate is added to a solution of the cobaltous salt containing a little pyridine, the precipitated complex salt is filtered off, and the excess of thiocyanate titrated with standard silver nitrate solution.

Procedure. The sample should contain 0·05-0·1 g. of cobalt as cobaltous salt. Dissolve it in 150 mI. of water in a 250-mI. volumetric flask, acidify with dilute nitric acid (to litmus), add 3 mI. of pure pyridine, and excess of standard 0·1 N-ammonium thiocyanate (1). The cobalt is precipitated as \(\text{[Co(C}_6\text{H}_5\text{N})_4](\text{CNS})_2\), which settles readily and filters easily. Dilute to the mark, and mix thoroughly. Filter a portion of the solution through a quantitative filter-paper, and discard the first few mI. of the filtrate. Transfer 50 mI. of the filtrate to a beaker or conical flask, dilute to 100 mI., add 1 mI. of concentrated nitric acid, and then a known excess of standard 0·1 N-silver nitrate. Add 5 mI. of ferric indicator (2), and titrate the excess of silver nitrate with 0·1 N-ammonium thiocyanate in the usual way (Section III, 31).

Calculate the weight of cobalt \(w\) from the formula:

\[
w = [\text{mI. of } \text{NH}_4\text{CNS} \times N - 5(\text{mI. of } \text{AgNO}_3 \times N)] \times 0·02947
\]

* Also called hydrosulphites and dithionites.
Notes. 1. Standardise the 0·1N-ammonium thiocyanate against standard 0·1N-silver nitrate; the latter may be standardised, if necessary, against A.R. sodium chloride.

2. Dissolve 5 g. of A.R. iron alum in a mixture of 40 ml. of water and 10 ml. of 6N-nitric acid.

III. 38. Determination of nickel.—The procedure is similar to that given in the preceding Section for Cobalt. The complex has the formula \([\text{Ni(C}_5\text{H}_5\text{N})_4](\text{ONS})_2\) (compare Section IV, 32C). The weight of nickel \(w\) is calculated from the formula:

\[
w = \left[\text{ml. of NH}_4\text{CNS} \times N - 5(\text{ml. of AgNO}_3 \times N)\right] 0·02935
\]

Note. The method may also be applied to the determination of copper (Section IV, 19E), cadmium (Section IV, 18D), and zinc (Section IV, 34D).

III. 39. Determination of fluoride as lead chlorofluoride.—Discussion.

This method is based upon the precipitation of lead chlorofluoride, \(\text{PbCIF}\), which can be weighed as such, or, more conveniently, the chloride is determined by Volhard’s method from which the fluorine content can be calculated. The advantages of the method are: the precipitate is granular, settles readily, and is easily filtered; the factor for conversion to fluorine is low; the volumetric procedure is carried out at \(pH\) 3·6-5·6, so that substances which might be co-precipitated, such as phosphates, sulphates, chromates, and carbonates, do not interfere. Aluminium must be entirely absent, since even very small quantities cause low results; a similar effect is produced by boron (> 0·05 g.), ammonium (> 0·5 g.), and sodium or potassium (> 10 g.). Iron must be removed, but zinc is without effect. Silica does not vitiate the method, but causes difficulties in filtration.

For practice, the student may determine the percentage of fluorine in sodium fluoride.

Procedure. Weigh out accurately about 1·5 g. of dry sodium fluoride, dissolve it in water, and make up to 250 ml. in a volumetric flask. Shake well. Pipette 25 ml. of the solution into a 400-ml. beaker,* add 2 drops of bromo-phenol blue indicator, 3 ml. of 10 per cent sodium chloride, and dilute the mixture to 250 ml. Add dilute nitric acid until the colour just changes to yellow, and then add dilute sodium hydroxide solution until the colour just changes to blue. Treat with 1 ml. of concentrated hydrochloric acid, then with 5·0 g. of A.R. lead nitrate, and heat on the steam-bath. Stir gently until the lead nitrate has dissolved, and then immediately add 5·0 g. of crystallised sodium acetate and stir vigorously. Digest on the steam-bath for 30 minutes, with occasional stirring, and allow to stand overnight.

Meanwhile, a washing solution of lead chlorofluoride is prepared as follows. Add a solution of 10 g. of lead nitrate in 200 ml. of water to 100 ml. of a solution containing 1·0 g. of sodium fluoride and 2 ml. of concentrated hydrochloric acid, mix it thoroughly, and allow the precipitate to settle. Decant the supernatant liquid, wash the precipitate by decantation with 5 portions of water, each of about 200 ml. Finally add 1 litre of water to the precipitate, shake the mixture at intervals during an hour, allow the precipitate to settle, and filter the liquid. Further quantities of wash liquid may be prepared as needed by treating

* The details apply to a volume of solution corresponding to 0·01-0·1 g. of fluorine.
the precipitate with fresh portions of water. The solubility of lead chlorofluoride in water is 0.325 g. at 25°C.

Separate the original precipitate by decantation through a Whatman No. 542 or No. 42 paper. Transfer the precipitate to the filter, wash once with cold water, four or five times with the saturated solution of lead chlorofluoride, and finally once more with cold water. Transfer the precipitate and paper to the beaker in which precipitation was made, stir the paper to a pulp in 100 ml. of 5 per cent nitric acid, and heat on the steam-bath until the precipitate has dissolved (5 minutes). Add a slight excess of standard 0.1N-silver nitrate, digest on the steam-bath for a further 30 minutes, and allow to cool to room temperature while protected from the light. Filter the precipitate of silver chloride through a sintered-glass crucible, wash with a little cold water, and titrate the residual silver nitrate in the filtrate and washings with standard 0.1N-thiocyanate. Subtract the amount of silver found in the filtrate from that originally added. The difference represents the amount of silver that was required to combine with the chlorine in the lead chlorofluoride precipitate.

Calculate the percentage of fluorine in the sample.

\[ 1 \text{ ml. } N-\text{AgNO}_3 = 0.01900 \text{ g. F} \]

III. 40. Determination of arsenic as silver arsenate.—Discussion.
Arsenates in solution are precipitated as silver arsenate, \( \text{Ag}_3\text{AsO}_4 \), by the addition of neutral silver nitrate solution: the solution must be neutral, or if slightly acid, an excess of sodium acetate must be present to reduce the acidity; if strongly acid, most of the acid should be neutralised by aqueous sodium hydroxide. The silver arsenate is dissolved in dilute nitric acid, and the silver titrated with standard thiocyanate solution. The silver arsenate has nearly six times the weight of the arsenic, hence quite small amounts of arsenic may be determined by this procedure.

Arsenites must first be oxidised by treatment with nitric acid. Small amounts of antimony and tin do not interfere, but chromates, phosphates, molybdates, tungstates, and vanadates, which precipitate as the silver salts, should be absent. An excessive amount of ammonium salts has a solvent action on the silver arsenate.

A general method applicable to all arsenic compounds will be described.

Procedure. Fuse 0.5 g. (or less, according to the amount of As present) of the finely powdered substance with 3–5 g. of a 1:1 mixture of A.R. sodium carbonate and A.R. potassium nitrate, placing about one-third of the mixture on top of the charge, or, alternatively, use ten to twelve times the weight of sodium peroxide. Extract the cooled melt with hot water, and filter. Acidify the filtrate, containing the soluble arsenate, with dilute nitric acid, boil to expel carbon dioxide, and cool. Add sufficient sodium hydroxide solution to give an alkaline reaction to phenolphthalein, and then discharge the red colour from the solution by just acidifying with acetic acid. Add a slight excess of silver nitrate solution with vigorous stirring, and allow the precipitate to settle in the dark. Pour off the supernatant liquid through a sintered-glass crucible, wash the precipitate by decantation with cold distilled water, transfer the precipitate to the crucible, and wash it free from silver nitrate solution. Wash out the receiver
Amlonic Analysis

thoroughly. Dissolve the silver arsenate in dilute nitric acid (ca. N) (which leaves any silver chloride undissolved), wash with very dilute nitric acid, and make up the filtrate and washings to 250 ml. in a volumetric flask. Titrate a convenient aliquot portion with standard ammonium (or potassium) thiocyanate solution in the presence of ferric alum as indicator (Section III, 31). Calculate the percentage of arsenic in the sample.

1 ml. N-thiocyanate = 0.02497 g. of As

III, 41. Determination of cyanides.—Discussion. The theory of the titration of cyanides with silver nitrate solution according to Liebig (1851) has been given in Section I, 40. All silver salts except the sulphide are readily soluble in excess of a solution of an alkali cyanide, hence chloride, bromide, and iodide do not interfere. The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide is often precipitated in a curdy form, which does not readily re-dissolve, and, moreover, the end point is not easy to detect with accuracy.

There are two methods for overcoming these disadvantages. In the first the precipitation of silver argentocyanide at the end point can be avoided by the addition of ammonia solution, in which it is readily soluble:

\[
\text{Ag[Ag(CN)\textsubscript{2}]} + 4\text{NH}_4\text{OH} = 2[\text{Ag(NH}_3\text{)}\textsubscript{2}]\text{CN}^* + 4\text{H}_2\text{O}
\]

If a little potassium iodide solution is added before the titration is commenced, the sparingly soluble silver iodide, which is insoluble in ammonia solution, will be precipitated at the end point.

\[
2[\text{Ag(NH}_3\text{)}\textsubscript{2}]\text{CN} + 2\text{KI} + 4\text{H}_2\text{O} = 2\text{AgI} + 2\text{KCN} + 4\text{NH}_4\text{OH}
\]

At the end point, the cyanide, in which silver iodide is soluble, is no longer present to keep it in solution, and since, unlike the silver argentocyanide, it is insoluble in ammonia solution, silver iodide is precipitated. The precipitation is best seen by viewing against a black background.

In the second method diphenylcarbazide is employed as an adsorption indicator. The end point is marked by the pink colour becoming pale violet (almost colourless) on the colloidal precipitate in dilute solution (ca. 0.01N) before the opalescence is visible. In 0.1N solutions, the colour change is observed on the precipitated particles of silver argentocyanide.

For practice, the student may determine the percentage of KCN in potassium cyanide (“single salt”).

NOTE. Potassium cyanide and all other cyanides are deadly poisons, and extreme care must be taken in their use.

Procedure A. (KCN in potassium cyanide.) Weigh out accurately about 3.5 g. of potassium cyanide (single salt) from a glass-stoppered weighing-bottle, dissolve it in water and make up to 250 ml. in a volumetric flask. Shake well. Transfer 25 ml. of this solution by means of a burette and NOT a pipette to a 250-ml. conical flask, add 75 ml. of water, 5–6 ml. of 6N-ammonia solution, and 2 ml. of 10 per cent potassium iodide solution. Place the flask on a sheet of black paper, and titrate with standard 0.1N-silver nitrate. Add the silver nitrate solution dropwise as soon as the yellow silver iodide shows any signs for the end point.

* Or [Ag(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{+} + [Ag(CN)\textsubscript{2}]\textsuperscript{2-}. 
Quantitative Inorganic Analysis

of persisting. When 1 drop produces a permanent turbidity, the end point has been reached. Repeat the titration with two other 25-ml. portions of the cyanide solution.

Calculate the KCN content of the sample.

1 ml. \( N\text{-AgNO}_3 \) = 0.05204 g. CN = 0.1304 g. KCN

Procedure B. Transfer 25 ml. of the cyanide solution, prepared as detailed in Procedure A, by means of a burette and NOT a pipette to a 250-ml. conical flask, add 2 to 3 drops of the diphenylcarbazide indicator, and titrate against the standard 0.1\( N \)-silver nitrate until a permanent violet colour is just produced. Repeat the titration with two other 25-ml. portions of the cyanide solution.

The diphenylcarbazide indicator is prepared by dissolving 0.1 g. of diphenylcarbazide in 100 ml. of alcohol.

Calculate the percentage of KCN in the sample.

III, 42. Determination of nickel by potassium cyanide.—Discussion. This method depends upon the fact that nickel ions can react with potassium cyanide in slightly ammoniacal solution to form a complex anion, \( [\text{Ni}(\text{CN})_4]^{2-} \):

\[
[\text{Ni(NH}_3)_6]^{2+} + 4\text{KCN} + 6\text{H}_2\text{O} = \text{K}_4[\text{Ni(CN)}_4] + 6\text{NH}_4\text{OH} + 2\text{KCl}
\]

If the ammoniacal solution of nickel contains a little silver iodide in suspension and potassium cyanide solution is added, the turbidity will not disappear until all the nickel has been converted into the complex cyanide. The slightest excess of cyanide is therefore indicated by the clearing of the liquid; this excess may be determined exactly by adding standard silver nitrate solution until the turbidity is reproduced.

\[
\text{AgI} + 2\text{KCN} = \text{K}[\text{Ag(CN)}_2] + \text{KI}
\]

\[
\text{Ag}^+ + \text{I}^- = \text{AgI}
\]

Copper, cobalt, and zinc, which form complex cyanides, must be absent; the addition of alkali pyrophosphate, however, renders zinc harmless. Aluminium, manganese, and iron are kept in solution by the addition of citric acid, tartaric acid, or sodium pyrophosphate.

The potassium cyanide solution is standardised against standard 0.1\( N \)-silver nitrate as described in Section III, 41. It is evident that:

\[
\text{AgNO}_3 = 2\text{KCN} = \text{Ni}/2
\]

i.e.,

1 ml. \( N\text{-AgNO}_3 \) = 0.1304 g. KCN = 0.02935 g. Ni

For practice in this determination, the student may determine the percentage of nickel: (a) in pure nickel ammonium sulphate and (b) in a steel.

Procedure (Ni in nickel ammonium sulphate). Dissolve 14 g. of A.R. potassium cyanide in 1 litre of distilled water in a volumetric flask, and shake well. Prepare a solution of 10 g. of A.R. potassium iodide in 100 ml. of water. Standardise the potassium cyanide solution against standard 0.1\( N \)-silver nitrate (Section III, 41).

Weigh out accurately about 5 g. of pure nickel ammonium sulphate \( \text{NiSO}_4(\text{NH}_4)_2\text{SO}_4.6\text{H}_2\text{O} \),* dissolve it in water containing a little dilute sulphuric acid, and make up to 250 ml. in a volumetric flask. Shake

* The A.R. product may be obtained, e.g., from the Mallinckrodt Chemical Works, 70-74 Gold St., New York 8, N.Y., U.S.A.
well. Pipette 25 ml. of this solution into a 250-ml. conical flask, add 125 ml. of water, followed by 6N-ammonia solution until the fluid smells slightly of it, and then add a further 3 ml. If a precipitate forms, it will re-dissolve if a little ammonium chloride solution is added. Then add 5 ml. of the potassium iodide solution and a small measured volume, say 0.5-1 ml., of the standard 0.1N-silver nitrate. The silver iodide produced should cause the liquid to become cloudy. Titrate with the standard potassium cyanide solution from a burette until the turbidity just disappears. This will take place when the potassium cyanide added is equivalent to the nickel in the solution plus the silver in the known volume (0.5-1 ml.) of silver nitrate solution added. Add standard 0.1N-silver nitrate dropwise from a burette until the cloudiness due to silver iodide reappears. The excess of potassium cyanide solution, which is equivalent to the silver nitrate solution, is thus accurately determined.

Repeat the titration with two other 25-ml. portions of the nickel solution.

Calculate the volume of the standard potassium cyanide solution which has reacted with the nickel, and therefrom the percentage of nickel in the sample.

Procedure (Ni in nickel steel). The most accurate method for the analysis of any steel containing nickel is to precipitate the nickel as the dimethylglyoxime complex, and to determine the nickel in the latter.

Weigh out accurately about 1 g. of the nickel steel * into a 350-ml. conical flask, add 15 ml. of 8N-nitric acid, and place a funnel in the mouth of the flask to prevent mechanical loss. When the first violent action is over, boil gently until all the steel has dissolved, adding a little concentrated hydrochloric acid if necessary. Continue the boiling for 5 minutes in order to expel oxides of nitrogen. Dilute to 200 ml., and add 8 g. of pure tartaric acid. When all the tartaric acid has dissolved, neutralise with concentrated ammonia solution, and add ca. 1 ml. in excess. If any insoluble material is present, filter it through a quantitative filter-paper, and wash the latter with hot water. Acidify the solution with hydrochloric acid, heat to 80° C., and add 20-25 ml. of a 1 per cent alcoholic solution of dimethylglyoxime. Add ammonia solution until the liquid is slightly alkaline, and allow to stand for 30-60 minutes, preferably on a water-bath. Filter the precipitate through a Gooch or Jena sintered-glass crucible, and wash the precipitate thoroughly with hot water. Dissolve the precipitate in 25 ml. of 6N-nitric acid, add 20 ml. of 9N-sulphuric acid and boil for 20 minutes. Add 6 g. of citric acid, render the solution slightly ammoniacal, and, when cold, titrate the nickel as described above.

Calculate the percentage of nickel in the steel.

For another method involving the precipitation of the nickel with dicyandiamidine sulphate and titration of the precipitated complex with 0.1N-hydrochloric acid, see Section IV, 32D.

III, 43. Determination of thiocyanates.—Discussion. The method consists in the titration of the thiocyanate in dilute nitric acid solution with a standard solution of mercuric nitrate, using a little iron alum

* Either Ridsdale's "Nickel steel, No. 22a" (one of the Analysed Samples for Students) or the Bureau of Analysed Samples "Nickel Steel, No. 222" (a British Chemical Standard) is suitable.
solution as indicator. Immediately the thiocyanate is completely converted into the mercuric salt, the solution becomes water-white. The end point is very sharp.

The method may also be applied to the determination of **thiocyanate and chloride in admixture** when the chloride is present in comparatively small amount (say, 5 per cent of the thiocyanate). The neutral solution containing the thiocyanate and chloride is treated with excess of bismuth nitrate solution. The precipitated bismuth oxychloride is separated, the filtrate acidified with dilute nitric acid, and the thiocyanate determined as above.

**Procedure.** The following solutions should be prepared:

- **N-Mercuric nitrate.** 100·3 Grams of dry A.R. mercury are heated in a 600-ml. beaker (fume cupboard) with 250 ml. of distilled water, and concentrated nitric acid is added until all the mercury is dissolved. The action of the acid is rather energetic, especially when hot, and the acid should be added a little at a time. The solution is boiled to drive off all nitrous fumes, cooled, transferred to a standardised litre flask, and diluted to 1000 ml. The 0·1N solution is prepared by diluting the N solution. Since the mercury is pure and can be accurately weighed, the solution requires no standardisation.

Mercuric sulphate may replace the nitrate, but offers no advantage; mercuric chloride cannot be used.

- **Dilute nitric acid.** One hundred and fifty ml. of concentrated nitric acid are added to 400–500 ml. of distilled water, boiled to drive off nitrous gases, and diluted to 1000 ml.

- **Iron alum solution.** Twenty-five grams of A.R. iron alum are dissolved in water, and diluted to 500 ml.

The solution containing about 0·2 g. of thiocyanate is diluted to 150–200 ml. with distilled water, and 10 ml. of the dilute nitric acid and 2 ml. of the iron alum solution are added. The solution is titrated against the standard 0·1N-mercuric nitrate solution with constant agitation until the red colour of the ferric thiocyanate just disappears, leaving the solution water-white.

\[
1 \text{ ml. } 0.1N-\text{Hg(NO}_3)_2 = 0.005809 \text{ g. CNS}
\]

**Thiocyanate and chloride in admixture.** A solution of bismuth nitrate is required and is prepared as follows. Ten grams of pure crystallised bismuth nitrate and 50 ml. of A.R. glacial acetic acid are warmed in a 200-ml. beaker, and 30 ml. of distilled water are added gradually until complete dissolution has been effected, the solution being stirred between each addition. When the salt has completely dissolved, the solution is diluted to 500 ml. with distilled water. Ten ml. of this solution are required to precipitate approximately 0·01 g. of chloride, calculated as sodium chloride.

The neutral solution containing approximately 0·2 g. of thiocyanate and 0·01 g. of chloride (calculated as NaCl) is diluted to 150 ml. with distilled water, and 10 ml. of the bismuth nitrate solution are added. The mixture is shaken, left for 10–15 minutes in the cold, filtered through a quantitative filter-paper, and the precipitate well washed. The filtrate should give no precipitate upon the addition of a few ml. of the bismuth nitrate solution. The filtrate is then acidified with dilute nitric acid, and, after adding 2 ml. of the iron solution, titrated with 0·1N-mercuric nitrate solution as above. The chloride may be deter-
minded by any of the usual methods by dissolving the basic chloride on the filter-paper in dilute nitric acid.

**III. 44. Determination of barium and of sulphates.**—Barium solutions, weakly acid with hydrochloric acid, give a red precipitate of barium "rhodizonate" with a freshly prepared solution of the sodium salt of rhodizonic acid (dihydroxydiquinoyl, C₆O₄(OH)₂):

\[
\begin{align*}
\text{CO} & \quad \text{C} \quad \text{ONa} \\
\text{CO} & \quad \text{C} \quad \text{ONa} \\
\text{CO} & \quad \text{C} \quad \text{O} \\
\text{BaCl₂} & = \\
\text{Ba} & + 2\text{NaCl}
\end{align*}
\]

The solubility of the red compound is much greater than that of barium sulphate, hence upon the addition of a sulphate solution to a solution of a barium salt, the barium will be completely precipitated when the red colour changes to colourless (in weakly acid solution) or to yellow (in neutral solution). This forms the basis of a volumetric method for the determination of barium. To obtain the best results, it is advisable to work with concentrated solutions (volume up to 10 ml. — 0.2-0.5N).

The indicator is freshly prepared as required by dissolving 15 mg. of sodium "rhodizonate" in 5 ml. of water. Ten drops are used for each titration.

**A. Barium.** The concentrated solution of the barium salt (5-10 ml.) is treated with 10 drops of indicator and 1-2 ml. of alcohol. It is then titrated whilst shaking vigorously with (a) 0.2N-potassium sulphate (prepared from the A.R. solid) until the colour changes sharply from red to yellow, or (b) with 0.2N-sulphuric acid until the colour changes from red to colourless.

**B. Sulphate.** Sulphate in acid solution cannot be titrated directly against a solution of a barium salt, because rhodizonic acid is unstable and soon decomposes. A known excess of barium chloride solution (0.2-0.5N) is added to the sulphate solution, and the excess of barium titrated as above. Here also the solutions should be concentrated (0.2-0.5N) and the volume small (10-25 ml.).

Satisfactory results may be obtained as follows. A known volume of the neutral alkali sulphate solution (say, 10-20 ml.) is placed in a glass-stoppered conical flask, 1 g. of pure ammonium chloride added, followed by a known excess of 0.2N-barium chloride (prepared from the A.R. salt) and 10 drops of the freshly prepared indicator. The mixture is thoroughly shaken, and 3 drops of 10 per cent hydrochloric acid added; the further addition of one-third the volume of alcohol improves the end point. The mixture is then titrated with 0.2N-potassium sulphate until the colour begins to fade. The alkali sulphate solution is then added dropwise, with vigorous shaking and waiting for a short time between the drops, until the red colour has completely disappeared. The titration is repeated until consistent results are obtained.

By subtracting the volume of 0.2N-potassium sulphate from that of the 0.2N-barium chloride originally employed, the volume of the latter equivalent to the sulphate present in the initial solution is found, since \( \text{Ba} = \text{SO}_4 \).
GENERAL DISCUSSION

The student should be familiar with the general theory of oxidation-reduction given in Chapter I; in particular, he should read:

Section I, 23—Equivalent weights. Normal solutions.
Sections I, 43-51—Theory of oxidation-reduction reactions (including potentiometric titration).

With this groundwork, he should experience no difficulty in carrying out oxidation-reduction titrations intelligently and, when once he has had practice in the fundamental simple titrations, the student should be in a position to apply his combined theoretical and practical knowledge to more complex cases and to various practical problems.

The standard solutions of oxidising agents employed in the titration of reducing agents include those of potassium permanganate, potassium dichromate, ceric sulphate, manganic sulphate, iodine, potassium iodate, potassium bromate, and chloramine-T. The standard solutions of reducing agents, used in the titration of oxidising agents, include those of sodium thiosulphate, arsenious oxide, sodium oxalate, oxalic acid, ferrous salts, titanous sulphate or chloride, chromous sulphate or chloride, and vanadous sulphate or chloride. The mode of use and applications of each of these will be given in the following Sections.

OXIDATIONS WITH POTASSIUM PERMANGANATE

III, 46. Discussion.—This valuable and powerful oxidising agent was first introduced into volumetric analysis by F. Margueritte in 1846 for the titration of ferrous iron. In acid solutions, the reduction can be represented by the following equation:

\[ \text{MnO}_4^- + 8H^+ + 5e^- \rightarrow \text{Mn}^{II} + 4H_2O \]

from which it follows that the equivalent weight is one-fifth of the formula weight (1/5 mol.)*, or 158.03/5, or 31.606.

Sulphuric acid is the most suitable acid, as it has no action upon permanganate in dilute solution. With hydrochloric acid, there is the likelihood of the reaction:

\[ 2\text{KMnO}_4 + 16\text{HCl} = 2\text{KCl} + 2\text{MnCl}_2 + 5\text{Cl}_2 + 8\text{H}_2\text{O} \]

taking place, and some permanganate may be consumed in the formation of chlorine. This reaction is particularly liable to occur with iron salts unless special precautions are adopted (see below). With a small excess of free acid, a very dilute solution, low temperature and slow titration with constant shaking, the danger from this cause is minimised. There are, however, some titrations, such as those with arsenious acid, for elementary students, the equivalent weight may be deduced from the hypothetical equation:

\[ 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 5\text{O} \]

It follows that the equivalent weight is one-fifth of the molecular weight (KMnO₄/5).
oxide, trivalent antimony, and hydrogen peroxide, which can be carried out in the presence of hydrochloric acid.

In the analysis of iron ores, solution is frequently effected in concentrated hydrochloric acid, the ferric iron is reduced with a slight excess of stannous chloride solution, and the excess of the latter removed with mercuric chloride solution (Zimmermann–Reinhardt process): the ferrous iron is then determined in the resultant solution. To do this, it is best to add about 25 ml. of Zimmermann and Reinhardt's solution (this is sometimes termed preventive solution), which is prepared by dissolving 50 g. of crystalline manganese sulphate MnSO₄·4H₂O in 250 ml. of water, adding a cooled mixture of 100 ml. of concentrated sulphuric acid and 300 ml. of water, followed by 100 ml. of syrupy phosphoric acid. The manganous sulphate lowers the oxidation potential of the permanganate (compare Sections I, 46, 47 and Fig. I, 49, 2) and thereby makes it a weaker oxidising agent; the tendency of the permanganate to oxidise chloride ions is thus reduced. The manganous ion also acts as a catalyst in promoting the speed of the reduction of the permanganate ion, and as a negative catalyst for the oxidation of the chloride ion. The phosphoric acid combines with the yellow ferric ions to form colourless complex ions, thus rendering the end point more clearly visible. The main purpose of the phosphoric acid is, however, to lower the oxidation potential of the ferric–ferrous system (Section I, 46) and thus to increase the reducing power of the ferrous iron.

For the titration of colourless or slightly coloured solutions, the use of an indicator is unnecessary, since as little as 0·01 ml. of 0·01N-potassium permanganate imparts a pale-pink colour to 100 ml. of water. The intensity of the colour in dilute solutions may be enhanced, if desired, by the addition of an oxidation-reduction indicator, such as diphenylamine, diphenylbenzidine, sodium diphenylamine sulphonate, erioglaucine, tri-ortho-phenanthroline ferrous sulphate or N-phenylanthranilic acid, near the end point of the reaction; this is usually not required.

Potassium permanganate also finds some application in strongly alkaline solutions. Here two consecutive partial reactions take place:

(i) the relatively rapid reaction:

\[
\text{MnO}_4^- + e^- = \text{MnO}_4^{2-}
\]

and (ii) the relatively slow reaction:

\[
\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2e^- = \text{MnO}_2 + 4\text{OH}^- 
\]

By suitably controlling the experimental conditions, it is possible to arrange that reaction (i) occurs almost exclusively; the equivalent weight is then 1 mol. Excess of 0·1M-potassium permanganate which is 1–2N with respect to sodium hydroxide is added to a solution of the substance to be oxidised. After 10–20 minutes the excess of permanganate is back-titrated either in an alkaline medium with a standard solution of sodium formate

\[
(2\text{MnO}_4^- + 30\text{H}^- + \text{HCO}_3^- = 2\text{MnO}_4^{2-} + \text{CO}_3^{2-} + 2\text{H}_2\text{O})
\]

or in an acid medium with oxalic acid.*

* For further experimental details and an account of the numerous applications of this method, the reader is referred to W. Bottger and R. E. Oesper, Neuer Methoden der Volumetrischen Chemischen Analyse, 1938, p. 85. (D. Van Nostrand : Chapman and Hall.)
Potassium permanganate is not a primary standard. It is difficult to obtain the substance perfectly pure and free from manganese dioxide. Moreover, ordinary distilled water is likely to contain reducing substances (traces of organic matter, etc.) which will react with the potassium permanganate to form manganese dioxide. The presence of the latter is very objectionable because it catalyses the auto-decomposition of the permanganate solution on standing. For these reasons, potassium permanganate solution is never made up exactly by weight, but after removal of the manganese dioxide by filtration through purified glass wool or through a sintered-glass filter-crucible (porosity, No. 4) is standardised by one of several methods. These methods include the use of the following substances: sodium oxalate $Na_2C_2O_4$, arsenious oxide $As_2O_3$, metallic iron, anhydrous potassium ferrocyanide $K_4[Fe(CN)_6]$, ferrous ammonium sulphate $FeSO_4\cdot(NH)_2SO_4\cdot6H_2O$, oxalic acid $H_2C_2O_4\cdot2H_2O$, and potassium tetroxalate $KHC_2O_4\cdotH_2C_2O_4\cdot2H_2O$.

Of these substances sodium oxalate was formerly regarded as the most trustworthy, since it is readily obtained pure and anhydrous. The U.S. Bureau of Standards supplies a product of 99·95 per cent guaranteed purity, and the ordinary A.R. substance has a purity of at least 99·9 per cent. The experimental procedure hitherto employed was due to R. S. McBride (1912). A solution of the oxalate, acidified with dilute sulphuric acid and warmed to 80–90°C., was treated slowly (10–15 ml. per minute) and with constant stirring with the permanganate solution until the first permanent faint pink colour was obtained; the temperature near the end point was not allowed to fall below 60°C. R. M. Fowler and H. A. Bright (1935) have, however, shown that with McBride’s procedure the results may be 0·1–0·45 per cent high; the titre depends upon the acidity, the temperature, the rate of addition of the permanganate solution, and upon the speed of stirring. These authors recommend a more rapid addition of 90–95 per cent of the permanganate solution (about 25–35 ml. per minute) to a solution of sodium oxalate in 2N-sulphuric acid at 25–30°C., the solution is then warmed to 55–60°C. and the titration completed, the last 0·5–1-ml. portion being added dropwise. The method is accurate to 0·06 per cent. Full experimental details are given in Procedure B below.

$$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

The procedure of H. A. Bright (1937), which utilises arsenious oxide as a primary standard and potassium iodide or potassium iodate as a catalyst for the reaction, is more convenient in practice and promises to take first place as a trustworthy method for the standardisation of permanganate solutions. Like sodium oxalate, A.R. arsenious oxide has a purity of at least 99·8 per cent, and the U.S. Bureau of Standards supplies a product of 99·99 per cent guaranteed purity.* The results by this method agree to within 1 part in 3000 with the sodium oxalate procedure of Fowler and Bright. Full experimental details are given in Procedure A.

$$5As_2O_3 + 4MnO_4^- + 12H^+ = 5As_4O_6 + 4Mn^{++} + 6H_2O$$
$$5As_2O_3 + 4KMnO_4 + 12HCl = 4MnCl_2 + 4KCl + 5As_2O_5 + 6H_2O$$

* A.R. arsenious oxide of the Mallinckrodt Chemical Works, U.S.A., has an assay value of 99·95 per cent.
Iron wire of 99·9 per cent purity is available commercially. The A.R. reagent is a suitable standard, particularly if the potassium permanganate solution is subsequently to be employed in the determination of iron. If the wire exhibits any sign of rust, it should be drawn between two pieces of fine emery cloth, and then wiped with a clean, dry cloth before use. The reaction which occurs is:

\[2\text{KMnO}_4 + 10\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}\]

A.R. potassium ferrocyanide may also be used for standardisation. Either the anhydrous compound (prepared by dehydrating the A.R. product to constant weight at 110° C.) or the trihydrate (the finely powdered A.R. hydrated crystals are dried to constant weight over a saturated solution of sodium bromide) is suitable, although the former is generally preferred. It is essential that the solution of the ferrocyanide be dilute and that a large excess of dilute sulphuric acid be present (to avoid the formation of a precipitate of \(\text{K}_2\text{Mn}[\text{Fe(CN)}_6]\)):

\[5\text{H}_3\left[\text{Fe(CN)}_6\right]^+ + \text{MnO}_4^- + 3\text{H}^+ = 5\text{H}_3[\text{Fe(CN)}_6] + \text{Mn}^{++} + 4\text{H}_2\text{O}\]

Excellent results are obtained by potentiometric titration in 2N-sulphuric acid (see Chapter VI).

The use of crystallised oxalic acid, potassium tetroxalate, and ferrous ammonium sulphate (Mohr’s salt) for standardisation is not recommended for accurate work; they may, however, be employed for elementary students in work in which great accuracy is not required. All these substances are hydrated, and unless special precautions are taken in drying and storage, the water content may be open to suspicion. Furthermore, for potassium tetroxalate and Mohr’s salt it is difficult to be quite sure that the constituent salts are present in exactly equimolecular proportions. The A.R. substances have the following assay values: \(\text{H}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O} < 99.8\) per cent; \(\text{KH}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O} < 99.9\) per cent; and \(\text{FeSO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O} 99.0-100.5\) per cent. Apart from the objections already mentioned, it is evident that A.R. ferrous ammonium sulphate cannot be used directly for standardisation, even for work of moderate accuracy. It must first be dissolved in warm water, and the solution rapidly cooled to ensure the production of small crystals; these are filtered at the pump, washed with a little distilled water, repeatedly pressed between sheets of clean filter-paper, and placed in a current of air to dry thoroughly. The substance is dry when the small grains no longer adhere to each other or to the paper in which they are contained, and is then preserved in a stoppered bottle for use.

III, 47. Preparation of 0·1N-potassium permanganate.—Weigh out about 3·2-3·25 g. of A.R. potassium permanganate on a watch glass, transfer it to a 1500-ml. beaker, add 1 litre of water, cover the beaker

* The author has found the “Iron Wire Analytical Reagent” supplied by the Mallinckrodt Chemical Works, U.S.A., in sealed glass vials to be very satisfactory. The assay value is 99·9 per cent Fe, and the percentages of impurities are given on the label. If the vials are carefully re-sealed with wax after each opening, and care be taken to prevent the introduction of moisture from the hands and other sources, the iron wire retains its original bright surface for long periods.

272

Quantitative Inorganic Analysis

with a clock glass (or Fisher "speedyvap" beaker-cover), heat the solution to boiling, boil gently for 15-30 minutes and allow the solution to cool to the laboratory temperature. Filter the solution through a funnel containing a plug of purified glass-wool, or through a Gooch crucible provided with a pad of purified asbestos, or, most simply, through a porous-porcelain or sintered-glass filter-crucible or funnel. Collect the filtrate in a vessel which has been cleaned with chromic acid mixture and then thoroughly washed with distilled water. The filtered solution should be stored in a clean, glass-stoppered bottle, and kept in the dark or in diffuse light except when in use: alternatively, it may be kept in a bottle of dark-brown-coloured glass.

III, 48. Standardisation of permanganate solutions.—Procedure A. With arsenious oxide (H. A. Bright, 1937). Dry some A.R. arsenious oxide at 105-110°C for 1-2 hours, and allow to cool in a desiccator. Accurately weigh approximately 0.25 g. of the dry oxide, and transfer it to a 400-ml. beaker. Add 10 ml. of a cool solution of sodium hydroxide, prepared from 20 g. of sodium hydroxide and 100 ml. of water (1). Allow to stand for 8-10 minutes, stirring occasionally. When solution is complete, add 100 ml. of water, 10 ml. of pure concentrated hydrochloric acid, and 1 drop of 0.0025M-potassium iodide or potassium iodate (2). Add the permanganate solution from a burette until a faint pink colour persists for 30 seconds. Add the last 1-1.5 ml. dropwise, allowing each drop to become decolorised before the next drop is introduced. (For the most accurate work it is necessary to determine the volume of permanganate solution required to duplicate the pink colour at the end point. This is done by adding permanganate solution to a solution containing the same amounts of alkali, acid, and catalyst as were used in the test. The correction should not be more than 0.03 ml.*). Repeat the determination with two other similar quantities of arsenious oxide. Calculate the normality of the potassium permanganate solution. Duplicate determinations should agree within 0.1 per cent.

Notes. 1. For elementary students, it is sufficient to weigh out accurately about 1.25 g. of A.R. arsenious oxide, dissolve this in 50 ml. of a cool 20 per cent solution of sodium hydroxide, and make up to 250 ml. in a volumetric flask. Shake well. Remove 25 ml. of this solution by means of a burette and not with a pipette (caution—the solution is highly poisonous), transfer to a 250-350-ml. conical flask, add 100 ml. of water, 10 ml. of pure concentrated hydrochloric acid, 1 drop of potassium iodide solution, and titrate with the permanganate solution to the first permanent pink colour as detailed above. Repeat with two other 25-ml. portions of the solution. Successive titrations should agree within 0.1 ml.

2. 0.0025M-potassium iodide = 0.41 g. KI per litre; 0.0025M-potassium iodate = 0.54 g. KIO₃ per litre.

Calculation. It is evident from the equation given in Section III, 46 and also from the equation:

\[ \text{As}_2\text{O}_3 + 2\text{O} = \text{As}_2\text{O}_5 \]

that the equivalent weight of arsenious oxide is one quarter of the

* The end point can also be determined with tri-ortho-phenanthroline ferrous sulphate as indicator. As the end point is approached one drop of the indicator (Section III, 63) is added. The permanganate solution is then added dropwise until the pink colour of the indicator changes to a very faint blue. The blank correction should average about 0.03 ml.
molecular weight, 197.82/4 or 49.46 g. One ml. of a normal solution contains the milli-equivalent weight, or 0.04946 g. If the weight of arsenious oxide be divided by the number of ml. of potassium permanganate solution to which it is equivalent as found by titration, we have the weight of primary standard equivalent to 1 ml. of the permanganate solution. If this last value be divided by the milli-equivalent of arsenious oxide, the normality of the permanganate solution is obtained (for details of an actual calculation, see under Sodium Carbonate, Section III, 4A).

In the method described in Note 1, the normality of the arsenious oxide solution is calculated from the weight of arsenious oxide used (1 litre of a N solution contains 49.46 g. of As₂O₃). The normality of the permanganate solution is then computed from the relation:

\[ V_A \times n_A = V_B \times n_B \]

(compare Section III, 4A).

**Procedure B.** With sodium oxalate (R. M. Fowler and H. A. Bright, 1935). Dry some A.R. sodium oxalate at 105–110° C. for 2 hours, and allow it to cool in a desiccator. Weigh out accurately from a weighing-bottle about 0.3 g. of the dry sodium oxalate into a 600-ml. beaker, add 240 ml. of water, and 12.5 ml. of concentrated sulphuric acid (caution).* Cool to 25–30° C., and stir until the oxalate has dissolved (1). Add 90–95 per cent of the required quantity of permanganate solution from a burette at a rate of 25–35 ml. per minute while stirring slowly (2). Heat to 55–60° C. (use a thermometer as stirring-rod), and complete the titration by adding permanganate solution until a faint pink colour persists for 30 seconds. Add the last 0.5–1 ml. dropwise, with particular care to allow each drop to become decolorised before the next is introduced. (For the most exact work, it is necessary to determine the excess of permanganate solution required to impart a pink colour to the solution. This is done by matching the colour produced by adding permanganate solution to the same volume of boiled and cooled diluted sulphuric acid at 55–60° C. This correction usually amounts to 0.03–0.05 ml.) Repeat the determination with two other similar quantities of sodium oxalate.

Calculate the normality of the potassium permanganate solution. Duplicate determinations should agree within 0.1–0.2 per cent.

**Notes.** 1. For elementary students, it is sufficient to weigh out accurately about 1.7 g. of A.R. sodium oxalate, transfer it to a 250-ml. volumetric flask, and make up to the mark. Shake well. Use 25 ml. of this solution per titration and add 150 ml. of ca. 2N-sulphuric acid. Carry out the titration rapidly at the ordinary temperature until the first pink colour appears throughout the solution, and allow to stand until the solution is colourless. Warm the solution to 50–60° C. and continue the titration to a permanent faint pink colour. It must be remembered that oxalate solutions attack glass, so that the solution should not be stored more than a few days.

2. An approximate value of the volume of permanganate solution required can be computed from the weight of sodium oxalate employed. In the first titration about 75 per cent of this volume is added, and the determination is completed at 55–60° C. Thereafter, about 90–95 per cent of the volume of permanganate solution is added at the laboratory temperature.

* Or 250 ml. of approximately 2N-sulphuric acid, prepared by adding 50 ml. of concentrated sulphuric acid cautiously to 550 ml. of water.
Calculation. This is similar to that described under Procedure A. The equivalent weight of sodium oxalate is \( \frac{3}{2} \) mol. or 67.01 g.

1 ml. \( N-Na_2C_2O_4 \) = 0.06701 g. \( Na_2C_2O_4 \)

Procedure C. With metallic iron. Use A.R. iron wire of 99.9 per cent assay value (see relevant footnote in Section III, 46). Insert a well-fitting rubber stopper provided with a bent delivery tube into a 350-ml. conical flask and clamp the flask in a rotogr stand in an inclined position, the tube being bent so as to dip into a small beaker containing saturated sodium bicarbonate solution or 20 per cent potassium bicarbonate solution (prepared from the A.R. solids) (Fig. III, 48, 1). Place 100 ml. of 3N-sulphuric acid (from 92 ml. of water and 8 ml. of concentrated sulphuric acid) in the flask, and add 0.5-1 g. of A.R. sodium bicarbonate in two portions; the carbon dioxide produced will drive out the air. Meanwhile, weigh out accurately about 0.15 g. of the iron wire, place it quickly into the flask, replace the stopper and bent tube, and warm gently until the iron has dissolved completely. Cool the flask rapidly under a stream of cold water,* and then run in the permanganate solution cautiously from a burette, with constant shaking, until the faint pink colour is permanent. The addition of about 5 ml. of pure syrpy phosphoric acid facilitates the detection of the end point. Repeat the determination with two other samples of the iron wire.

The reaction is:

\[
2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O
\]

Calculation. The weight of iron wire taken, multiplied by 0.999, will give the weight of pure iron used in each titration.

1 ml. \( N-KMnO_4 \) = 0.05584 g. Fe

Procedure D. With anhydrous potassium ferrocyanide. Prepare anhydrous potassium ferrocyanide by drying the powdered A.R. crystallised salt at 110° C. to constant weight, and cooling in a desiccator over calcium chloride.

The reaction in dilute solution, which should be about 2N with respect to sulphuric acid, is:

\[
5H_4[Fe(CN)_6] + MnO_4^- + 3H^+ = 5H_4[Fe(CN)_6] + Mn^{++} + 4H_2O
\]

Prepare a 0.1N solution of potassium ferrocyanide by dissolving 9-209 g. of the anhydrous salt in water and making up to 250 ml. with boiled-out water in a volumetric flask. (The equivalent weight and molecular weight is 368.34.) Pipette 25 ml. of the solution into a 350-ml. conical flask, add 100 ml. of boiled-out water, 20 ml. of 8N-

* As the flask cools, the bicarbonate solution is automatically drawn in until the pressure of the carbon dioxide inside the flask is equal to the atmospheric pressure.
Volumetric Analysis

sulphuric acid, and 0·5 ml. of N-phenylanthranilic acid indicator. Titrate with the potassium permanganate solution to the first sharp colour change. Carry out two or at most three titrations: these should not differ by more than 0·05 ml.

Alternatively, weigh out accurately 0·4-g. portions of anhydrous potassium ferrocyanide into 350-ml. conical flasks, dissolve in boiled-out water, and proceed with the titrations as detailed in the previous paragraph.

Calculate the normality of the potassium permanganate solution.

**Procedure E.** With ferrous ammonium sulphate. Weigh out accurately about 9·8 g. of the A.R. salt: this should preferably be recrystallised as detailed in Section III, 48. Transfer to a 350-ml. volumetric flask, add 200 ml. of water and 5 ml. of concentrated sulphuric acid (or 200 ml. of N-sulphuric acid). Shake until the solid has dissolved and make up to the mark with distilled water. Shake well. Remove 25 ml. of the solution with a pipette, add 25 ml. of N-sulphuric acid, and titrate with the permanganate solution to the first permanent pink colour. Here also the addition of a few ml. of syrupy phosphoric acid improves the colour change at the end point. Carry out two or at most three titrations. These should not differ by more than 0·1 ml.

**Calculation.** The equivalent weight of ferrous ammonium sulphate in this reaction is the molecular weight or 392·13 (2FeO + O = Fe₃O₄).

Compute the normality of the potassium permanganate solution from the relation:

\[ V_A \times n_A = V_B \times n_B \]

(Section I, 24).

**Procedure F.** With oxalic acid or potassium tetraoxalate. Weigh out accurately either about 1·6 g. of A.R. \( \text{H}_2\text{C}_2\text{O}_4,\text{H}_2\text{O} \) or about 1·6 g. of A.R. \( \text{KHC}_2\text{O}_4,\text{H}_2\text{C}_2\text{O}_4,2\text{H}_2\text{O} \), and make up to 250 ml. in a volumetric flask. Shake well. Remove 25-ml. portions with a pipette, add 150 ml. of ca. 2N-sulphuric acid, and titrate with the permanganate solution as detailed under Procedure B (sodium oxalate). Successive titrations should agree within 0·1 ml.

**Calculation.** The partial equation for both reactions is:

\[ \text{C}_3\text{O}_4^{--} + 2\varepsilon = 2\text{CO}_2 \]

hence the equivalent weight of \( \text{H}_2\text{C}_2\text{O}_4,\text{H}_2\text{O} \) is 0·5 mol. or 63·03, and that for \( \text{KHC}_2\text{O}_4,\text{H}_2\text{C}_2\text{O}_4,2\text{H}_2\text{O} \) is 0·25 mol. or 63·55. Calculate the normality of the potassium permanganate solution as already detailed.

**III. 48. Permanence of potassium permanganate solutions.**—A pure permanganate solution, provided it is kept free from dust, organic matter, precipitated manganese dioxide, and reducing vapours, will keep for a long time. For very accurate work, however, it is advisable to standardise the solution frequently, preferably with arsenious oxide. If filtered solutions of permanganate are to be diluted, it is best to use water which has been re-distilled from alkaline permanganate, e.g., conductivity water (Section II, 100). The addition of 10 g. of potassium hydroxide per litre increases the stability of the solution.

The student is reminded that owing to the decomposition of permanganate solution by organic matter of any kind, it cannot be filtered through filter-paper, nor can it be used in a clip burette, because it is decomposed by the india-rubber tube. Filtration is carried out through purified glass wool, asbestos, or a sintered-glass funnel.
ANALYSES INVOLVING THE USE OF STANDARD POTASSIUM
PERMANGANATE SOLUTIONS

III, 50. Determination of ferrous iron.—The detailed experimental
method has already been given under Procedures C and E of Section
III, 48; the solution is acidified with dilute sulphuric acid. If chloride
ion is present high results are obtained, because the reaction between
ferrous iron and permanganate induces the oxidation of hydrochloric
acid to chlorine (or to hypochlorous acid). The chloride ion is rendered
almost harmless by the addition of a manganous salt, preferably in the
form of the so-called Zimmermann–Reinhardt or preventive solution
(Section III, 46), and by slow titration.

As an exercise, the student should determine the percentage of iron
in crystallised ferrous sulphate, FeSO₄·7H₂O. Weigh out accurately
about 7 g. of ferrous sulphate crystals, dissolve in 200 ml. of N-sulphuric
acid (195 ml. of water and 5 ml. of concentrated sulphuric acid) in a
250-ml. volumetric flask, and make up to the mark with distilled water.
Shake well. Remove 25 ml. of the solution with a pipette into a
250-ml. conical flask, add 25 ml. of N-sulphuric acid, and titrate with
standard 0·1N-potassium permanganate to the first permanent faint
pink colour. Repeat with two other 25-ml. portions of the ferrous
solution. Successive titrations should agree within 0·1 ml.

Calculate the percentage of ferrous iron in the crystals.

\[
2\text{KMnO}_4 + 10\text{FeSO}_4 + 8\text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Fe}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}
\]

1 ml. N-KMnO₄ = 0·05585 g. Fe

III, 51. Reduction of ferric to ferrous iron.—Iron often occurs in the
ferric state, or as a mixture of ferrous and ferric iron in ores and other
materials. For the volumetric determination of iron, the ferric iron
must be first quantitatively reduced to the ferrous state. The following
methods, in decreasing order of importance and application, are avail­
able: (A) with stannous chloride; (B) with amalgamated zinc pre­
ferably in the Jones reductor, or with the cadmium reductor (Section
II, 39B); (C) with titanous salts; (D) with sulphurous acid; (E) with
hydrogen sulphide; and (F) with zinc or magnesium and dilute sul­
phuric acid. Methods A and B are widely used. Method C is described
in Section III, 86. Method F has been largely displaced by B.

A. Reduction with stannous chloride solution. Many iron ores are
brought into solution with concentrated hydrochloric acid. In such
cases the reducing agent frequently employed is stannous chloride:

\[
2\text{FeCl}_3 + \text{SnCl}_2 = 2\text{FeCl}_2 + \text{SnCl}_4
\]

The hot iron solution (70–90° C.), from about 0·3 g. of iron ore, which
should occupy a volume of 25–30 ml.*, be 5–6N with respect to
hydrochloric acid, is reduced by adding concentrated stannous chloride
solution dropwise from a separating-funnel or a burette, with stirring,
until the yellow colour of the solution has nearly disappeared. The
reduction is then completed by diluting the concentrated solution of
stannous chloride with 2 volumes of dilute hydrochloric acid, and
adding the dilute solution dropwise, with agitation after each addition,

* If the volume is greater than this, it must be reduced by careful evaporation.
Volumetric Analysis

until the liquid has a faint green colour, quite free from any tinge of yellow. The solution is then rapidly cooled under the tap, with protection from the air, and the slight excess of stannous chloride present removed by adding 10 ml. of a saturated solution (ca. 5 per cent) of mercuric chloride rapidly in one portion. A slight silky white precipitate of mercurous chloride should be obtained:

$$2\text{HgCl}_2 + \text{SnCl}_2 = \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$$

The oxidising agent has no appreciable effect upon the small amount of mercurous chloride in suspension. If a heavy precipitate forms, or a grey or black precipitate is obtained, too much stannous chloride has been used; the results are inaccurate and the reduction must be repeated. Finely divided mercury is oxidised by potassium permanganate (and by potassium dichromate).

After the addition of the mercuric chloride solution, the whole is allowed to stand for 5 minutes, and transferred quantitatively to a 600-ml. beaker or casserole with the aid of about 400 ml. of water. Twenty-five ml. of the Zimmermann–Reinhardt solution (the so-called “preventive solution”) are added, and the mixture titrated slowly and with constant stirring with standard 0.1N-potassium permanganate.

The end point is not the permanent pink colour which is obtained in the absence of a chloride, but is the first pink coloration seen throughout the whole solution; this coloration fades after about 15 seconds. The fading is due to the reaction between the permanganate solution and the mercurous chloride, and also to the following reaction, which is, however, very slow in cold acid solution:

$$2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} = 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$

Blank runs on the reagents should be carried through all the operations, and corrections made, if necessary.

The concentrated solution of stannous chloride is prepared by dissolving 12 g. of pure tin or 30 g. of A.R. crystallised stannous chloride (SnCl$_2$·2H$_2$O) in 100 ml. of concentrated hydrochloric acid and diluting to 200 ml. with water.

Details of the Zimmermann–Reinhardt or preventive solution are given in Section III, 46.

B. Reduction with amalgamated zinc. The Jones reductor. Amalgamated zinc is an excellent reducing agent for ferric iron:

$$2\text{Fe}^{+++} + \text{Zn} = 2\text{Fe}^{++} + \text{Zn}^{++}$$

The metal can be purchased in the pure state: A.R. granulated zinc contains less than 0.002 per cent of iron. Zinc reacts rather slowly with acids, but upon treatment with a dilute solution of a mercuric salt, the metal is covered with a thin layer of mercury; the amalgamated metal reacts quite readily. Reduction with amalgamated zinc is usually carried out in the “reductor,” due to C. Jones (1888–89)*. This consists of a column of amalgamated zinc contained in a long glass tube provided with a stopcock, through which the solution to be reduced may be drawn. A large surface is exposed, and consequently such a zinc column is much more efficient than pieces of zinc placed in the solution.

* The use of amalgamated zinc spirals is described in Section II, 39D.
A suitable form of the Jones reductor, with approximate dimensions, is shown in Fig. III, 51, 1. A perforated porcelain plate, covered with purified asbestos or glass wool, supports the zinc column. The tube below the tap passes through a tightly fitting one-holed rubber stopper into a 750-ml filter-flask. It is advisable to connect another filter-flask in series with the water-pump, so that if any water "sucks back" it will not spoil the determination. The amalgamated zinc is prepared as follows. About 300 g. of A.R. granulated zinc (or zinc shavings, or pure 20-30-mesh zinc) are covered with 2 per cent mercuric chloride solution in a beaker. The mixture is stirred for 5-10 minutes, then the solution is decanted from the zinc, and washed three times with water by decantation. The resultant amalgamated zinc should have a bright silvery luster. The porcelain plate is placed in position, covered with a layer of purified asbestos or glass wool and then the amalgamated zinc added; the latter should reach to the shoulder of the tube. The zinc is washed with distilled water (500 ml.), using gentle suction. If the reductor is not to be used immediately, it must be left full of water in order to prevent the formation of basic salts by atmospheric oxidation, which impair the reducing surface.

To use the reductor for the reduction of ferric iron, proceed as follows. The zinc is activated by filling the cup (which holds about 50 ml.) with 2N (ca. 5 per cent) sulphuric acid, the tap being closed. The flask is connected to a filter-pump, the tap opened, and the acid slowly drawn through the column until it has fallen just above the level of the zinc; the tap is then closed and the process repeated twice. The tap is shut, the flask detached, cleaned, and replaced. The reductor is now ready for use. It is important to note that during use the level of the liquid should always be just above the top of the zinc column. The solution to be reduced should have a volume of 100-150 ml., contain not more than 0.25 g. of iron, and be about 2N in sulphuric acid. The cold ferric iron solution is passed through the reductor, using gentle suction, at a rate not exceeding 75-100 ml. per minute. As soon as the reservoir is nearly emptied of the solution, 100 ml. of 2-5 per cent sulphuric acid is passed through in two portions, followed by 100-150 ml. of water. The last washing is necessary in order to wash out all of the reduced compound and also the acid, which would otherwise cause unnecessary consumption of the zinc. Disconnect the flask from the reductor, wash the end of the delivery tube, and titrate immediately with standard 0-1N-potassium permanganate.

Carry out a blank determination, preferably before passing the iron solution through the reductor, by running the same volumes of acid and water through the apparatus as are used in the actual determination. This should not amount to more than about 0.1 ml. of 0-1N-permanganate, and should be deducted from the volume of permanganate solution used in the subsequent titration.
It must be emphasised that if hydrochloric acid has been employed in the original solution of the iron-bearing material, the volume should be reduced to ca. 25 ml. and then diluted to ca. 150 ml. with 5 per cent sulphuric acid. The estimation is carried out as detailed above, but 25 ml. of the Zimmermann–Reinhardt or preventive solution must be added before titration with the standard potassium permanganate solution. A better method is to expel the hydrochloric acid by careful evaporation with an excess of sulphuric acid before the solution is reduced; the addition of the Zimmermann–Reinhardt solution is then unnecessary, and the end point is more stable.

For the determination of total iron in hydrochloric acid solution, it is more convenient to reduce the solution in a silver reductor (Section II, 390) and to titrate the reduced solution with either standard potassium dichromate or standard ceric sulphate solution (vide infra).

Applications and limitations of the Jones reductor.—1. Solutions containing 1–10 per cent by volume of sulphuric acid or 3–15 per cent by volume of concentrated hydrochloric acid can be used in the reductor. Sulphuric acid is, however, generally used, as hydrochloric acid may interfere in the subsequent titration, e.g., with potassium permanganate.

2. Nitric acid must be absent, for this is reduced to hydroxylamine and other compounds which react with permanganate. If nitric acid is present, evaporate the solution just to dryness, wash the sides of the vessel with about 3 ml. of water, carefully add 3–4 ml. of concentrated sulphuric acid, and evaporate until fumes of the latter are evolved. Repeat this operation twice to ensure complete removal of the nitric acid, dilute to 100 ml. with water, add 5 ml. of concentrated sulphuric acid, and proceed with the reduction.

3. Organic matter (acetates, etc.) must be absent. It is removed by heating to fumes of sulphuric acid in a covered beaker (best with a cover of the Fisher “speedyvap” type), then carefully adding drops of a saturated solution of potassium permanganate until a permanent colour is obtained, and finally continuing the fuming for a few minutes.

4. Solutions containing compounds of copper, tin, arsenic, antimony, and other reducible metals must never be used. These must be removed before the reduction by treatment with hydrogen sulphide.

5. Other elements which are reduced in the reductor to a definite valency stage are titanium to Ti$$^{+++}$$, chromium to Cr$$^{++}$$, molybdenum to Mo$$^{+++}$$, and vanadium to V$$^{++}$$.

With the exception of ferrous iron and quadrivalent uranium, the reduced solutions are extremely unstable and readily re-oxidise upon exposure to air. These are best caught in a five-fold excess of a solution of ferric alum (150 g. of A.R. iron alum and 150 ml. of concentrated sulphuric acid per litre; approximately 0.3N with respect to iron) contained in the filter-flask. The ferrous iron formed is then titrated with a standard solution of a suitable oxidising agent. Titanium and chromium are completely oxidised and liberate an equivalent amount of ferrous sulphate; molybdenum is reoxidised to the quinquevalent...
(red) stage, which is fairly stable in air, and complete oxidation is effected by the permanganate, but the net result is the same, viz., \( \text{Mo}^{III} \rightarrow \text{Mo}^{VII} \); vanadium is re-oxidised to the quadrivalent condition, which is stable in air, and the final oxidation is completed by slow titration with potassium permanganate solution or with ceric sulphate solution. For further details, see Section III, 91 et seq.

D. Reduction with sulphurous acid. The solution must be feebly acid and fairly dilute, say, 500 ml. for 0.5 g. of iron. If the concentration of the acid exceeds 5\(N\), sulphurous acid will oxidise ferrous solutions. Hydrochloric acid–chloride solutions are reduced more rapidly than sulphuric acid–sulphate solutions. Either sulphur dioxide from a siphon of the liquid gas or freshly prepared sulphurous acid solution or ammonium bisulphite solution may be used. The operation is best carried out in an all-glass special wash bottle or, if this is not available, in a flask fitted with a rubber stopper carrying two "wash-bottle" tubes.

Treat the hydrochloric acid or sulphuric acid solution of the iron slowly and with constant shaking with dilute ammonia solution until a faint permanent precipitate is obtained. Dilute to about 100 ml., pass sulphur dioxide through the solution for 2–3 minutes, and then gradually heat to boiling, still continuing the passage of the gas. When the solution is colourless (15–30 minutes), replace the sulphur dioxide by a stream of washed carbon dioxide (from a Kipp's apparatus or cylinder), and boil vigorously until all the sulphur dioxide is expelled (20–30 minutes) as shown by passing the escaping gas for 30 seconds through dilute sulphuric acid containing 2 drops of 0.1\(N\)-permanganate. Allow the solution to cool in a stream of carbon dioxide, add more acid, and titrate with a standard solution of a suitable oxidising agent.

A simpler method is to place the acidified iron solution in a conical flask, add dilute ammonia solution slowly until a faint permanent precipitate is obtained, and then add either 25 ml. of a freshly prepared saturated solution of sulphur dioxide or excess of freshly prepared ammonium bisulphite solution; in the latter case, boiling water followed by a little dilute sulphuric acid is added. A small funnel is placed in the mouth of the flask, and the mixture boiled for 30 minutes. All the sulphur dioxide will then have been expelled. Cool the solution in an atmosphere of carbon dioxide, add 10 ml. of dilute sulphuric acid (1:6), and titrate at once with a standard solution of the oxidising agent.

Members of the hydrogen sulphide group of metals must be absent. If present, they must be removed first.

E. Reduction with hydrogen sulphide. This method is not frequently employed. The best experimental conditions are as follows. About 100 ml. of a cold 2.5 per cent sulphuric acid solution of the iron compound is treated with a current of washed hydrogen sulphide for 30 minutes, and then for a further 15 minutes during which the solution is heated to boiling. Fifteen ml. of sulphuric acid (1:1) are added, and the solution is boiled down to about 50 ml. during 30–60 minutes whilst a stream of oxygen-free carbon dioxide is passed through. The solution is allowed to cool in a stream of the gas, diluted to 200 ml. with distilled water, and titrated with standard permanganate solution. The precipitated sulphur is coagulated during the concentration, and usually need not be removed before titration. The results are slightly high.
Volumetric Analysis

F. Reduction with zinc and sulphuric acid. This method has been largely replaced by that employing amalgamated zinc, but is given here for the sake of completeness. The solution to be reduced should be dilute (e.g., not more than 0.15 g. of iron per 200 ml.; for this quantity about 10 g. of zinc and 25 ml. of sulphuric acid are necessary). Place 150 ml. of the iron solution in a 350-ml. conical or flat-bottomed flask, add cautiously 20 ml. of concentrated sulphuric acid and 10 g. of A.R. zinc. The reaction will usually be slow, and is accelerated by the addition of two to three drops of copper sulphate solution. Warm very gently and allow the reaction to continue until the solution appears quite colourless (or pale green): a short funnel should be placed in the neck of the flask to prevent loss by spray. Test for the presence of ferric salt by removing a drop of the solution on the end of a thin glass rod, or at the end of a capillary tube, and bringing it into contact with a drop of potassium or ammonium thiocyanate solution upon a porcelain "spot" plate. No red colour should appear, or at most only a faint pink tint, if all the ferric iron has been reduced; otherwise a red coloration is formed. When all the iron has been reduced, close the flask by means of a one-holed rubber stopper carrying a Bunsen valve (Fig. III, 51, 2), and boil the mixture gently until all the zinc has dissolved. (A Bunsen valve consists of a piece of glass tubing carrying a short length of rubber tubing, which is closed at the upper end by a short glass rod. The rubber tube has a vertical slit, about 1–2 cm. long, forming the valve; this allows gas or vapour to pass out, but is closed by atmospheric pressure when the evaporation ceases, thus preventing the entrance of air.) When the zinc has completely dissolved, allow the solution to cool, remove the stopper, and titrate the contents of the flask with standard permanganate solution.

For reduction with liquid zinc amalgam, see Section III, 90.

III, 52. Determination of iron in ferric ammonium sulphate.—In order to obtain experience in the various methods of reduction described in the preceding Section, the student is recommended to determine the percentage of iron in ferric alum, \((\text{NH}_4)_2\text{SO}_4\cdot\text{Fe}_2(\text{SO}_4)_a\cdot24\text{H}_2\text{O}\). It is best to employ the A.R. material, as some check can be made by calculation upon the accuracy of the result obtained.

Weigh out accurately about 24 g. of A.R. ferric alum, transfer it to a 500-ml. volumetric flask, dissolve it in water containing about 100 ml. of dilute sulphuric acid (2N; ca. 5 per cent), and make up to the mark with water. Shake well. Reduce the iron in 25-ml. portions: (i) by the stannous chloride method, (ii) by the sulphurous acid method, and (iii) by the Jones reductor, if available. In all cases the final solution should be titrated with standard 0.1N-potassium permanganate. Individual determinations should agree within 0.1 ml. of the permanganate solution.

Calculate the percentage of iron in the compound for each method of reduction.

\[
\text{1 ml. } N\text{-KMnO}_4 = 0.05584 \text{ g. Fe}
\]

The volume of permanganate solution used is multiplied by its nor-
Quantitative Inorganic Analysis

mality; this gives the volume of \( N \) solution to which it is equivalent. If the latter volume is multiplied by the milli-equivalent of iron (0.00584 g.), the weight of iron in the volume of solution titrated is obtained, from which the percentage of iron is readily calculated.

III, 53. Determination of the total iron in an iron ore.—For practice, the student may employ either spathic iron ore (largely ferrous carbonate)* or the iron ore supplied by the instructor. Weigh out accurately about 2 g. of the finely ground ore and dissolve it in 100 ml. of dilute hydrochloric acid (1 : 1) in a conical flask carrying a short funnel in the neck. Warm gently, and continue the heating until the residue is free from coloured material. Rinse down the funnel and the neck of the flask with distilled water, cool, and filter the liquid through a hardened quantitative filter-paper into a 250-ml. volumetric flask. Wash with very dilute hydrochloric acid and allow the washings to pass into the flask. Remove the funnel and make up to the mark. Shake well. Remove 50 ml. of the liquid by means of a pipette to a conical flask, heat to boiling, and reduce the ferric salt by the stannous chloride method (Section III, 51A). Pour the reduced solution into 400 ml. of water containing 25 ml. of the Zimmermann–Reinhardt solution (Section III, 46), and titrate slowly with standard 0.1N-potassium permanganate to the first pink colour which is stable for 15 seconds. Repeat the titration with two other 50-ml. portions of iron in the iron ore.

III, 54. Determination of calcium in calcium carbonate.—Discussion. Metals, such as calcium, copper, lead, and zinc, which give slightly soluble oxalates may be determined by dissolving the washed precipitate in dilute sulphuric acid and titrating with standard permanganate solution. The method is widely used for the estimation of calcium. The calcium is precipitated as the oxalate by the addition of ammonium oxalate solution to a dilute hydrochloric acid solution of the element, followed by neutralisation of the acid with dilute ammonia solution. The washed precipitate is dissolved in dilute sulphuric acid, and the liberated oxalic acid titrated with standard permanganate solution.

\[
\begin{align*}
\text{CaC}_2\text{O}_4 + \text{H}_2\text{SO}_4 &= \text{CaSO}_4 + 2\text{C}_2\text{O}_4 \\
2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{C}_2\text{O}_4 &= \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}
\end{align*}
\]

It must be pointed out that the above method is not quite satisfactory for the determination of lead, because of the formation of a coating of lead sulphate over the lead oxalate. In this case the following procedure, which can be applied to all the elements given above, should be used. The oxalate of the metal is precipitated by a known excess of oxalic acid or ammonium oxalate solution in the presence of ammonia solution (details are given below), the precipitate is filtered and well washed, and the excess of oxalate in the filtrate and washings determined by titration with standard potassium permanganate solution in the usual manner.

Procedure. Weigh out accurately 0.15–0.2 g. of calcium carbonate, preferably of A.R. grade, into a 400-ml. beaker. Add 20 ml. of water and cover the beaker with a clock glass. Add 10 ml. of dilute hydrochloric acid (1 : 1) and warm until the solid has dissolved. Rinse the

* Suitable iron ores are Ridgesdale's 'Iron Ore, No. 17' (one of the Analyzed Samples for Students) and 'Iron Ore A' (a British Chemical Standard) of the Bureau of Analyzed Samples.
sides of the vessel and the clock glass, dilute to 200 ml., and add a few drops of methyl red indicator. Heat the solution to boiling, and add a clear solution of 1.5 g. of ammonium oxalate dissolved in 25 ml. of water slowly and with constant stirring; some calcium oxalate may be precipitated in the acid solution owing to the large excess used. To the hot solution (70–80° C.) add dilute ammonia solution (1:1) dropwise and with stirring from a burette until the liquid is neutral or faintly alkaline (colour change from red to yellow). Allow the solution to stand for an hour in a warm place. Decant the clear supernatant liquid through a Whatman No. 40 or No. 540 filter-paper; test the filtrate for the presence of calcium with ammonium oxalate. Transfer the precipitate quantitatively to the filter (Section II, 28), and wash the precipitate on the filter repeatedly with small quantities of cold water until the washings are oxalate- and chloride-free. Pierce a hole in the filter with a pointed glass rod, and wash the bulk of the precipitate through the funnel into a conical flask with hot water. Treat the filter with small quantities of dilute sulphuric acid (1:8), and again wash into the flask. Finally wash the filter-paper thoroughly with hot water. When the precipitate has completely dissolved (add more dilute sulphuric acid, if necessary), dilute the solution to about 200 ml., and titrate with standard 0.1N-potassium permanganate (for details, see Section III, 48, Procedure B).

The calcium oxalate precipitate may also be filtered through a sintered-glass or porous-porcelain crucible. The precipitate is then washed with dilute sulphuric acid (5 per cent) until dissolved. The sulphuric acid is added in small portions, and is allowed to remain in contact with the precipitate before being drawn into the suction flask. The solution in the flask is diluted and titrated with standard 0.1N-permanganate.

Repeat the determination with two other samples of the calcium carbonate.

Calculate the percentage of calcium in the calcium carbonate.

1 ml. N-KMnO₄ = 0.02004 g. Ca = 0.02804 g. CaO

III, 55. Analysis of hydrogen peroxide.—Discussion. Hydrogen peroxide is marketed in four concentrations, "10-", "20-", "40-", and "100-volume" concentrations. The "10-volume" solution refers to the fact that the solution, when fully decomposed by heat, yields 10 times its volume of oxygen measured at 0° C. and 760 mm.

2H₂O₂ = 2H₂O + O₂
2 × 34.02 g. 22.4 litres (at N.T.P.)

A "10-volume" preparation should contain about 3 per cent H₂O₂. The following reaction occurs when potassium permanganate solution is added to hydrogen peroxide solution acidified with dilute sulphuric acid:

2KMnO₄ + 3H₂SO₄ + 5H₂O₂ = K₂SO₄ + 2MnSO₄ + 8H₂O + 5O₂

This forms the basis of the following method of analysis.

Procedure. Transfer 25 ml. of the "10-volume" solution by means of a burette (1) to a 250-ml measuring-flask, and dilute with water to the mark. Shake thoroughly. Transfer 25 ml. of this solution to a conical flask, dilute with 200 ml. of water, add 20 ml. of dilute sulphuric
acid (1 : 5), and titrate with standard 0.1N-potassium permanganate to the first permanent, faint pink colour. Repeat the titration; two consecutive determinations should agree within 0.1 ml.

Calculate: (i) the weight of hydrogen peroxide per litre of the original solution and (ii) the "volume strength," i.e., the number of ml. of oxygen at N.T.P. that can be obtained from 1 ml of the original solution.

\[ 1 \text{ ml. } N\text{-KMnO}_4 = 0.01701 \text{ g. } \text{H}_2\text{O}_2 \]

Note. 1. If the percentage is required by weight, the specific gravity of the original solution may be taken as unity. A better procedure is to weigh out the original sample in a weighing-bottle.

III, 56. Analysis of sodium peroxide.—In this analysis, precautions must be taken to prevent loss of active oxygen. Prepare a cold mixture of 100 ml of water, 5 ml of concentrated sulphuric acid, and 5 g. of pure boric acid.* Transfer gradually about 0.5 g. of the sodium peroxide from a weighing-bottle to the mixture, which is kept vigorously stirred. Make up the solution to 250 ml in a measuring-flask, and shake well. Titrate 50-ml portions of this solution with standard 0.1N-potassium permanganate.

Calculate the percentage purity of the sample.

\[ 1 \text{ ml. } N\text{-KMnO}_4 = 0.03900 \text{ g. } \text{Na}_2\text{O}_2 \]

Note. Barium peroxide may be evaluated by dissolving a weighed quantity (say 1 g.) in 200 ml of N-hydrochloric acid, and making up to 250 ml in a volumetric flask. Fifty-ml portions are titrated with standard 0.1N-potassium permanganate.

\[ 1 \text{ ml. } N\text{-KMnO}_4 = 0.08468 \text{ g. } \text{BaO}_2 \]

The use of the Zimmermann and Reinhardt's solution is not necessary in this case (compare Section III, 46).

III, 57. Determination of manganese dioxide in pyrolusite.—Discussion. Manganese dioxide occurs in nature as the mineral pyrolusite. For many purposes, a knowledge of the percentage of MnO_2 is required. This may be determined by treatment with an excess of an acidified solution of a reducing agent, such as ferrous sulphate, sodium oxalate, or arsenious oxide.

\[
\begin{align*}
\text{MnO}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 & = \text{Fe}_2(\text{SO}_4)_3 + \text{MnSO}_4 + 2\text{H}_2\text{O} \\
\text{MnO}_2 + \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 & = \text{MnSO}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O} \\
2\text{MnO}_2 + \text{As}_2\text{O}_3 + 2\text{H}_2\text{SO}_4 & = 2\text{MnSO}_4 + \text{As}_2\text{O}_5 + 2\text{H}_2\text{O}
\end{align*}
\]

The excess of reducing agent is determined by titration with standard permanganate solution. The disadvantage of using ferrous sulphate solution is that the operation must be carried out in an atmosphere free from air (e.g., carbon dioxide) in order to prevent the aerial oxidation of the ferrous salt. Both sodium oxalate and arsenious oxide which are primary standards and are stable in air, are more convenient. Arsenious oxide is somewhat more trustworthy in this estimation than is sodium oxalate, because oxalic acid decomposes very slowly at high temperatures into carbon monoxide and carbon dioxide, the

* This is added in order that the relatively stable "perboric acid" may be formed upon the addition of the sodium peroxide.
decomposition being catalysed by manganous salts; the extent of decomposition under ordinary circumstances is, however, very small. Both procedures will be described.

Procedure A (arsenious oxide method). Dry the finely powdered sample of pyrolusite at 120° C. to constant weight. Weigh out accurately from a weighing-bottle about 0·2 g. of the sample into a 250-ml. conical flask, add 50 ml. of standard 0·1N-arsenious oxide (Section III, 48A, Note 1) and 10 ml. of concentrated sulphuric acid. Place a short funnel in the mouth of the flask, and boil until the pyrolusite has decomposed completely; no brown or black particles should then be present. Cool the solution, add 1 drop of 0·0025M-potassium iodide solution, and titrate the excess of arsenious oxide with standard 0·1N-potassium permanganate. Repeat the determination with two other samples of the solid.

Calculate the percentage of MnO₂ in the pyrolusite from the amount of arsenious oxide consumed in the titration.

\[
1 \text{ ml. } N\text{-KMnO}_4 = 1 \text{ ml. } N\text{-As}_2\text{O}_3 = 0.04346 \text{ g. MnO}_2
\]

Procedure B (sodium oxalate method). Weigh out accurately about 0·2 g. of the finely powdered, dry pyrolusite into a conical flask, add 50 ml. of standard 0·1 N-sodium oxalate (Section III, 48B, Note 1), add 50 ml. of 4N-sulphuric acid (ca. 10 per cent), and place a short funnel in the mouth of the flask. Boil the mixture gently until no black particles remain. Allow to cool, and titrate the excess of oxalate with standard 0·1N-potassium permanganate as detailed in Section III, 48, Procedure B. Repeat the determination with two other samples of similar weight.

Calculate the amount of sodium oxalate consumed in the reaction, and from this the percentage of MnO₂ in the pyrolusite.

\[
1 \text{ ml. } N\text{-KMnO}_4 = 1 \text{ ml. } N\text{-Na}_2\text{C}_2\text{O}_4 = 0.04346 \text{ g. MnO}_2
\]

Note on the analysis of red lead. A weighed quantity (about 0·3 g.) of red lead is heated with about 30 ml. of 2N-nitric acid. The following reaction occurs:

\[
Pb_2O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O
\]

When the reaction is over, 50 ml. of 0·1N-sodium oxalate is added, and the mixture boiled until the solution is almost clear and colourless. The excess of the oxalate is then titrated with standard 0·1N-potassium permanganate.

III, 58. Determination of nitrites.—Discussion. Nitrites react in warm acid solution (ca. 40° C.) with permanganate solution in accordance with the equation:

\[
2\text{KMnO}_4 + 3H_2SO_4 + 5HNO_2 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O
\]

If a solution of a nitrite is titrated in the ordinary way with potassium permanganate, poor results are obtained, because the nitrite solution has first to be acidified with dilute sulphuric acid. Nitrous acid is liberated, which being volatile and unstable, is partially lost. If, however, a measured volume of standard potassium permanganate solution, acidified with dilute sulphuric acid, is treated with the nitrite solution, added from a burette, until the permanganate is just decolorised, results accurate to 0·5–1 per cent may be obtained. This is due
to the fact that nitrous acid does not react instantaneously with the permanganate. More accurate results may be secured by adding the nitrite to an acidified solution in which permanganate is present in excess (the tip of the pipette containing the nitrite solution should be below the surface of the liquid during the addition), and back-titrating the potassium permanganate with a solution of ferrous ammonium sulphate which has recently been compared with the permanganate solution.

For practice in this estimation, the student may determine the purity of commercial potassium nitrite.

**Procedure.** Weigh out accurately about 1.1 g. of commercial potassium nitrite, dissolve it in cold water, and dilute to 250 ml. in a volumetric flask. Shake well. Measure out 25 ml. of standard 0.1N-potassium permanganate into a 500-ml. flask, add 300 ml. of 0.75N-sulphuric acid, and heat to 40° C. Place the nitrite solution in the burette, and add it slowly and with constant stirring until the permanganate solution is just decolorised. Better results are attained by allowing the tip of the burette to dip under the surface of the diluted permanganate solution. Towards the end the reaction is sluggish, so that the nitrite solution must be added very slowly. Repeat the titration with two other 25-ml. portions of the permanganate solution.

Calculate the percentage of KNO₂ in the commercial sample.

1 ml. N-KMnO₄ = 0.02351 g. HN0₂ = 0.04256 g. KNO₂

**III. 59. Determination of persulphates.—Discussion.** Alkali persulphates can readily be evaluated by adding to their solutions a known excess of an acidified ferrous salt solution, and determining the excess of ferrous iron by titration with standard potassium permanganate solution.

\[ \text{K}_2\text{S}_2\text{O}_8 + 2\text{FeSO}_4 + \text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 2\text{KHSO}_4 \]

Another procedure utilises standard oxalic acid solution. When a sulphuric acid solution of a persulphate is treated with excess of standard oxalic acid solution in the presence of a little silver sulphate as catalyst, the following reaction occurs:

\[ \text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{C}_2\text{O}_4 = 2\text{H}_2\text{SO}_4 + 2\text{CO}_2 \]

The excess of oxalic acid is titrated with standard potassium permanganate solution.

For practice, the student may determine the purity of potassium persulphate, preferably of A.R. quality.

**Procedure A.** Prepare an approximately 0.1N solution of ferrous ammonium sulphate as described in Section III, 48, Procedure E, and titrate this against standard 0.1N-potassium permanganate. Weigh out accurately about 0.3 g. of potassium persulphate into a conical flask fitted with a Bunsen valve (Fig. III, 57, 2). Remove the rubber stopper carrying the valve, displace the air by carbon dioxide, add 50 ml. of the acidified ca. 0.1N-ferrous solution, followed by 150–200 ml. of boiling water so as to raise the temperature to at least 80° C. Close the flask and mix the contents thoroughly. When the solid has dissolved, cool the solution by immersion in cold water, and titrate the excess of ferrous iron with standard 0.1N-potassium permanganate.
Repeat the titration with two further quantities of the potassium persulphate.

From the difference between the volume of 0.1N-permanganate required to oxidise 50 ml. of the ferrous solution and that required to oxidise the ferrous salt remaining after the addition of the persulphate, calculate the percentage purity of the sample.

\[ \text{1 ml. } \text{N-KMnO}_4 = 0.1352 \text{ g. } \text{K}_2\text{S}_2\text{O}_8 \]

**Procedure B.** Prepare a 0.1N solution of oxalic acid (Section III, 48F). Weigh out accurately 0.3–0.4 g. of potassium persulphate into a 350-ml. conical flask, add 50 ml. of 0.1N-oxalic acid, followed by 0.2 g. of silver sulphate dissolved in 20 ml. of 10 per cent sulphuric acid. Heat the mixture in a water-bath until no more carbon dioxide is evolved (15–20 minutes), dilute the solution to about 100 ml. with water at about 40°C, and titrate the excess of oxalic acid with standard 0.1N-potassium permanganate.

Calculate the percentage purity of the sample.

**III, 60. Determination of manganese in steel. A. Bismuthate method.**—Discussion. Sodium bismuthate of commerce is a brown powder of somewhat indefinite composition; the oxidising component is usually taken as NaBiO₃. The A.R. product contains about 85 per cent of NaBiO₃. Manganese salts are oxidised to permanganic acid by excess of sodium bismuthate in the presence of nitric acid:

\[ 2\text{Mn(NO}_3\text{)}_2 + 5\text{NaBiO}_3 + 16\text{HNO}_3 = 2\text{HMnO}_4 + 5\text{Bi(NO}_3\text{)}_3 + 5\text{NaNO}_3 + 7\text{H}_2\text{O} \]

The permanganic acid is very stable in a cold solution containing 20–40 per cent of nitric acid. If the steel is dissolved in nitric acid and the resultant cold solution treated with excess of sodium bismuthate, permanganic acid is formed. The excess of bismuthate is removed by filtration, and a measured excess of standard ferrous solution added to reduce the permanganate to a manganous salt:

\[ \text{MnO}_4^- + 5\text{Fe}^{++} + 8\text{H}^+ = \text{Mn}^{++} + 5\text{Fe}^{+++} + 4\text{H}_2\text{O} \]

The excess of ferrous iron is then determined by titration with standard potassium permanganate solution.

The solution should be free from cobalt, chromium, and chloride.

**Procedure.** Prepare the following solutions:

**0.03N-Potassium permanganate.** Dissolve 1 g. of A.R. potassium permanganate in 1 litre of water (Section III, 47).

**0.03N-Ferrous ammonium sulphate.** Dissolve 12 g. of A.R. ferrous ammonium sulphate in 1 litre of 5 per cent sulphuric acid (Section III, 48, Procedure E).

**3 Per cent nitric acid free from nitrous acid.** Boil concentrated nitric acid (d 1.42) for a short time (fume cupboard). Dilute in the proportion of 3 ml. of the concentrated acid to 100 ml. of water. (One ml. of nitric acid, d 1.42, contains nearly 1 g. of HNO₃. The above is therefore a 3 per cent solution both by volume and by weight.)

Standardise the permanganate solution against A.R. sodium oxalate either by weighing out accurately about 0.1 g. of the dry oxalate and proceeding as in Section III, 48 (Procedure B) or by preparing an approximately 0.03N solution (0.5 g. per 250 ml.) and following the experi-
Quantitative Inorganic Analysis

mental procedure of Section III, 48, Procedure B, Note 1. Alternatively, the arsenious oxide method (Section III, 40, Procedure A) may be used.

Weigh out accurately about 1 g. of the sample containing 0·2–1 per cent of manganese,* and dissolve it in 50 ml. of dilute nitric acid (1 : 3) in a 250-ml. conical flask. Filter, if necessary, through a sintered-glass crucible. Boil for 5 minutes, cool, add 0·5 g. of A.R. sodium bismuthate, and boil again for 5 minutes. A pink colour due to permanganic acid and/or a precipitate of manganese dioxide should appear; if neither a coloration nor a precipitate is produced, add a further 0·5 g. of sodium bismuthate and boil again for 5 minutes (1). Then add dropwise a concentrated solution of freshly prepared sulphurous acid or of sodium sulphite until the solution clears. Boil until all oxides of nitrogen are expelled (2). Cool the solution to about 15° C., add A.R. sodium bismuthate until no further appreciable alteration in colour ensues (about 0·25 g. NaBiO₃ for each 0·01 g. of Mn), add a further 0·5 g. excess, and stir the mixture for 2–3 minutes. Add 50 ml. of the prepared 3 per cent nitric acid, and filter through a porous-porcelain or sintered-glass crucible into a 350-ml. conical flask. Wash the residue well with the 3 per cent nitric acid until free from permanganic acid; this will generally require 50–100 ml., and the approximate volume should be noted. Run in slowly the ferrous ammonium sulphate solution from a burette until a slight excess is present (note the exact volume) as indicated by the disappearance of the permanganate colour (3). Titrate immediately with the 0·03N-potassium permanganate to the first faint pink coloration (4). The addition of 3 ml. of syrupy phosphoric acid improves the end point.

Standardise the ferrous ammonium solution by running a blank in the following manner. Into a 350-ml. Erlenmeyer flask place 50 ml. of 1 : 3 nitric acid, add a little sodium bismuthate, dilute with 50–100 ml. (use the volume of the wash liquid) of 3 per cent nitric acid, add an equal volume of the ferrous solution as was used in the determination, and titrate against the standard potassium permanganate solution. The difference between the titrations represents the permanganate equivalent of the permanganic acid formed in the determination.

Calculate the percentage of manganese in the sample of steel.

1 ml. N-KMnO₄ = 0·01099 g. Mn

Notes. 1. This preliminary oxidation with sodium bismuthate is to destroy any reducing substances, including carbonaceous matter, present which would subsequently slowly react with the permanganate.

2. All oxides of nitrogen must be removed, since these react with the permanganate. The reduction will also dissolve any manganese compounds that may have separated from the solution through the decomposition of the permanganic acid owing to the vigorous boiling.

3. The ferrous solution must be added as soon as the filtration and washing are complete, because the permanganic acid slowly decomposes.

4. This titration must be carried out immediately the ferrous solution has been added, because the ferrous solution reacts slowly with the nitric acid.

* Either Riddelde's 'Medium Carbon Steel, No. 2a' (one of the Analyzed Samples for Students) or the Bureau of Analyzed Samples 'Carbon Steel 'F'' or 'R' (a British Chemical Standard) is suitable. The British Standardised Steel Sample, No. 11, may also be used.
B. Persulphate–arsenite method.—Discussion. Manganese salts are oxidised to permanganic acid by persulphate in the presence of silver nitrate solution as catalyst:

\[ 2\text{MnSO}_4 + 5(\text{NH}_4)_2\text{S}_2\text{O}_8 + 8\text{H}_2\text{O} = 2\text{HMnO}_4 + 5(\text{NH}_4)_2\text{SO}_4 + 7\text{H}_2\text{SO}_4 \]

If the oxidation with persulphate is carried out in the presence of phosphoric acid, it is possible to oxidise as much as 50 mg. of manganese to permanganic acid without the separation of oxides of manganese. No satisfactory method is known for removing the excess of persulphate; boiling will destroy it, but some permanganic acid will be decomposed at the same time. Use is made of the fact that an arsenite solution reacts rapidly with permanganic acid in the cold, but no reaction occurs with the persulphate. A little chloride is added to precipitate the silver catalyst and thus prevent the re-oxidation of the manganous salt formed by reduction. The reduction of the permanganic acid by the arsenite does not proceed completely to bivalent manganese, and it is therefore advisable to standardise the arsenite solution against a steel of known manganese content.

Chromium is oxidised to chromate, but the yellow colour is not serious if the chromium content does not exceed 10 mg. per 100 ml.

Procedure. Weigh out accurately about 1 g. of the steel into a 350-ml. conical flask and add successively 15 ml. of water, 3 ml. of concentrated sulphuric acid, 4 ml. of 85 per cent phosphoric acid, and 8 ml. of concentrated nitric acid. Heat until solution is complete, and boil to expel oxides of nitrogen. Add 100 ml. of water, 5 ml. of 0.1M-silver nitrate solution, and 2.5 g. of pure ammonium persulphate dissolved in a little water. Heat to boiling and boil briskly for \( \frac{1}{2} \) minute. Cool rapidly to 25° C. or lower, add 75 ml. of cold water, and 5 ml. of 0.2M-sodium chloride solution. Titrate immediately with 0.025N-sodium arsenite solution (1) to a clear yellow end point which does not change upon the addition of more arsenite solution.

Standardise the arsenite solution against a similar steel of known manganese content.

Note. 1. Prepare the 0.025N-sodium arsenite solution by dissolving 1.230 g. of A.R. arsenuous oxide in a solution of 10 g. of A.R. sodium hydroxide in 30 ml. of water, warming if necessary. Dilute to about 500 ml., neutralise by the addition of 21 ml. of concentrated hydrochloric acid, then add 10 g. of A.R. sodium bicarbonate, and dilute to 1 litre in a volumetric flask.

(For a potentiometric titration method in pyrophosphate solution with standard potassium permanganate solution, see Section VI, 12; this is superior to either of the two preceding procedures).

III, 61. Determination of formates and of formic acid.—Discussion. Potassium permanganate reacts slowly with formic acid in cold acid solutions; in hot solutions, loss by volatilisation occurs. Formates in the presence of an alkali carbonate, e.g., sodium or potassium carbonate, react quantitatively with potassium permanganate:

\[ 2\text{KMnO}_4 + 3\text{HCOOK} = \text{KHC}_2\text{O}_3 + 2\text{K}_2\text{CO}_3 + 2\text{MnO}_2 + \text{H}_2\text{O} \]

This is one of the rare examples in which potassium permanganate has an equivalent weight of \( \frac{3}{5} \) of the formula weight or \( \frac{3}{5} \) mol.:

\[ \text{MnO}_4^- + 2\text{H}_2\text{O} + 3e = \text{MnO}_2 + 4\text{OH}^- \]
Quantitative Inorganic Analysis

or reacts in accordance with the hypothetical formula \( K_2Mn_2O_8 = K_2O_2MnO_3 \). In this method, the formic acid or formate is treated with an excess of sodium carbonate, and the standard potassium permanganate solution allowed to run into the hot formate solution until the clear liquid above the precipitate is just coloured pink. Some difficulty may be experienced in detecting the exact end point in the presence of the brown precipitate. The following procedure is therefore recommended. After the solution has acquired a distinct pink colour, it is strongly acidified with dilute sulphuric acid, a known excess of approximately 0·1N-sodium oxalate solution added, and the mixture warmed until the precipitate has dissolved. The excess of oxalate is then titrated with standard potassium permanganate solution.

In the modified procedure, the final end point is produced in acid solution. The final products of a chemical reaction are independent of the stages by which that reaction has been brought to completion, hence the permanganate reacts in accordance with the ionic equation:

\[
MnO_4^- + 8H^+ + 5e^- = Mn^{++} + 4H_2O
\]

(or as \( K_2O_2MnO_3 \) and its equivalent is \( \frac{1}{2} \) mol. The oxidation of the formic acid is essentially:

\[
\text{H·COOH} + \text{O} = \text{H}_2\text{O} + \text{CO}_2
\]

hence 1 ml. \( N\)-KMnO\(_4\) = 0·02301 g. HCOOH.

The method is unreliable in the presence of much chloride.

For practice, the student may determine the purity of commercial sodium formate.

Procedure. Weigh out accurately about 1·7 g. of sodium formate and dissolve it in 500 ml. of water in a volumetric flask. Shake well. Transfer 25 ml. of this solution into a conical flask, add excess of sodium carbonate solution, warm and then add standard 0·1N-potassium permanganate from a burette to the hot solution until the liquid has a distinct pink colour. Acidify strongly with dilute sulphuric acid, add 25 ml. of 0·1N-sodium oxalate, and warm until the precipitate has dissolved and the permanganate colour has disappeared. Titrated the excess of oxalate with the standard permanganate solution. Titrated 25 ml. of the sodium oxalate solution with the permanganate solution; the difference between this result and the total permanganate solution used gives the quantity of permanganate required to oxidise the formate. Repeat the determination with two other 25-ml. portions of the formate solution.

Calculate the percentage purity of the sample of sodium formate.

III, 62. Determination of selenium.—Method A. The selenious acid or selenite corresponding to about 0·1 g. of selenium is dissolved in 25 ml. of 40 per cent sulphuric acid, and diluted to 150 ml. Twelve grams of sodium phosphate (or phosphoric acid) is added (to prevent formation of manganese dioxide), followed by a considerable excess, at least 10 ml., of standard 0·1N-potassium permanganate. After 30 minutes, the residual potassium permanganate is determined by the addition of a slight excess of 0·1N-ferrous ammonium sulphate and back titration with standard 0·1N-permanganate.

\[
1 \text{ ml.} \ N\text{-KMnO}_4 = 0\cdot03948 \text{ g. Se}
\]
Method B.* The reaction:

$$\text{H}_2\text{SeO}_3 + 4\text{HI} = \text{Se} + 2\text{I}_2 + 3\text{H}_2\text{O}$$

is quantitative if carbon disulphide is present to prevent the liberated iodine from being adsorbed on the selenium. 100 ml. of an aqueous solution containing 0·05–0·10 g. of selenium as selenious acid are placed in a 250-ml. glass-stoppered bottle containing 10 ml. of 25 per cent hydrochloric acid and 20 ml. of carbon disulphide. Ten ml. of 10 per cent potassium iodide solution are added in a fine stream whilst the liquid is rotated. Shaking is continued for 1 minute, and the liberated iodine is then titrated with standard 0·1N-sodium thiosulphate with shaking, starch being added as indicator.

$$1 \text{ ml. } N^-\text{Na}_2\text{S}_2\text{O}_3 = 0·01974 \text{ g. Se}$$

Method C.* An alternative procedure to B utilises a relatively large volume of starch solution, which serves to maintain the selenium in colloidal solution (thus preventing the adsorption of iodine) and also as an indicator.

100–300 ml. of an aqueous solution containing up to 0·15 g. of selenium as selenious acid are placed in a 500–750-ml. conical flask, and 15 ml. of 2 per cent starch solution and 6 ml. of 1:1-hydrochloric acid are introduced. (For results of the highest accuracy, the oxygen present in the solution and the titration flask is expelled by the addition of 2 × 0·20 g. portions of pure sodium bicarbonate.) Add 10–20 ml. of 10 per cent potassium iodide solution in a thin stream whilst swirling the contents of the flask. After 1 minute titrate with 0·1N-sodium thiosulphate until the colour changes from blue through an intermediate dirty brown to violet red. If the titration is unnecessarily prolonged, the selenium flocculates before the end point is attained.

Note. A mixture of selenious and tellurous oxides or acids can be determined as follows. By the use of 0·1N-potassium permanganate both oxides or acids are oxidised to the sexavalent condition. With 0·1N-potassium dichromate, tellurium alone (see Section III, 80, Method B) is so oxidised. Hence by carrying out each oxidation on a different portion of the solution, each element can be determined.

It is not essential, however, to carry out titrations with two different samples, for if one portion is titrated with potassium dichromate solution, the tellurous tellurium will be oxidised; the titration can then be completed with potassium permanganate solution. The pink colour appears sharply; at the true end point the green colour of the chromic salt and the first drop of excess of permanganate solution gives a neutral grey tint. The effect is similar to that of "screened" methyl orange; the colour change is green → grey → red.

* This method should be given under Iodimetry and Iodometry, but is described here in order to have both methods for the determination of selenium together.
OXIDATIONS WITH POTASSIUM DICHROMATE

III, 63. General discussion.—Potassium dichromate is not so powerful an oxidising agent as potassium permanganate (compare oxidation potentials in Table XVI, and also Fig. I, 49, 2), but it has, however, several advantages over the latter substance. It can be obtained pure, is stable up to its fusion point, and is therefore an excellent primary standard. Standard solutions of exactly known strength can be prepared by weighing out the pure dry salt and dissolving it in the proper volume of water. Furthermore, the aqueous solutions are stable indefinitely. Potassium dichromate is used only in acid solution, and is reduced rapidly at the ordinary temperature to a green chromic salt. It is not reduced by cold hydrochloric acid, provided the acid concentration does not exceed 1 or 2N. Dichromate solutions are also less easily reduced by organic matter than are those of permanganate. Potassium dichromate is therefore of particular value in the determination of iron in iron ores: the ore is usually dissolved in hydrochloric acid, and the ferrie iron reduced to the ferrous state with stannous chloride solution (see Section III, 51A):

\[
K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O
\]

In acid solution, the reduction of potassium dichromate may be represented as:

\[
Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O
\]

from which it follows (compare Section I, 23) that the equivalent weight is one-sixth of the molecular weight, 294/6 or 49.035 g. A 0.1N solution therefore contains 4.9035 g. per litre.*

With regard to the determination of the end point in titrations with potassium dichromate solutions three methods are available: (i) with an external indicator, (ii) with an internal indicator, and (iii) potentiometrically. A general discussion of the principles underlying the potentiometric method has been given in Section I, 51.

The external indicator method was formerly widely used, but has become obsolete since the introduction of suitable oxidation-reduction indicators. It will only be described here for the sake of completeness, and also as an illustration of the use of an external indicator. Its widest application was in connexion with the titration of ferrous iron. A small crystal of pure potassium ferricyanide is repeatedly washed with distilled water in order to remove the superficial coating of the ferrocyanide. The washed crystal is dissolved in distilled water (∼0.1 per cent solution) and drops of the solution, which should appear almost colourless or pale yellow, are placed on a white tile with the aid

* For elementary students, the equivalent weight may be deduced from the hypothetical equations:

\[
K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O
\]

\[
K_2Cr_2O_7 + 8HCl = 2KCl + 2CrCl_3 + 4H_2O + 3O
\]

From either of these equations, it follows that the equivalent weight is one-sixth of the molecular weight (\(K_2Cr_2O_7/6\)).
of a stirring-rod. The acidified ferrous solution is titrated with the standard potassium dichromate solution. A drop of the ferrous solution is withdrawn from time to time with a thin glass rod and placed adjacent to a drop of the indicator; the two drops are carefully allowed to coalesce.* At first a deep blue colour is produced where the drops mix, but as the addition of the dichromate solution is continued, this is replaced by a bluish green, then green shade, and the titration is completed when there is no trace of green and no change is apparent in the mixed drops. After the first titration, the dichromate solution is run in slowly into the diluted ferrous solution without testing to within 0.5 ml. of the previously determined end point, and then added a drop at a time, the liquid being tested after the addition of each drop.

The first internal indicator to be used for this titration was a 1 per cent solution of diphenylamine in concentrated sulphuric acid (J. Knop, 1924). Subsequently a 1 per cent solution of diphenylbenzidine in concentrated sulphuric acid and also a 0.2–0.3 per cent aqueous solution of sodium diphenylamine sulphonate were introduced. With these three indicators, phosphoric acid must be added; the reason for this is that the phosphoric acid lowers the oxidation potential of the ferrous–ferrous system by forming a complex with the ferric ions (for further details, see Section I, 50). These indicators impart a green colour to the ferrous solution, which deepens to a blue-green shortly before the end of the titration. At the end point an intense purple or blue-violet coloration is obtained, which remains permanent after shaking. The addition of phosphoric acid may be avoided by the use of  \( N \)-phenylanthranilic acid or of tri-ortho-phenanthroline ferrous sulphate. The former is comparatively inexpensive, and is prepared by dissolving 1.07 g. of  \( N \)-phenylanthranilic acid in 20 ml. of 5 per cent sodium carbonate solution and diluting to 1 litre; about 0.5 ml. is used in a titration. Tri-ortho-phenanthroline ferrous sulphate † is an expensive indicator; since only one drop is necessary for each titration in a volume of 100–150 ml. owing to the intense coloration produced, the cost is in reality not high. With both indicators it is best to work in a volume of approximately 300 ml. and the solution should be about 2\( N \) with respect to sulphuric acid; satisfactory results are also obtained when the solution is about 2\( N \) with respect to hydrochloric acid. If the dichromate solution is placed in the burette, the colour change at the end point is from orange to pale green for ferroin, and from green to violet red for  \( N \)-phenylanthranilic acid. The reverse titration, dichromate with ferrous solution, is slower but definite, and the end point must be approached more slowly.

It has already been mentioned that a standard solution of potassium dichromate can be prepared by weighing out accurately the requisite quantity of the pure dry salt and dissolving it in the appropriate

---

* The above procedure may be replaced by the following, which, although more time-consuming, has the advantage that the potassium ferriyanide solution is not exposed to the atmosphere of the laboratory for longer than is absolutely necessary. One drop of the indicator is set out on a white tile with a thin glass rod, the latter is washed and then employed to withdraw a drop of the titrated liquid, and the drops allowed to mix as described. The process is then repeated—the rod is washed, a drop of the ferriyanide solution placed on the tile, the rod washed again, a drop of the solution removed, etc., until the end point is reached.

† The abbreviation "ferroin" will be employed in all subsequent references to this indicator.
quantity of water. Further standardisation is unnecessary. Sometimes, however, the problem of standardising a dichromate solution does arise. The best method is to use A.R. iron wire of 99-9 per cent purity (see Section III, 48). Ferrous ammonium sulphate may be employed in elementary work or in work requiring only moderate accuracy (see Section III, 48).

III, 64. Preparation of 0·1 N-potassium dichromate.—A.R. potassium dichromate has a purity of not less than 99-9 per cent.* Powder finely about 6 g. of the A.R. product in a glass or agate mortar, and heat for 30–60 minutes in an air oven at 140–150°C. Allow to cool in a desiccator. Weigh out accurately about 4·9 g. of the dry potassium dichromate into a weighing-bottle and transfer the salt quantitatively to a 1-litre measuring-flask (Section II, 6A (iii)), using a small funnel to avoid loss. Dissolve the salt in the flask in water and make up to the mark; shake well. Alternatively, place a little over 4·9 g. of potassium dichromate in a weighing-bottle, and weigh accurately. Empty the salt into a litre volumetric flask, and weigh the bottle again. Dissolve the salt in water, and make up to the mark. Mix thoroughly.

Calculate the exact normality by dividing the actual weight of the potassium dichromate employed by the theoretical weight for 1 litre of normal solution (49·035 g.). An exactly 0·1000 N solution may be prepared by weighing out 4·904 g. of the salt and dissolving it in 1 litre of water in a measuring-flask.

III, 65. Standardisation of potassium dichromate solution against iron.—For practice in this determination, use the 0·1N-potassium dichromate prepared in the previous Section. Use the method described in Section III, 48, Procedure C with 0·2 g., accurately weighed, of A.R. iron wire. Alternatively, a flask fitted with a Bunsen valve (Fig. III, 51, 2) may be employed: the air in the flask is similarly displaced by carbon dioxide. Titrate the cooled solution immediately with the dichromate solution, using either sodium diphenylamine sulphonate or N-phenylanthranilic acid as indicator. If the former is selected, add 6–8 drops of the indicator, followed by 5 ml. of syrupy phosphoric acid: titrate slowly with the dichromate solution, stirring well, until the pure green colour changes to a grey-green. Then add the dichromate solution dropwise until the first tinge of blue-violet, which remains permanent on shaking, appears. If the latter indicator is selected, add 200 ml. of 2N-sulphuric acid, then 0·5 ml. of the indicator; add the dichromate solution, with shaking until the colour changes from green to violet-red. Repeat the determination with two similar quantities of iron.

Calculate the normality of the potassium dichromate solution.

\[ 1 \text{ ml.} \ N-K_2Cr_2O_7 = 0.05584 \text{ g. Fe} \]

Note. For work requiring only moderate accuracy, A.R. ferrous ammonium sulphate may be used for standardisation. An approximately 0·1 N solution is prepared by weighing out accurately about 9·8 g. of the

* If a greater purity is required, or if only a pure grade of commercial salt is available, or if there is some doubt as to the purity of the salt, the following method of purification should be used. A concentrated solution of the salt in hot water is prepared and filtered. The crystals which separate on cooling are filtered on a sintered-glass filter-funnel (Section II, 12A) and sucked dry. The resultant crystals are recrystallised again. The purified crystals are then dried at 180–200°C, ground to a fine powder in a glass or agate mortar, and again dried at 140–160°C to constant weight.
solid and dissolving it in 250 ml. of 5 per cent sulphuric acid in a volumetric flask (Section III, 48, Procedure E). This is slowly titrated with the dichromate solution, using sodium diphenylamine sulphonate, N-phenylanthranilic acid or ferroin as indicator.

**ANALYSES INVOLVING THE USE OF STANDARD POTASSIUM DICHROMATE SOLUTIONS**

**III, 66. Determination of ferrous iron.**—For practice in the titration, the student should determine the percentage of iron in crystallised ferrous sulphate FeSO₄·7H₂O, preferably of A.R. grade.

Weigh out accurately about 14 g. of ferrous sulphate crystals, dissolve in 450 ml. of 5 per cent sulphuric acid in a 500-ml. measuring-flask and make up to the mark with distilled water. Shake well. Titrate 25-ml. portions against the standard 0·1N-potassium dichromate with sodium diphenylamine sulphonate (I)* and with N-phenylanthranilic acid (II) as examples of internal indicators, and with potassium ferrioyanide as an external indicator.

Use 8 drops (say 0·4 ml.) of the indicator I, add 200 ml. of 2·5 per cent sulphuric acid, followed by 5 ml. of 85 per cent phosphoric acid, and titrate slowly, whilst stirring constantly, with the standard dichromate until the solution assumes a bluish-green or greyish-blue tint near the end point. Continue the titration, adding the dichromate solution dropwise and maintaining an interval of a few seconds between each drop, until the addition of 1 drop causes the formation of an intense purple or violet-blue coloration, which remains permanent after shaking and is unaffected on the further addition of the dichromate. Carry out two or at most three titrations; these should agree within 0·1 ml.

Use 0·5 ml. of indicator II. Add about 200 ml. of 2N-sulphuric acid and then titrate with the 0·1N-potassium dichromate until the colour changes from green to violet-red. This titration is sharp to within 1 drop. Carry out two or three further titrations, which should agree within 0·1 ml.

For the determination with the external indicator, use 25 ml. of the ferrous solution, add 100 ml. of N (ca. 2·5 per cent) sulphuric acid, and proceed as detailed in Section III, 63. As in previous instances, carry out about three titrations; two successive values should agree within 0·1 ml.

Compare the mean volumes of the dichromate solution consumed in the three titrations with different indicators. These should not differ by more than 0·1 ml. Calculate the percentage of iron in the crystals.

1 ml. N-K₂Cr₂O₇ = 0·05584 g. Fe

**III, 67. Determination of ferric iron (iron in ferric ammonium sulphate).**—Weigh out accurately about 12 g. of A.R. ferric alum (NH₄)₂SO₄·Fe₂(SO₄)₃·24H₂O, transfer to a 250-ml. volumetric flask, dissolve in water containing about 50 ml of 2N (ca. 5 per cent) sulphuric acid, and make up to the mark with water. Shake well.

Of the various methods which can be employed for the reduction of the ferric iron, the stannous chloride method is very convenient, and,

* Or with diphenylamine or diphenylbenzidine; use 3 drops of the 1 per cent solution in concentrated sulphuric acid.
furthermore, illustrates the advantage of the use of dichromate solution when hydrochloric acid is present (compare Section III, 46).

Remove 25 ml. of the ferric solution, and reduce it with stannous chloride solution as described in Section III, 51A. Then add 200 ml. of 2·5 per cent sulphuric acid, 5 ml. of syrupy phosphoric acid, and 0·3-0·4 ml. of sodium diphenylamine sulphphonate indicator. * Titrate slowly and with constant stirring against standard 0·1N-potassium dichromate to the first permanent violet-blue coloration. Carry out two further titrations; these should agree within 0·1 ml.

Calculate the percentage of iron in ferric alum.

III, 68. Determination of the total iron in an iron ore.—The iron ore of Section III, 53, may be used, if desired. Weigh out accurately about 2 g. of the iron ore, dissolve it in dilute hydrochloric acid, and proceed exactly as described in Section III, 53, to the point where a solution in a 250-ml. volumetric flask is obtained. Remove 50 ml. of this solution, heat to boiling, and reduce the ferric iron by the stannous chloride method (Section III, 51A). Complete the determination as detailed in the previous Section. Carry out three separate titrations, which should agree within 0·1 ml., and take the mean of the results.

Calculate the percentage of iron in the ore.

Alternatively, 50 ml. of the prepared solution diluted to about 75 ml. may be reduced in the silver reductor (Section II, 396, Fig. II, 39, 1). Pass the solution through the silver reductor at the rate of about 25 ml. per minute, and collect the solution in a 600-ml. beaker. Wash the silver with six 25-ml. portions of dilute hydrochloric acid (1 : 10) when the first portion has fallen to a level about 5 mm. above the top of the silver column, turn off the stopcock and add a new portion, etc. Titrate the solution with 0·1N-potassium dichromate using either N-phenylanthranilic acid or sodium diphenylamine sulphphonate as indicator; with the latter indicator add 5 ml. of 85 per cent phosphoric acid. Carry out three separate titrations, which should agree within 0·1 ml., and take the mean of the results. The indicator blank may be as high as 0·05 ml., and should be determined if great accuracy is desired.

Calculate the percentage of iron in the ore.

III, 69. Determination of ferrous and ferric iron in an iron ore.—For this estimation, spathic iron ore or any other suitable iron ore may be used. Determine first the total iron by the method described in the preceding Section.

Determine the ferrous iron as follows. Weigh out accurately about 0·4 g. of the finely powdered iron ore into a 350-ml. flask fitted with wash-bottle tubes; displace the air by carbon dioxide from a Kipp's apparatus or from a cylinder of the gas fitted with a reducing valve. Open the flask momentarily and pour in 30 ml. of 1 : 1-hydrochloric acid. Replace the rubber stopper and tubes, and warm in a slow stream of carbon dioxide until the ore has been completely attacked and no further solution takes place. A whitish residue of silica remains in most cases. Cool in a stream of carbon dioxide, wash down the tubes and the neck of the vessel with a little cold, air-free distilled water, dilute with 200 ml. of 2·5 per cent sulphuric acid (which has been pre-

* Alternatively 3 drops of diphenylamine or of diphenylbenzidine indicator may be used.
pared with air-free water), add 5 ml. of syrupy phosphoric acid and 0.3–0.4 ml. of sodium diphenylamine sulphonate indicator, and titrate slowly and with constant stirring against standard 0.1N-potassium dichromate to the first permanent violet-blue coloration. Alternatively, 1 or 2 drops of ferroin may be used as indicator; here the addition of phosphoric acid is superfluous. Repeat the determination with two other similar quantities of the ore.

Calculate the percentages of total iron and ferrous iron in the ore. The difference between these two values gives the percentage of iron present in the ferric state.

III, 70. Determination of chromium in a chromic salt.—Discussion. Chromic salts are oxidised to dichromates by boiling with excess of a persulphate solution in the presence of a little silver nitrate (catalyst). The excess of persulphate remaining after the oxidation is complete is destroyed by boiling the solution for a short time. The dichromate content of the resultant solution is determined by the addition of excess of a standard ferrous solution and titration of the excess of the latter with standard 0.1N-potassium dichromate.

For practice in this determination, the student may determine the percentage of chromium in A.R. chrome alum, K$_2$SO$_4$Cr$_2$(SO$_4$)$_3$·24H$_2$O.

Procedure. Weigh out accurately about 2.5 g. of chrome alum, and dissolve it in 50 ml. of distilled water. Add 20 ml. of 0.1N-silver nitrate solution, followed by 50 ml. of a 10 per cent solution of ammonium or potassium persulphate. Boil the liquid gently (using a Fisher "speedyvap” beaker cover) for 20 minutes. Cool, and dilute to 250 ml. in a volumetric flask. Remove 50 ml. of the solution with a pipette, add 50 ml. of 0.1N-ferrous ammonium sulphate solution (Section III, 48, Procedure E), 200 ml. of 2N-sulphuric acid, and 0.5 ml. of N-phenylanthranilic acid indicator. Titrate the excess of the ferrous salt with standard 0.1N-potassium dichromate until the colour changes from green to violet-red.

Standardise the ferrous ammonium sulphate solution against the 0.1N-potassium dichromate, using N-phenylanthranilic acid as indicator (Section III, 68). Calculate the volume of the ferrous solution which was oxidised by the dichromate originating from the chrome alum, and from this the percentage of chromium in the sample.

\[1 \text{ ml. } \text{N-Fe}^{++} = 0.01734 \text{ g. Cr}\]

III, 71. Determination of chromium in chromite.—Discussion. The highly refractory mineral chromite is brought into solution by fusion with excess of sodium peroxide:

\[2\text{FeCr}_2\text{O}_4 + 7\text{Na}_2\text{O}_2 = 2\text{NaFeO}_2 + 4\text{Na}_2\text{CrO}_4 + 2\text{Na}_2\text{O}\]

Upon leaching the melt with water, the sodium chromate dissolves and the iron is precipitated as ferric hydroxide:

\[\text{NaFeO}_2 + 2\text{H}_2\text{O} = \text{NaOH} + \text{Fe(OH)}_3\]
\[2\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} = 4\text{NaOH}\]

The excess of peroxide is decomposed by boiling the alkaline solution. The precipitate is filtered off after diluting the solution; the filtrate is acidified with hydrochloric acid, a known volume of excess of ferrous
ammonium sulphate solution is added, and the excess of ferrous salt is
titrated with standard potassium dichromate solution.

\[
2\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{HCl} = \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl} + \text{H}_2\text{O}
\]

\[
\text{Na}_2\text{Cr}_2\text{O}_7 + 6\text{FeSO}_4 + 14\text{HCl} = 2\text{CrCl}_2 + 2\text{NaCl} + 2\text{Fe}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O}
\]

Procedure. Weigh out accurately about 0·5 g. of the very finely
powdered ore * into a 30-35-mI. nickel, or heavy-walled porcelain,
crucible, add 4 g. of sodium peroxide, and mix thoroughly by means of
a thin glass rod. Remove any powder adhering to the rod by stirring
about 1 g. of sodium peroxide with it; cover the mixture in the crucible
with this peroxide. Place the lid on the crucible, and gently heat the
covered crucible in the fume cupboard over a small flame until the
mass is quite liquid (about 10 minutes); keep fused for a further 10
minutes at a dull red heat. Allow to cool, and when a solid crust has
formed, add 4 g. more of the sodium peroxide, and fuse the mixture
again at a cherry-red heat for 10 minutes. Allow the crucible to cool
and place it in a 60-mI. Pyrex beaker containing a little distilled water.
Cover the beaker with a clock glass (or with a Fisher "speedyvap"
beaker cover), add a little warm water, and, after the violent action has
subsided, remove the crucible and wash it thoroughly, collecting the
washings in the same beaker. Boil the liquid for 30 minutes, keeping
the beaker covered (this decomposes the hydrogen peroxide), add 250
ml. of boiling water, and allow the precipitate to settle. Filter through
a hardened 15-cm. filter-paper or, better, through a sintered-glass
 crucible,† and wash the residue thoroughly with boiling water until free
from chromate. (The residue should be completely soluble in concen-
trated hydrochloric acid; no black gritty particles should remain.
If this is not the case, decomposition is not complete, and the determina-
tion must be started afresh.) Evaporate the filtrate to about 200 ml.,
cool, and add 9N-sulphuric acid cautiously until acid. Cool, transfer
to a 250-mI. measuring-flask, and make up to the mark with distilled
water. Shake well. Remove 50 ml. of this solution with a pipette,
add 50 ml. of 0·1N-ferrous ammonium sulphate (Section III, 48,
Procedure E), 200 ml. of 2N-sulphuric acid, and 0·5 ml. of N-phenyl-
anthranilic acid indicator. Titrate with standard 0·1N-potassium
dichromate until the colour changes from green to violet-red. Alterna-
tively, take 50 ml. of the solution, add 50 ml. of 0·1N-ferrous ammonium
sulphate, 5 ml. of syrupy phosphoric acid, and 0·4 ml. of sodium di-
phenylamine sulphonate indicator; dilute to 200 ml., and titrate with
standard 0·1N-potassium dichromate until the green colour changes
to violet-blue. Repeat until two titrations agree within 0·1 ml.

The ferrous ammonium sulphate solution must be standardised by
titration with the 0·1N-potassium dichromate; the same indicator as
was employed in the above determination must be used.

Calculate the volume of the ferrous solution which was oxidised by
the dichromate originating from the chromite, and from this the per-
centage of chromium in the original ore.

\[
1\text{ml. } N\text{-Fe}^{++} = 1\text{ml. } N\text{-K}_2\text{Cr}_2\text{O}_7 = 0·02534\text{ g. } \text{Cr}_2\text{O}_3 = 0·01734\text{ g. } \text{Cr}
\]

* Ridsdale's "Chrome Iron Ore, No. 40G" (one of the Analyzed Samples for Students)
is suitable for this determination.
† If the latter is used, it is unnecessary to add more than 160 ml. of boiling water;
the subsequent concentration is then avoided.
III. 72. Determination of manganese in steel or in manganese ore. (Pattinson’s method).—Discussion. When a solution containing iron, zinc, and manganese salts is treated with bromine water and calcium carbonate, all the manganese is precipitated in the quadrivalent condition as the manganite (e.g., \( \text{ZnO}_2\text{MnO}_3 \)). The precipitate is dissolved in excess of ferrous solution, and the excess of the latter titrated with standard potassium dichromate solution.

\[
\text{MnO}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 = \text{Fe}_2(\text{SO}_4)_3 + \text{MnSO}_4 + 2\text{H}_2\text{O}
\]

Procedure. Weigh out 2.5 g. of the steel or 1 g. of the manganese ore* and dissolve it in 50 ml. of concentrated hydrochloric acid in a covered beaker. Oxidise with a little nitric acid and evaporate to a small volume in order to expel the excess of acid. Transfer to a 250-ml. measuring-flask, after filtering through a sintered-glass crucible, if necessary. Make up to the mark with distilled water, and shake thoroughly. Transfer 50 ml. of the solution into a litre beaker, add 30 ml. of 3 per cent zinc chloride solution, and then add pure calcium carbonate in small quantities at a time until the liquid is almost neutralised, but still remains clear. Add 100 ml. of saturated bromine water, and then more calcium carbonate with constant stirring until an excess of about 1 g. remains undissolved. Add 700 ml. of boiling water to the contents of the beaker, stir well, and allow the insoluble residue to settle for a few minutes. If the supernatant liquid is violet due to permanganic acid, add 1–2 drops of alcohol, boil until colourless, and again allow the precipitate to settle. Decant the liquid through a funnel containing a large hardened filter-paper; it is better to allow the latter to rest on a Whatman filter-cone (hardened, No. 51), so that suction may be applied. Wash the precipitate four times by decantation, using 300 ml. of hot water each time. Transfer the precipitate to the filter, rinsing out the beaker well without making any attempt to remove the precipitate which adheres to the glass. Wash the precipitate with hot water until the filtrate no longer turns starch–potassium iodide–paper blue. Place the filter-paper and precipitate in the original beaker, add 50 ml. of freshly standardised 0.1N-ferrous ammonium sulphate and 50 ml. of 9N-sulphuric acid. Stir the mixture until the precipitate has entirely dissolved. Titrate the excess of ferrous salt with standard 0.1N-potassium dichromate. Repeat the estimation with two other 50-ml. portions of the solution.

Calculate the percentage of manganese in the sample.

\[
1 \text{ ml. } N\text{-K}_2\text{Cr}_2\text{O}_7 = 0.02747 \text{ g. Mn}
\]

(For a potentiometric titration method in pyrophosphate solution with standard potassium permanganate solution, see Section VI, 12; this is one of the best methods for the volumetric determination of manganese.)

* Suitable samples are Riddalde’s “Steel, No. 21” and “Pyrolusite (Mn) Ore, No. 18” (Analysed Samples for Students) or the Bureau of Analysed Samples “Carbon Steel, No. 161” and “Mang. Ore, No. 176” (British Chemical Standards).
OXIDATIONS WITH CERIC SULPHATE

III, 73. General discussion.—Ceric sulphate is a powerful oxidising agent; its oxidation potential in 1-8N-sulphuric acid at 25° C. is 1·43 ± 0·05 volts (compare Section I, 46). It can be used only in acid solution, best in 0-5N or higher concentrations: in neutral or alkaline solutions, basic ceric or perceric salts respectively may be formed. The solution has an intense yellow colour, and in hot solutions which are not too dilute the end point may be detected without an indicator; the latter procedure, however, necessitates the application of a blank correction, and it is therefore preferable to add a suitable indicator. It should be noted, however, that the self-colour of ceric solutions is less pronounced than that of permanganate solutions, and the titration with an oxalate cannot be so readily carried out (compare Section III, 76).

The advantages of ceric sulphate as a standard oxidising agent are:

1. Ceric sulphate solutions are remarkably stable over prolonged periods. They need not be protected from light, and may even be boiled for a short time without appreciable change in concentration. The stability of sulphuric acid solutions covers the wide range of 10–40 ml. of concentrated sulphuric acid per litre. It is evident, therefore, that an acid solution of ceric sulphate surpasses a permanganate solution in stability.

2. Ceric sulphate may be employed in the determination of reducing agents in the presence of a high concentration of hydrochloric acid (contrast potassium permanganate, Section III, 46).

3. Ceric solutions in 0·1N solution are not too highly coloured to obstruct vision when reading the meniscus in burettes and other volumetric apparatus.

4. It was formerly generally assumed that the reaction involved the simple valency change:

\[ \text{Ce}^{+++} + e \rightleftharpoons \text{Ce}^{++} \]

the equivalent weight of a ceric salt is therefore the molecular weight. With permanganate, of course, a number of reduction products are possible according to the experimental conditions.

The work of G. F. Smith and Getz (1938) upon the single electrode potentials of the ceric, cerous system in the presence of varying concentrations of sulphuric, nitric, and perchloric acids has yielded the following results:

<table>
<thead>
<tr>
<th>Acid Concentration</th>
<th>Single Electrode Potential Values (Volts).</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.</td>
<td>H$_2$SO$_4$</td>
</tr>
<tr>
<td>1</td>
<td>1·44</td>
</tr>
<tr>
<td>2</td>
<td>1·44</td>
</tr>
<tr>
<td>4</td>
<td>1·43</td>
</tr>
<tr>
<td>6</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>1·42</td>
</tr>
</tbody>
</table>
Since the single electrode potential varies considerably with the anion of the acid used, but only slightly with its concentration, these authors conclude that the results support the view that the following equilibria are present in the three solutions respectively:

\[
\begin{align*}
\frac{[\text{Ce}^{+++}] \times [\text{SO}_4^{--}]}{[\text{Ce}^{+++}] \times [\text{NO}_3^-]} &= \frac{[\text{Ce}^{+++}] \times [\text{ClO}_4^-]}{[\text{Ce}^{+++}] \times [\text{ClO}_4^-]}
\end{align*}
\]

No measurements are at present available of the instability constants of the various ions (Section I, 12), but it would appear that the ionic equilibria present, say, with ceric sulphate in the presence of concentrations of sulphuric acid in excess of that required to prevent hydrolysis could be represented by:

\[
\text{H}_4[\text{Ce}^{(SO_4)_4}] \rightleftharpoons 4\text{H}^+ + [\text{Ce}^{(SO_4)_4}]^{---} \rightleftharpoons 4\text{H}^+ + \text{Ce}^{+++} + 4\text{SO}_4^{--}
\]

Hence the actual reaction which takes place in the presence of a reducing agent, particularly for ceric sulphate in sulphuric acid solution which has been most extensively studied, may still be regarded as:

\[
\text{Ce}^{+++} + e \rightleftharpoons \text{Ce}^{+++}
\]

G. F. Smith terms the acid sulphatoceric acid and the ammonium salt, previously formulated as \(\text{Ce}^{(SO_4)_4}2(\text{NH}_4)_2\text{SO}_42\text{H}_2\text{O}\), tetra-ammonium sulphatocerate \(\text{(NH}_4)_4[\text{Ce}^{(SO_4)_4}]2\text{H}_2\text{O}\). The original term ceric sulphate will be used throughout this book where the reagent is employed in the presence of excess of sulphuric acid.

5. The cerous ion is colourless (compare colourless manganous ion from potassium permanganate, and green chromic ion from potassium dichromate).

6. Ceric sulphate is a very versatile oxidising agent. It may be employed in most titrations in which permanganate has been used, and also for other estimations.

7. The indicators which have been used in ceric sulphate titrations include: diphenylamine, diphenylbenzidine, sodium diphenylamine sulphonate (with these three indicators, phosphoric acid must be present), erioflavine, erio green, xylene cyanol FF, ferroin, and \(N\)-phenylanthranilic acid. The last two indicators give the most striking colour changes, and thus render the determination of the correct end point a very easy matter: moreover, the addition of phosphoric acid is unnecessary.

8. Ceric sulphate solutions can be readily standardised against arsenious oxide, pure iron, anhydrous potassium ferrocyanide, anhydrous sodium thiosulphate, and also ferrous solutions, and also indirectly against sodium oxalate (Section III, 76).

Solutions of ceric sulphate may be readily prepared by dissolving pure ceric sulphate or the more soluble ceric ammonium sulphate \(\text{Ce}^{(SO_4)_4}2(\text{NH}_4)_2\text{SO}_42\text{H}_2\text{O}\) (more correctly termed tetra-ammonium sulphatocerate \(\text{(NH}_4)_4[\text{Ce}^{(SO_4)_4}]2\text{H}_2\text{O}\)) in dilute sulphuric acid. These solid reagents are relatively expensive. Ceric ammonium nitrate, more correctly termed ammonium hexanitratocerate \(\text{(NH}_4)_5[\text{Ce}^{(NO_3)_5}]\), technical quality,\(^*\) is inexpensive: two recrystallisations from hot dilute nitric acid \((1:3)\) in the presence of a little ammonium nitrate, followed by drying at 80–85° C., gives a product with a purity exceeding 99 per cent. For most purposes one recrystallisation suffices and the

\(^*\) The product obtainable from Johnson, Matthey and Co., Ltd., Hatton Garden, London, E.C.1, costs 8s. per pound (1950).
product is 93–95 per cent pure; the yield is about 60 per cent. The purified ceric ammonium nitrate (which may be purchased, but is relatively expensive) may be dissolved in 2N-sulphuric acid and employed for many purposes for which ceric sulphate is used. The conversion of ammonium hexanitratocerate into ceric sulphate by evaporation with concentrated sulphuric acid is a simple process, and the resulting ceric sulphate may be dissolved in warm 2N-sulphuric acid. The author recommends that this be done; any possible harmful effects of nitrate ions are thus avoided. For smaller quantities, i.e., sufficient to produce 500 ml. or 1 litre of 0·1N-ceric sulphate, it is more convenient to dissolve the purified ceric ammonium nitrate in water, add an excess of dilute ammonia solution, filter off the precipitated ceric hydroxide on a sintered-glass funnel, wash well with water to remove ammonium nitrate, and to dissolve the precipitate in warm 2N- or 4N-sulphuric acid: the conversion of ceric ammonium nitrate into ceric sulphate by this process is practically quantitative. This simple procedure provides a very facile and inexpensive method for preparing ca. 0·1N-ceric sulphate solution.

III, 74. Preparation of 0·1N-ceric sulphate.—Method A. Recrystallise 125 g. of ceric ammonium nitrate (ammonium hexanitratocerate), technical, by warming with 100 ml. of dilute nitric acid (1 : 3 by volume) and 40 g. of ammonium nitrate until dissolved, filtering the boiling solution if necessary through a sintered-glass funnel, and cooling in ice. Filter the solid which separates through a sintered-glass funnel, wash well with water to remove ammonium nitrate, and to dissolve the precipitate in warm 2N- or 4N-sulphuric acid: the conversion of ceric ammonium nitrate into ceric sulphate by this process is practically quantitative. This simple procedure provides a very facile and inexpensive method for preparing ca. 0·1N-ceric sulphate solution.

Dissolve about 28 g. of the dry, recrystallised ceric ammonium nitrate (equivalent and molecular weight = 548·27) in 100 ml. of water in a 600-ml. beaker, add dilute ammonia solution slowly and with stirring until a slight excess is present (about 60 ml. of ca. 2·5N-ammonia solution are required). Filter the precipitated ceric hydroxide with suction through a 7-cm. sintered-glass funnel, and wash with five 50-ml. portions of water to remove ammonium nitrate; leave the precipitate “on the water-pump” for about 30 minutes to remove as much water as possible. Transfer the precipitate back to the original beaker as far as possible and remove the residual ceric hydroxide on the sintered-glass filter by washing with four 50-ml. portions of 4N-sulphuric acid previously warmed to about 60° C. (1). Add the washings to the precipitate in the beaker, and warm until the precipitate dissolves completely. Allow to cool, transfer the solution to a 500-ml. volumetric flask, and make up to the mark with distilled water. The resulting solution of ceric sulphate is about 0·1N, and requires standardisation before use.

Note. 1. Experienced workers will probably prefer to allow the four 50-ml. portions of 4N-sulphuric acid at 60° C. to percolate through the precipitate (no suction is applied). All the precipitate will have dissolved during the addition of the fourth portion of acid. An almost quantitative conversion of the ceric ammonium nitrate into ceric sulphate is thus obtained. The filtrate is allowed to cool and then diluted to 500 ml.
The following alternative procedure may be used for the preparation of large volumes of ceric sulphate solution. Evaporate 55.0 g. of dry ceric ammonium nitrate almost to dryness with excess (48 ml.) of concentrated sulphuric acid either in a Pyrex evaporating-dish or in a shallow ("Baco") beaker. Dissolve the resulting ceric sulphate in 2N-sulphuric acid (28 ml. of concentrated sulphuric acid to 500 ml. of water), transfer to a 1-litre volumetric flask, add 2N-sulphuric acid until near the graduation mark, and make up to the mark with distilled water. Shake well.

**Method B.** The molecular weight and also the equivalent weight of ceric sulphate $\text{Ce(SO}_4\text{)}_2$ and ceric ammonium sulphate (tetra-ammonium sulphatocerate) $(\text{NH}_4)_4[\text{Ce(SO}_4\text{)}_4]_2\text{H}_2\text{O}$ are 333.25 and 632.57 respectively.

Weigh out 35-36 g. of pure ceric sulphate into a 600-ml. beaker, add 56 ml. of 1 : 1 sulphuric acid and stir, with frequent additions of water and gentle warming, until the salt is dissolved. Transfer to a glass-stoppered volumetric flask and, when cold, dilute to the mark with distilled water. Shake well.

Weigh out 64-66 g. of ceric ammonium sulphate into a solution prepared by adding 28 ml. of concentrated sulphuric acid to 500 ml. of water: stir the mixture until the solid has dissolved. Transfer to a 1-litre measuring-flask, and make up to the mark with distilled water. Shake well.

**III, 75. Standardisation of ceric sulphate solutions.—Discussion.** The most trustworthy method for standardising ceric sulphate solutions is with pure arsensious oxide. The reaction between ceric sulphate (sulphatoceric acid) and arsensious oxide is very slow at the ordinary temperature; it is necessary to add a trace of osmium tetroxide as catalyst. The arsensious oxide is dissolved in sodium hydroxide solution, the solution acidified with dilute sulphuric acid, 2 drops of "osmic acid" solution * added, followed by the indicator, and the resulting solution is titrated with the ceric sulphate solution to the first sharp colour change. As already pointed out (Section III, 78) the most satisfactory indicators are: (i) 0.025M-tri-ortho-phenanthroline ferrous sulphate or ferroin † (1 or 2 drops), and (ii) 0.005M-phenylanthranilic acid ‡ (0.5 ml.). The colour changes are respectively: (i) orange-red to very pale blue, and (ii) yellowish-green to purple.

\[
\begin{align*}
\text{As}_2\text{O}_3 + 6\text{NaOH} &= 2\text{Na}_2\text{AsO}_3 + 3\text{H}_2\text{O} \\
2\text{Na}_2\text{AsO}_3 + 3\text{H}_2\text{SO}_4 &= 2\text{H}_2\text{AsO}_3 + 3\text{Na}_2\text{SO}_4 \\
\text{H}_2\text{AsO}_3 + 2\text{Ce(SO}_4\text{)}_2 + \text{H}_2\text{O} &= \text{H}_3\text{AsO}_4 + \text{Ce}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 \\
\text{or [Ce(SO}_4\text{)}_4]^{4-} + \text{AsO}_3^{3-} + \text{H}_2\text{O} &= 2\text{Ce}^{3+} + \text{AsO}_4^{3-} + 2\text{H}^+ + 8\text{SO}_4^{2-}
\end{align*}
\]

Four other direct methods are available for standardising ceric sulphate solutions, viz., with pure iron, with pure anhydrous potassium ferrocyanide, with pure anhydrous sodium thiosulphate, and with pure ferrous ammonium sulphate.

* The "osmic acid" solution (or 0.01M-osmium tetroxide solution) is prepared by dissolving 0.1 g. of osmium tetroxide in 10 ml. of 0.1N-sulphuric acid.
† The 0.025M-ferroin, $(\text{C}_6\text{H}_5\text{N}_3)_2\text{FeSO}_4$, may be purchased or may be prepared, if desired, as follows. Dissolve 1.485 g. of ortho-phenanthroline monohydrate $\text{C}_6\text{H}_5\text{N}_3\text{H}_2\text{O}$ in 100 ml. of 0.025M-ferrous sulphate (0.005 g. of ferrous sulphate $\text{FeSO}_4\cdot7\text{H}_2\text{O}$ in 100 ml. of water).
‡ Dissolve 1.07 g. of N-phenylanthranilic acid in 20 ml. of 5 per cent sodium carbonate solution, and dilute to 1 litre.
A known weight of pure iron is dissolved in dilute sulphuric acid, and the resulting ferrous sulphate solution is titrated with the ceric sulphate solution:

\[ 2\text{FeSO}_4 + 2\text{Ce}(\text{SO}_4)_2 = \text{Fe}_2(\text{SO}_4)_3 + \text{Ce}_2(\text{SO}_4)_3 \]

The best indicators are ferroin and N-phenylanthranilic acid. Good results are obtained with erioglaucine (0.5 ml. of a 0.1 per cent solution); the colour change is from greenish-yellow to pink. Erioglaucine (0.5 ml. of a 0.1 per cent solution) may also be used, but the colour change at the equivalence point is less marked than for erioglaucine. For work not requiring a very high degree of accuracy, pure ferrous ammonium sulphate may be used (see remarks in the last paragraph of Section III, 46).

Pure anhydrous potassium ferrocyanide is readily obtained, and possesses the advantage of a high molecular weight (368.34). The reaction is:

\[ 2\text{K}_4[\text{Fe(ON)}_6] + 2\text{Ce}(\text{SO}_4)_2 = 2\text{K}_3[\text{Fe(CN)}_6] + \text{Ce}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 \]

N-Phenylanthranilic acid and erioglaucine are suitable indicators; ferroin cannot be used, owing to the formation of a dark precipitate when it is added to the ferrocyanide solution.

Pure anhydrous sodium thiosulphate (Section III, 101) may be easily prepared from the A.R. pentahydrate. Its use in the standardisation of ceric sulphate solutions is based upon the following reactions:

\[ 2\text{Ce}^{+++} + 2\text{I}^- = 2\text{Ce}^{+++} + \text{I}_2 \]
\[ \text{I}_2 + 2\text{S}_2\text{O}_3^{--} = 2\text{I}^- + \text{S}_4\text{O}_6^{--} \]

Upon the addition of excess of potassium iodide solution and a little starch solution and titration with ceric sulphate, the equivalence point will be indicated by the first appearance of a blue colour. It is important that the experimental conditions given below be closely followed: the results are then highly satisfactory.

The direct standardisation of ceric sulphate solutions against pure sodium oxalate in hot dilute sulphuric acid is best carried out potentiometrically (Chapter VI); most oxidation-reduction indicators are oxidised before the equivalence point is reached. An indirect procedure is given in Section III, 76.

Procedure A. Standardisation with arsenious oxide. Weigh out accurately about 0.25 g. of A.R. arsenious oxide, previously dried at 105–110°C for 1–2 hours, and transfer to a 400-ml. beaker or to a 350-ml. conical flask. Add 20 ml. of 5 per cent sodium hydroxide solution, and warm the mixture gently until the arsenious oxide has completely dissolved (1). Cool to room temperature, and add 100 ml. of water, followed by 25 ml. of 1:5-sulphuric acid. Then add 3 drops of 0.01M-osmium tetroxide solution (0.25 g. of osmium tetroxide dissolved in 100 ml. of 0.1N-sulphuric acid) and 0.5 ml. of N-phenylanthranilic acid indicator (or 0.5 ml. of erioglaucine, or 1–2 drops of ferroin). Titrate with the 0.1N-ceric sulphate solution until the first sharp colour change occurs (see Discussion above). Repeat with two other samples of approximately equal weight of arsenious oxide.

Calculate the normality of the ceric sulphate solution (for details, see Section III, 48, Procedure A).
Note. 1. Elementary students may prepare 250 ml. of an approximately 0·1N-arsenious oxide solution, and titrate 25 ml. of this with the ceric solution as described above. Full details for the preparation of the solution and the method for the calculation of the result will be found in Section III, 48, Procedure A, Note 1.

Procedure B. Standardisation against pure iron. Weigh out accurately 0·15–0·20 g. of A.R. iron wire, and then proceed exactly as described in Section III, 48, Procedure C. Titrate the resulting ferrous solution with the ceric sulphate solution, using any of the indicators referred to in the Discussion.

Another method, which incidentally utilises the stannous chloride process of reduction, is the following. Weigh out accurately about 0·20 g. of A.R. iron wire into a 400-ml. beaker or into a 350-ml. conical flask. Add 5 ml. of water and 10 ml. of concentrated hydrochloric acid. Warm the solution until all the iron has dissolved. Heat the solution to boiling, and add freshly prepared 0·5N-stannous chloride, dropwise and with constant stirring, from a burette or separating-funnel (Section III, 51A) until the hot solution no longer shows any yellow colour and a few drops of the reducing agent causes the colour to change from yellow to very pale green. Cool, add 5 ml. of concentrated hydrochloric acid, dilute the solution with cold air-free water to 250 ml., and add 10 ml. of a saturated solution of mercuric chloride. A slight white silky precipitate of mercurous chloride should be formed, sometimes after 1–2 minutes. (If the precipitate is bulky or grey in colour, the solution should be rejected, and the estimation repeated.) Add a drop or two of ferroin (or 0·5 ml. of N-phenylanthranilic acid) and titrate slowly with the ceric sulphate solution until the sharp colour change from red to a faint yellow or green colour occurs. Alternatively, add 5 ml. of syrupy phosphoric acid, 0·5 ml. of sodium diphenylamine sulphonate, then titrate the mixture with the ceric sulphate solution (proceed slowly near the end point) until the solution assumes a distinct purple tint. Repeat with two other samples of the A.R. iron wire.

Calculate the normality of the ceric sulphate solution.

Procedure C. Standardisation against ferrous ammonium sulphate. As pointed out in Section III, 46, this method is only suitable for work requiring moderate accuracy or for elementary students. Prepare an approximately 0·1N-solution of ferrous ammonium sulphate (Section III, 48, Procedure E). Transfer 25 ml. of this solution to a conical flask, add 25 ml. of N-sulphuric acid, and the appropriate quantity of erio-glucine, ferroin, or N-phenylanlanilic acid (see Discussion above); titrate with the ceric sulphate solution to the first sharp colour change. Carry out two or at most three titrations; these should agree within 0·1 ml.

Alternatively, the ferrous solution may be placed in the burette, and 25-ml. portions of the ceric solution titrated. The end points are equally satisfactory, although when once the colour of the ceric solution has been bleached, it is advisable to add the ferrous solution slowly.

Calculate the normality of the ceric sulphate solution.

Procedure D. Standardisation against anhydrous potassium ferrocyanide. Dehydrate about 50 g. of A.R. potassium ferrocyanide trihydrate by heating the powdered solid to constant weight at 100–110°C., and allow to cool in a desiccator over anhydrous calcium chloride. Prepare a 0·1N solution by weighing out 18·415 g. of the anhydrous
Quantitative Inorganic Analysis

salt and dissolving it in 500 ml. of boiled-out water in a volumetric flask (1).

Dilute 25 ml. of the ferrocyanide solution with 25 ml. of water, add 50 ml. of 4N-sulphuric acid, and either 0·5 ml. of N-phenylanthranilic acid or 0·5 ml. of erioglaucine indicator, and titrate with the ceric sulphate solution to the first sharp colour change. Repeat the titration with two other 25-ml. portions of the ferrocyanide solution; these should give titres of ceric sulphate solution which agree well within 0·1 ml. Calculate the normality of the ceric sulphate solution.

Alternatively, weigh out accurately about 0·95 g. of the anhydrous potassium ferrocyanide into a 350-ml. conical flask or 400-ml. beaker, dissolve it in 100 ml. of 2N-sulphuric acid, add N-phenylanthranilic acid or erioglaucine indicator, and titrate with the ceric sulphate solution until the first sharp colour change occurs. Repeat with two other samples of approximately equal weight of anhydrous potassium ferrocyanide. Calculate the normality of the ceric sulphate solution.

Note. 1. The molecular weight and the equivalent weight of anhydrous potassium ferrocyanide is 388·34. The aqueous solution is stable for several days. A solution of potassium ferrocyanide in 2N-sulphuric acid is unstable; it soon develops a bluish-green coloration, and should therefore be titrated within an hour of its preparation.

Procedure E. Standardisation against anhydrous sodium thiosulphate. Weigh out accurately about 0·4 g. (1) of anhydrous sodium thiosulphate (Section III, 101) into a 500-ml. conical flask, dissolve it in water, add 0·3–0·4 g. of A.R. potassium iodide, 20 ml. of 0·2 per cent starch solution, dilute to 250 ml., and titrate with the ceric sulphate solution to the starch–iodine end point. Repeat the titration with two other similar portions of anhydrous sodium thiosulphate. Calculate the normality of the ceric sulphate solution.

Note. 1. Alternatively, a 0·1N solution of sodium thiosulphate may be prepared by weighing out 3·953 g. of anhydrous sodium thiosulphate (the equivalent and molecular weight is 158·13) and dissolving it in 250 ml. of boiled-out distilled water in a volumetric flask. Twenty-five-ml. portions are titrated as detailed above. The normality of the ceric sulphate solution is then calculated (see Section III, 4A).

ANALYSES INVOLVING THE USE OF STANDARD CERIC SULPHATE SOLUTIONS

Practically all the determinations described under potassium permanganate and potassium dichromate may be carried out with ceric sulphate. Use is made of the various indicators already detailed and also, in some cases where great accuracy is not required, of the pale yellow colour produced by the ceric sulphate itself. Only a few determinations will therefore be considered in some detail.

III, 76. Determination of oxalates ($H_2C_2O_4$ in crystallised oxalic acid). —Discussion. This determination will give the student practice in the titration of oxalates with ceric sulphate solution. Two methods may be used. In the first, the ceric sulphate solution is run into the hot solution of oxalic acid acidified with dilute sulphuric acid until the
solution acquires a pale yellow colour, the ceric solution thus acting as its own indicator.

\[
H_2C_2O_4 + 2Ce(SO_4)_2 = 2CO_2 + Ce_2(SO_4)_3 + H_2SO_4
\]

In the second procedure, a known excess of the ceric solution is added to the oxalic acid solution, the mixture warmed for 5 minutes at 50° C. in order to complete the reaction, and, after cooling, the excess of ceric sulphate is titrated with ferrous ammonium sulphate solution, using \(N\)-phenylanthranilic acid or ferroin as indicator.

The latter method provides an excellent means for standardising ceric sulphate solutions. Thus if roughly equivalent solutions (say, of about 0·1N strength) of ceric sulphate and of ferrous ammonium sulphate be titrated, the relative concentrations will be found. Now if a known weight of A.R. sodium oxalate be dissolved in dilute sulphuric acid, excess of the ceric sulphate solution added, the mixture heated at 50° C. for 5 minutes, and, after cooling, back titrated with the ferrous ammonium sulphate solution, then the volume of ceric sulphate solution equivalent to the known weight of the pure sodium oxalate is obtained. The normality of the ceric sulphate solution can then be readily calculated.

**Procedure.** Weigh out accurately about 3·15 g. of A.R. crystallised oxalic acid (\(H_2C_2O_4\cdot2H_2O\)), dissolve it in water, and make up to 500 ml. in a volumetric flask. Shake well. With a pipette transfer 25 ml. of this solution into a conical flask, add 25 ml. of \(N\)-sulphuric acid, heat to 70-80° C., and titrate with the 0·1N-ceric sulphate until the solution assumes a faint yellow colour. Repeat the titration with 50 ml. of \(N\)-sulphuric acid, heat to 70-80° C., and add the ceric sulphate solution until the solution has the same colour as in the previous titration. Subtract this blank correction from the volume of 0·1N-ceric sulphate consumed in the titration with the oxalic acid solution. Carry out two other titrations with the oxalic acid solution; the values should agree within 0·1-0·2 ml.

Calculate the percentage of \(H_2C_2O_4\) in the oxalic acid crystals.

\[
1 \text{ ml. } N-Ce(SO_4)_2 = 0·04502 \text{ g. } H_2C_2O_4
\]

For the alternative method, prepare an approximately 0·1N solution of ferrous ammonium sulphate (Section III, 48, Procedure E). Place this in the burette and titrate it against a mixture of 25 ml. of the 0·1N-ceric sulphate and 25 ml. of \(N\)-sulphuric acid, using ferroin (1 drop) or \(N\)-phenylanthranilic acid (0·5 ml.) as indicator. Measure out 25 ml. of the oxalic acid solution into a conical flask, add 50 ml. of 0·1N-ceric sulphate and 50 ml. of \(N\)-sulphuric acid. Warm the mixture at 50° C. for 5 minutes, cool, and titrate the excess of ceric sulphate with the ferrous solution, employing the same indicator as in the first titration. Repeat the determination with two other 25-ml. portions of the oxalic acid solution; the titrations should agree within 0·1 ml.

Calculate the volume of the 0·1N-ceric sulphate that has reacted with the oxalic acid, and hence the percentage of \(H_2C_2O_4\) in the oxalic acid crystals.

**III, 77. Determination of iron in an iron ore.**—The procedure is identical with that given in Section III, 68, except that after the reduction with stannous chloride, addition of excess of mercuric chloride solution, and 200 ml. of 2·5 per cent sulphuric acid, 1 or 2 drops of
Quantitative Inorganic Analysis

ferroin or 0·5 ml. of N-phenylanthranilic acid is added. The mixture is then titrated with 0·1N-meric sulphate to the first sharp colour change.

Calculate the percentage of iron in the ore.

\[ 1 \text{ ml. } N-\text{Ce(SO}_4\text{)}_2 = 0·05584 \text{ g. Fe} \]

In an alternative procedure the solution of the iron ore in hydrochloric acid is prepared as detailed in Section III, 53. Remove 50 ml. of the prepared solution, dilute to about 75 ml., and pass the solution through a silver reductor (Section II, 39C) at the rate of about 25 ml. per minute; collect the reduced solution in a beaker. Wash the silver column with five portions of dilute hydrochloric acid (1:10) of about 25 ml. each; close the stopcock when the level of the liquid has fallen to about 5 mm. above the top of the column before adding a further portion. Rinse the sides of the upper bulb occasionally. Add 10 ml. of concentrated hydrochloric acid to the cool solution immediately, then 2–3 drops of ferroin (or 0·5 ml. of N-phenylanthranilic acid), and titrate with standard ceric sulphate solution. Determine the indicator blank by taking an equal volume of water, adding 10 ml. of concentrated hydrochloric acid, and titrating to the same colour change.

III, 78. Determination of nitrates.—Discussion. Satisfactory results are obtained by adding the nitrite solution to excess of standard 0·1N-meric sulphate, and determining the excess of ceric sulphate with a standard ferrous solution (compare Section III, 58).

\[ 2\text{Ce}^{+++} + \text{NO}_2^- + \text{H}_2\text{O} = 2\text{Ce}^{++} + \text{NO}_3^- + 2\text{H}^+ \]

For practice, the student may determine the percentage of NO\textsubscript{2} in potassium nitrite, or the purity of sodium nitrite, preferably of A.R. quality.

Procedure. Weigh out accurately about 1·5 g. of sodium nitrite and dissolve it in 500 ml. of boiled-out water in a volumetric flask. Shake thoroughly. Place 50 ml. of standard 0·1N-meric sulphate in a conical flask, and add 10 ml. of 4N-sulphuric acid. Transfer 25 ml. of the nitrite solution to this flask by means of a pipette, and keep the tip of the pipette below the surface of the liquid during the addition. Allow to stand for 5 minutes, and titrate the excess of ceric sulphate against standard 0·1N-ferrous ammonium sulphate, using ferroin or N-phenylanthranilic acid as indicator. Repeat the titration with two further portions of the nitrite solution. Standardise the ferrous solution by titrating it with 25 ml. of the ceric solution in the presence of dilute sulphuric acid (Section III, 75C).

Determine the volume of the standard ceric sulphate solution which has reacted with the nitrite solution, and therefrom calculate the purity of the sodium nitrite employed.

\[ 1 \text{ ml. } N-\text{Ce(SO}_4\text{)}_2 = 0·02301 \text{ g. } \text{NO}_2 \]

III, 79. Determination of copper.—Discussion. Cupric copper is quantitatively reduced in 2N-hydrochloric acid solution by means of the silver reductor (Section II, 39C) to the cuprous state. The solution of the cuprous salt is collected in a solution of ferric alum, and the ferrous iron formed is titrated with standard ceric sulphate solution using ferroin or N-phenylanthranilic acid as indicator.

Comparatively large amounts of nitric acid, and also zinc, cadmium,
bismuth, tin, and arsenate have no effect upon the determination; the method may therefore be applied to determine copper in brass.

**Procedure (copper in crystallised copper sulphate).** For initial practice, the student may determine the copper content of A.R. cupric sulphate pentahydrate.

Weigh out accurately about 3·1 g. of A.R. copper sulphate crystals, dissolve in water, and make up to 250 ml. in a volumetric flask. Shake well. Pipette 50 ml. of this solution into a small beaker, add an equal volume of ca. 4N-hydrochloric acid. Pass this solution through a silver reductor at the rate of 25 ml. per minute, and collect the filtrate in a 350-ml. conical flask charged with 20 ml. of 0·5M-ferric alum solution (prepared by dissolving the appropriate quantity of A.R. iron alum in N-sulphuric acid). Wash the reductor column with six 25-ml. portions of 2N-hydrochloric acid (for details, see Section III, 77). Add 1 drop of ferroin indicator or 0·5 ml. of N-phenylanthranilic acid, and titrate with 0·1N-ceric sulphate solution. The end point is sharp, and the colour imparted by the cupric ions does not interfere with the detection of the equivalence point. Determine the volume of the 0·1N-ceric sulphate which has reacted with the ferrous salt produced, and calculate therefrom the percentage of copper in the sample of A.R. cupric sulphate.

\[
1 \text{ml. } N\text{-Ce(SO}_4\text{)}_2 = 0\cdot06357 \text{ g. Cu}
\]

**Procedure (copper in brass).** Weigh out accurately about 0·3 g. of brass* into a 250-ml. beaker, add 1 ml. of concentrated nitric acid and 4 ml. of concentrated hydrochloric acid, and heat until the solid has dissolved completely. Dilute to 150 ml.; neutralise the solution with ammonia solution, and add a slight excess to precipitate iron. If iron is present, filter through a quantitative filter-paper and wash well. Concentrate the combined filtrate and washings to 40 ml., and add sufficient hydrochloric acid to make the concentration 2N, and reduce the solution in the silver reductor as detailed above. Add a drop of ferroin or 0·5 ml. of N-phenylanthranilic acid to the filtrate from the silver reductor (collected in 20 ml. of 0·6M-ferric alum solution), and titrate the ferrous salt produced with 0·1N-ceric sulphate. Calculate the percentage of copper in the sample of brass.

**III, 80. Determination of molybdenum.—Discussion.** Molybdates (MoVII) are quantitatively reduced in 2N-hydrochloric acid solution at 60–80° C. by the silver reductor to quinquevalent molybdenum (MoV). The reduced molybdenum solution is sufficiently stable over short periods of time in air to be titrated against standard ceric sulphate solution with ferroin or N-phenylanthranilic acid as indicator (compare Section II, 39C). Nitric acid must be completely absent; the presence of phosphoric acid during the reduction of the molybdenum (MoVII) is not harmful and, indeed, increases the rapidity of the subsequent oxidation with ceric sulphate.

**Procedure.** Weigh out accurately about 2·5 g. of A.R. ammonium molybdate (NH₄)₆Mo₇O₂₄.4H₂O, dissolve in water, and make up to 250 ml. in a volumetric flask. Pipette 50 ml. of this solution into a small beaker, add an equal volume of 4N-hydrochloric acid, then 3 ml. of 85 per cent phosphoric acid, and heat the solution to 60–80° C. Pour

* Ridesdale’s "Brass, No. 5e" (one of the Analysed Samples for Students) may be used.
Quantitative Inorganic Analysis

hot 2N-hydrochloric acid through a silver reductor, and then pass the molybdate solution through the hot reductor at the rate of about 10 ml. per minute. Collect the reduced solution in a 400-ml. beaker or 350-ml. conical flask, and wash the reductor with six 25-ml. portions of 2N-hydrochloric acid; the first two washings should be made with the hot acid (rate: 10 ml. per minute) and the last four washings with the cold acid (rate: 20–25 ml. per minute). Cool the solution, add one drop of ferroin or 0·5 ml. of N-phenylanthranilic acid, and titrate with standard 0·1N-ceric sulphate. The precipitate of eerie phosphate, which is initially formed, dissolves on shaking. Add the last 0·5 ml. of the reagent dropwise and with vigorous stirring or shaking. Calculate the molybdenum content of the sample of ammonium molybdate.

1 ml. N-Ce(SO₄)₂ = 0·09595 g. Mo

III, 81. Determination of tellurium.—Method A. A measured excess of standard 0·1N-ceric sulphate is added to the tellurous solution (200 ml.) containing 10 ml. of concentrated hydrochloric acid and about 0·05 g. of chromium sulphate as catalyst.* The solution is boiled for 10 minutes, then cooled and back titrated with standard 0·1N-ferrous ammonium sulphate, using N-phenylanthranilic acid or ferroin as indicator. The tellurium is oxidised from the quadri- to the sexa-valent stage. Selenium does not interfere.

1 ml. N-Ce(SO₄)₂ = 0·06381 g. Te

Method B. The solution of tellurous acid or of a tellurite (200 ml.) is treated with 15 ml. of concentrated hydrochloric acid and a measured excess of standard 0·1N-potassium dichromate, and allowed to stand for 30 minutes. The residual potassium dichromate is then determined by the addition of excess of standard 0·1N-ferrous ammonium sulphate and back titration with 0·1N-potassium dichromate, using N-phenylanthranilic acid or ferroin as indicator (see Section III, 66). Selenium does not interfere.

1 ml. N-K₂Cr₂O₇ = 0·06381 g. Te

Method C. This is carried out similarly to Method A under selenium (Section III, 82). The solution should contain 0·15–0·20 g. of tellurous oxide or its equivalent.

1 ml. N-KMnO₄ = 0·06381 g. Te

III, 82. Determination of cerium.—Method A. The cerous salt in the form of sulphate in 100 ml. of 1 : 4-sulphuric acid is treated with 2 g. of ammonium sulphate, 1 g. of A.R. sodium bismuthate is added, and the solution heated to boiling. The mixture is cooled somewhat, 50 ml. of 2 per cent sulphuric acid added, filtered through a Gooch, porous-porcelain, or sintered-glass crucible, and washed with 100–150 ml. of 2 per cent sulphuric acid.

\[
2\text{Ce}_2\text{(SO}_4)_3 + 2\text{NaBiO}_3 + 6\text{H}_2\text{SO}_4 = 4\text{Ce(SO}_4)_2 + \text{Bi}_2\text{(SO}_4)_3 + \text{Na}_2\text{SO}_4 + 6\text{H}_2\text{O}
\]

* Ceric sulphate alone does not oxidise selenite or tellurite, but it oxidises chromium to the sexavalent state and this, in turn, oxidises tellurite (but not selenite) to the sexavalent condition; any chromium (VI) at the end is reduced by the ferrous sulphate. The ceric ion acts as a potential mediator (compare Section I, 50A).
Excess of $0.025N$-ferrous ammonium sulphate is added (as shown by the change from yellow to colourless, and the consequent complete reduction of the ceric to the cerous salt), and the excess of ferrous salt titrated with $0.1N$-potassium permanganate to the first appearance of a pink colour.

$$1 \text{ ml. } 0.025N-\text{FeSO}_4 = 0.003503 \text{ g. Ce}$$

**Method B.** 100–300 ml. of the solution, containing 0.1–0.3 g. of cerium and 2.5–7.5 ml. of concentrated sulphuric acid, are treated with 1–5 g. of A.R. ammonium persulphate and 10 drops of $0.1N$-silver nitrate solution (catalyst), and then boiled for 10 minutes. The solution is cooled to room temperature, and is ready for titration. Two procedures may be used.

(i) Add 10–20 ml. of 10 per cent potassium iodide solution, and titrate the liberated iodine with $0.1N$- or $0.025N$-sodium thiosulphate. To avoid the oxidation of the hydriodic acid by the air, the titration should be performed in an atmosphere of carbon dioxide.

$$1 \text{ ml. } N\text{-Na}_2S_2O_3 = 0.1401 \text{ g. Ce}$$

(ii) Titrate the solution with $0.1N$- or $0.025N$-ferrous ammonium sulphate, using erioglaucine, $N$-phenylanthonilic acid or ferroin as indicator (Section III, 75).

$$1 \text{ ml. } N\text{-FeSO}_4 = 0.1401 \text{ g. Ce}$$

**Note.** Ceric sulphate solution may be used for the analysis of hydrogen peroxide (compare Section III, 55). The diluted solution, which may contain nitric, sulphuric, or hydrochloric acid in any concentration between 0.5 and 3$N$, is titrated directly with standard ceric sulphate solution, using ferroin or $N$-phenylanthonilic acid as indicator. The reaction is:

$$2\text{Ce(SO}_4)_2 + \text{H}_2\text{O}_2 = \text{Ce}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 + \text{O}_2$$
OXIDATIONS WITH MANGANIC SULPHATE

III, 83. General discussion.—The introduction of aqueous manganic sulphate as a volumetric oxidising agent by A. R. J. P. Ubbelohde (1935) originated in an attempt to improve the poor end points which are sometimes obtained with potassium permanganate solutions, due to the slow rate of oxidation by the permanganate ion and to other causes. It was found that reactions involving only the removal of electrons were more rapid and yielded better end points, for example:

\[
\text{Fe}^{++} + \text{Mn}^{+++} = \text{Fe}^{+++} + \text{Mn}^{++}
\]

Manganic sulphate solutions gave satisfactory end points in the determination of ferrous salts in the presence of chloride ions (contrast potassium permanganate), nitrites, hydrogen peroxide, oxalates, and vanadous salts.

III, 84. Preparation and standardisation of manganic sulphate solutions.—Preparation. This is based upon the oxidation of manganous sulphate with potassium permanganate:

\[
8\text{MnSO}_4 + 2\text{KMnO}_4 + 8\text{H}_2\text{SO}_4 = 5\text{Mn}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 8\text{H}_2\text{O}
\]

Owing to the deep red tint and also the danger of hydrolysis in dilute solutions, it is best to work with ca. 0·07N solutions prepared in the following manner.

To 50 ml. of a solution of A.R. manganous sulphate (15·1 g. in 1 litre of 6N-sulphuric acid) add 3 ml. of concentrated sulphuric acid with water-cooling; then add 12 ml. of 0·5N-potassium permanganate solution, 2 ml. at a time, at intervals of about 3 minutes. After 8 ml. and after 12 ml. of the permanganate solution have been added, cautiously introduce a further 2 ml. of concentrated sulphuric acid. Store the solution for 4 hours before use. With the above precautions, reduction proceeds smoothly to manganic sulphate, and higher valency stages never accumulate in sufficient concentration to give rise to troublesome precipitates of higher oxides. If larger quantities of the solution are to be prepared, special precautions to ensure adequate cooling are necessary.

The solution of manganic sulphate has a deep-red colour. It must be stored in blue bottles and kept in a dark cupboard when not in use. On exposure to light in a clear bottle, a precipitate gradually appears owing to the formation and hydrolysis of quadrivalent manganese salts:

\[
2\text{Mn}^{+++} = \text{Mn}^{++} + \text{Mn}^{++++}
\]

Standardisation. This is effected by running the manganic sulphate solution into standard ferrous ammonium sulphate solution (Section III, 48, Procedure F); one drop in excess of the former gives a pink end point with a yellowish tinge. A better pink coloration, particularly for use in artificial light, is obtained on adding 2 drops of syrupy phosphoric acid.
III, 85. Applications of manganic sulphate solutions.—A. Ferrous salts in the presence of chloride ions. Satisfactory results are obtained up to a concentration of hydrochloric acid of $N$. When the concentration of acid exceeds 0.2$N$, 0.5–1 ml. of syrupy phosphoric acid is added to improve the end point, and the titration is carried out slowly and with vigorous shaking.

B. Nitrites. Excellent end points are obtained, and the titrations are rapid (contrast Section III, 58).

C. Hydrogen peroxide. Manganic sulphate solution reacts almost instantaneously with hydrogen peroxide, and the end point is sharp.

D. Oxalates. Titration is effected at 35° C., and the end point is sharp.

E. Vanadium. Vanadium salts are reduced with liquid zinc amalgam or with amalgamated zinc to the bivalent stage; the latter solution at 45–50° C., may be rapidly and satisfactorily oxidised by manganic sulphate solution to the quinquevalent stage. This procedure is superior to the permanganate method (Section III, 94).
REDUCTIONS WITH TITANOUS SALTS

III, 86. General discussion.—E. Knecht (1903) first suggested the use of titanous chloride for the determination of iron. This determination differs from those already described in that the iron is reduced instead of oxidised, for example:

$$\text{FeCl}_3 + \text{TiCl}_2 = \text{FeCl}_2 + \text{TiCl}_4$$

The end point of the reaction is judged by the use of an indicator such as methylene blue, which is reduced and decolorised when the titanous solution is present in slight excess, or of ammonium thiocyanate, which remains red as long as any ferric salt is present. The latter is generally preferred, because methylene blue is somewhat slow in reaction below about 35° C.; if, however, one drop of 10 per cent sodium salicylate solution is added, the change is instantaneous at the ordinary temperature.

Titanous chloride is a more powerful reducing agent than stannous chloride (compare Table XVI in Chapter I). It is oxidised rapidly in the air, and should be kept out of direct sunlight. A. S. Russell (1926) has shown that titanous sulphate in 4N sulphuric acid solution is more stable to air than is the chloride (compare ferrous chloride and ferrous sulphate), and, indeed, its titre against potassium permanganate solution when kept in a burette exposed to air remains unchanged for 12 hours. Nevertheless, for accurate analysis and for work requiring a large number of routine determinations, solutions of both titanous chloride and sulphate should be stored in an atmosphere of hydrogen; titrations, particularly of the chloride, are best carried out in an atmosphere of carbon dioxide.

Formerly titanous salts were employed for numerous quantitative estimations; * many of these determinations can now be made more simply by other methods. The chief present uses of the reagent are in the analysis of ferric salts, of organic nitro and nitroso-compounds, azo dyes, and various routine analyses. Only the first-named falls within the compass of this volume. The reaction with a nitro-compound may be written:

$$\text{R-NO}_2 + 6\text{Ti}^{+++} + 6\text{H}^+ = \text{R-NH}_2 + 6\text{Ti}^{+++} + 2\text{H}_2\text{O}$$

hence

$$\text{NO}_2 = 6\text{Ti}^{+++} \dagger$$

III, 87. Preparation of titanous solutions.—A. Titanous chloride solution. Boil 60 ml. of commercial titanous chloride solution (15–20 per cent TiCl₄) for 1 minute with 100 ml. of concentrated hydrochloric

* For complete details, see E. Knecht and E. Hibbert, New Reduction Methods of Volumetric Analysis, 1926 (Longmans, Green and Co.); W. M. Thornton, Titanium, 1927 (Chemical Catalog Co.).


314
acid * in a small flask, allow to cool in an atmosphere of nitrogen, and make up to about 2 litres with boiled-out water in the storage bottle (Fig. II, 25, 1). The solution should be thoroughly mixed by shaking and, when freshly prepared, should fill the bottle to the neck; otherwise air remains, which must be completely displaced by hydrogen.

The burette is first completely filled with the solution. The storage bottle, etc., is connected to a Kipp's apparatus generating hydrogen. The tap of the burette is opened so that the latter is emptied, and hydrogen is passed through the system in order to displace the residual air. The tap is now closed, and the burette filled with the solution by suitably rotating the tap. It is now ready for standardisation and for use.

B. Titanous sulphate solution. This is similarly prepared by boiling 60 ml. of commercial titanous sulphate solution (15–20 per cent Ti₂(SO₄)₃) for 2–3 minutes with 200 ml. of 1:3 sulphuric acid in a small flask, allowing to cool, and diluting exactly as detailed under titanous chloride.† If 3–4N-sulphuric acid is used for dilution, the stability of the solution is considerably increased. Another method is to reduce a solution of titanate sulphate in 4N-sulphuric acid with liquid zinc amalgam (Section III, 95) for 1–2 minutes, and then to decant the resultant titanous sulphate solution into a storage vessel or flask. This method is particularly valuable when relatively small volumes of the solution are required.

III, 88. Standardisation of the titanous sulphate (or titanous chloride) solution.—A. With pure iron. Weigh out accurately 1-001 g. of A.R. iron wire (assay value 99.9 per cent; see Section III, 46) into a long-necked flask held in an inclined position, or into a conical flask carrying a short funnel in the mouth, and add about 100 ml. of 5N-sulphuric acid. When all the iron has passed into solution, transfer quantitatively to a 500-ml. volumetric flask, add a further 200 ml. of 5N-sulphuric acid, and make up to the mark. Shake thoroughly. Pipette 25 ml. of this solution (≈ 0.0500 g. Fe) into a 250–350-ml. conical flask, fitted with a three-holed rubber stopper carrying tubes as described in Section III, 116B), and carefully oxidise with potassium permanganate solution of about 0.02N strength until a faint pink tinge is obtained. Boil vigorously to expel dissolved oxygen whilst a slow current of carbon dioxide is passed through the flask. Cool the solution, add 10–20 ml. of 10 per cent ammonium or potassium thiocyanate solution and run in the titanous sulphate (or chloride) solution until the red colour, due to “ferric thiocyanate,” has disappeared. The stream of carbon dioxide is maintained throughout the whole of the operation. The reduction of the last few mg. of the ferric salt is somewhat slow, and it is therefore best to add the titanous solution dropwise with intervals of several seconds between the drops when the end point has almost been reached. The use of a large excess of thiocyanate renders the end point much sharper. It is immaterial whether the iron is present in sulphuric or hydrochloric acid solution, but the presence of some mineral acid is essential, as otherwise the indicator is not sensitive.

* Commercial titanous chloride solution sometimes contains sulphides, which are eliminated as hydrogen sulphide on boiling.
† A more concentrated solution of titanous sulphate is generally used for the titration of nitro and other organic compounds. It is prepared by boiling 300 ml. of commercial titanous sulphate solution (15–20 per cent) with 600 ml. of 1:3 sulphuric acid for a few minutes, cooling, and making up to 1 litre.
Quantitative Inorganic Analysis

Repeat the titration with two other 25-ml. portions of the iron solution.

Calculate the weight of iron equivalent to 1 ml. of the titanous solution.

B. With ferrous ammonium sulphate. Weigh out accurately 3.511 g. of A.R. ferrous ammonium sulphate (Section III, 46), dissolve it in water, add about 150 ml. of 5N-sulphuric acid, and make up the solution to 250 ml. in a standard flask. Shake thoroughly. Pipette 25 ml. of this solution (= 0.0500 g. of Fe) into a 250-350-ml. conical flask and proceed as described under A. This method is less accurate than that employing pure iron (for reasons, see Sections III, 46, and III, 48, Procedure E).

A.R. ferric ammonium sulphate (iron alum) may also be used for the standardisation.

III, 89. Determination of iron in an ore.—Weigh out accurately about 2 g. of the iron ore,* dissolve it in 100 ml. of 1:1-hydrochloric acid, and make up the solution to 250 ml. in a volumetric flask as described in Section III, 53. Pipette 25 ml. of this solution into a 250-ml. conical flask, and precipitate the iron by the addition of ammonium hydroxide solution. Oxidise the ferrous hydroxide by adding excess of pure hydrogen peroxide solution. Boil for 10 minutes to decompose the excess of hydrogen peroxide. Cool, add concentrated hydrochloric acid until the acid content of the solution is about 10 per cent by volume, then 10 ml. of 10 per cent ammonium thiocyanate solution. Titrate with the standardised titanous sulphate (or chloride) solution in an atmosphere of carbon dioxide until the red colour just disappears (Section III, 88A). Repeat with two other 25-ml. portions of the solution.

From the results, calculate the percentage of total iron in the sample of ore used.

* Riddell’s “Iron Ore, No. 17” (one of the Analyzed Samples for Students) or the Bureau of Analyzed Samples “Iron Ore A” (one of the British Chemical Standards) may be used.
REDUCTIONS WITH AMALGAMATED ZINC AND WITH LIQUID AMALGAMS

III, 90. General discussion.—The use of amalgamated zinc as a reducing agent has been fully dealt with in Section III, 51B: full details are given in that Section of the manipulation of the very convenient Jones reductor. Experimental details, based upon the use of the Jones reductor, for the determination of uranium, titanium, molybdenum, and vanadium are given below.

Makazono (1921) introduced liquid zinc amalgam as a reducing agent in volumetric analysis, and subsequent Japanese workers have added liquid cadmium, bismuth, and lead amalgams. These amalgams have different reduction potentials (see Table XV in Chapter I); the order is zinc, cadmium, lead, bismuth, the first-named being the most powerful reductant. The final reduction products obtained with these amalgams for a few elements are collected in the table.

<table>
<thead>
<tr>
<th>Liquid Amalgam</th>
<th>Iron</th>
<th>Titanium</th>
<th>Molybdenum</th>
<th>Vanadium</th>
<th>Uranium</th>
<th>Tungsten</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>Fe²⁺</td>
<td>Ti⁺⁺</td>
<td>Mo⁺⁺⁺⁺⁺⁺⁺⁺</td>
<td>V⁺⁺⁺⁺</td>
<td>U⁺⁺⁺⁺</td>
<td>W⁺⁺⁺⁺</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Fe²⁺</td>
<td>Ti⁺⁺</td>
<td>Mo⁺⁺⁺⁺⁺⁺⁺⁺</td>
<td>V⁺⁺⁺⁺</td>
<td>U⁺⁺⁺⁺</td>
<td>W⁺⁺⁺⁺</td>
</tr>
<tr>
<td>Lead</td>
<td>Fe²⁺</td>
<td>Ti⁺⁺</td>
<td>Mo⁺⁺⁺⁺⁺⁺⁺⁺</td>
<td>V⁺⁺⁺⁺</td>
<td>U⁺⁺⁺⁺</td>
<td>W⁺⁺⁺⁺</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Fe²⁺</td>
<td>Ti⁺⁺</td>
<td>Mo⁺⁺⁺⁺⁺⁺⁺⁺</td>
<td>V⁺⁺⁺⁺</td>
<td>U⁺⁺⁺⁺</td>
<td>W⁺⁺⁺⁺</td>
</tr>
</tbody>
</table>

* The exact product depends upon the pH of the solution.

Zinc amalgam also reduces chromium to Cr⁺⁺.

In view of the poisonous character of mercury vapour—the effect is a cumulative one—the author prefers to recommend the use of the Jones reductor for most reductions in routine work. However, in determinations such as those of titanium (with zinc amalgam) and of tungsten (with lead amalgam), liquid amalgams offer certain advantages, and their use for these determinations is accordingly described below (Sections III, 95, 96). These Sections incidentally contain the methods of preparation of liquid zinc and lead amalgams; the amalgams of cadmium and bismuth are prepared similarly to that of zinc, except that for bismuth hydrochloric acid replaces sulphuric acid. Zinc amalgam is useful in the preparation of titanous, vanadous, and chromous salt solutions.

A special apparatus is described for the determination of titanium (Section III, 95). For many purposes (e.g., the reduction of ferric salts), however, the reduction may be carried out in a 250-ml reagent bottle fitted with a well-ground stopper. For the reduction of 50 ml of a solution of approximately deci-normal concentration, which should be 2–4N with respect to sulphuric acid, 30–50 ml of amalgam may be used; the reaction is complete after shaking for a few minutes. The contents of the bottle are then transferred to the titration flask or other vessel, the bottle rinsed two or three times with small volumes of boiled-
out water, the washings being, of course, added to the flask. The same amalgam can be used many times before it becomes exhausted.

III, 91. Determination of uranium.—The uranium solution (100 ml., about 0·25 g. U) should contain 5 per cent by volume of sulphuric acid, no compounds that are reduced in the Jones reductor, and be free from nitric acid. Add enough 0·1N-potassium permanganate to produce a permanent pink tint, cool the solution to 20–25° C., and pass it through a Jones reductor (Section III, 51B) at a rate of 50–100 ml. per minute. Part of the uranium is reduced to the trivalent state ($U^{III}$). Bubble a stream of air through the stirred solution for 5–6 minutes; the dirty dark-green colour changes to the bright apple-green characteristic of uranous salts. Titrate the solution with standard 0·1N-potassium permanganate. Carry out a blank determination with the reagents in the usual way, and subtract the blank correction from the volume of potassium permanganate required in the estimation.

\[1 \text{ ml. } N\text{-KMnO}_4 = 0·1190 \text{ g. U}\]

The cold sulphuric acid solution of quadrivalent uranium is stable to air for several hours, and even a rapid stream of air effects no change in 30 minutes.

Alternatively, the uranous salt ($U^{IV}$) may be titrated with 0·1N-ceric sulphate. The titration may be performed: (a) by adding an excess of standard ceric sulphate solution and, after 5 minutes, back-titrating the excess of ceric sulphate with standard ferrous ammonium sulphate solution, or (b) by direct titration at 50° C. with 0·1N-ceric sulphate, using ferroin or $N$-phenylanthranilic acid as indicator.

III, 92. Determination of titanium.—The titanium solution should be free from all metals that are reduced in a Jones reductor and also from all substances which are likely to react subsequently with potassium permanganate. 150 ml. of the solution, containing sulphuric acid and 0·12–0·15 g. of titanium, are treated with enough 0·1N-potassium permanganate to produce a permanent pink tint, and then passed through a Jones reductor (Section III, 51B); the reduced solution is collected in a five-fold excess of an acidified solution of A.R. ferric alum—100 ml. of a 10 per cent solution suffices for most purposes. The ferrous iron thus produced by reaction with the tervalent titanium is titrated with standard 0·1N-potassium permanganate. Subtract the blank correction determined in the usual manner.

\[1 \text{ ml. } N\text{-KMnO}_4 = 0·04790 \text{ g. Ti}\]

III, 93. Determination of molybdenum.—The molybdenum solution should be free from all metals that are reduced in a Jones reductor, and from all substances which are likely to react subsequently with the potassium permanganate. The cold solution, containing 0·08–0·10 g. of molybdenum and 3–10 per cent by volume of sulphuric acid, is treated with enough deci-normal potassium permanganate to produce a pink colour, and then passed through a Jones reductor; the reduced solution is collected in a five-fold excess of acidified A.R. iron alum solution (say, 30 ml. of a 10 per cent solution). Add a few ml. of syrupy phosphoric acid to the contents of the receiver and titrate the ferrous sulphate produced with standard 0·1N-potassium permanganate. Subtract the volume of permanganate required in a blank determination.
in which the reagents have been carried through all the steps of the process.

1 ml. \( N\text{-KMnO}_4 \) = 0.0320 g. Mo

Note. Owing to the instability of tervalent molybdenum compounds, exposure to air should be reduced to a minimum, and the lower tube of the reductor should pass under the surface of the iron solution.

For another procedure utilising the silver reductor and titration with standard ceric sulphate solution, see Section III, 80.

III, 94. Determination of vanadium.—Method A. The experimental details are similar to those described under Titanium (Section III, 92). The vanadium solution, containing sulphuric acid, is treated with enough 0.1N-potassium permanganate to produce a pink colour and is passed through a Jones reductor, whereupon it is reduced to the bivalent stage; the reduced solution is caught in excess of an acidified solution of A.R. iron alum, and the ferrous iron thus formed is titrated with standard 0.1N-potassium permanganate. Actually, the ferric salt oxidises the vanadous salt only to the quadrivalent condition, which is stable in air, and the oxidation to the quinteivalent state is completed by the potassium permanganate. The titration is somewhat slow towards the end, but the final point is quite definite; by heating the solution to 70–80°C towards the end of the titration, the oxidation is rapid.

1 ml. \( N\text{-KMnO}_4 \) = 0.01689 g. V

Method B. The vanadate solution should contain 2 per cent by volume of sulphuric acid, and be free from arsenic, antimony, iron, chromium, and other substances that are oxidised by potassium permanganate after reduction with sulphur dioxide. Heat the solution to boiling, add a strong solution of potassium permanganate until the solution is pink, fit the flask with wash-bottle tubes, and pass sulphur dioxide through the solution for 5–10 minutes; the solution acquires a pure blue colour (vanadyl sulphate) and is quite stable in the presence of sulphuric acid. Next pass a rapid stream of carbon dioxide through the boiling solution until it is free from sulphur dioxide, as tested by bubbling the issuing gas through an acidified and very dilute solution of potassium permanganate. Cool the solution to 60–80°C and titrate with standard 0.1N-potassium permanganate.

\[
2\text{H}_2\text{VO}_4 + \text{H}_2\text{SO}_4 + \text{H}_2\text{SO}_4 = 2(\text{VO})\text{SO}_4 + 5\text{H}_2\text{O}
\]
\[
5\text{V}_2\text{O}_7^{3+} + 2\text{MnO}_4^- + 22\text{H}_2\text{O} = 10\text{H}_2\text{VO}_4 + 2\text{Mn}^{2+} + 14\text{H}^+
\]

1 ml. \( N\text{-KMnO}_4 \) = 0.05095 g. V

Note. Since sulphur dioxide does not reduce molybdic acid, this procedure can be employed in the presence of molybdenum. Both molybdc and vanadic acids are reduced in the Jones reductor, hence the former may be determined by reducing both with amalgamated zinc and making allowance for the vanadium present.

III, 95. Determination of titanium (zinc amalgam method).—This method is based upon the use of liquid zinc amalganm as the reducing agent, whereby the titanium is quantitatively reduced to the tervalent state; the latter is titrated against standard ferric ammonium sulphate solution with potassium thioyuanate solution as indicator.
The apparatus employed for the titration is shown in Fig. III, 95, 1. A 250-ml. globular separating-funnel is closed with a rubber stopper \( A \) carrying a piece of 0.25-in. tubing \( B \), which is closed by a small cork \( C \). (Alternatively, the funnel may be closed with a three-holed rubber stopper carrying inlet and outlet tubes for carbon dioxide and a small stopper in the third hole.) The lower end of the funnel is connected by means of thick-walled ("pressure") tubing \( E \) to a 25-ml. flask \( D \) (this may consist of a 25-ml. volumetric flask, etc.); \( F \) is a pinch-cock.

A sample of the substance, equivalent to 0.1-0.2 g. of \( \text{TiO}_2 \) (1), is digested with 20 ml. of concentrated sulphuric acid and 15 g. of powdered A.R. ammonium sulphate until it is entirely dissolved. Bulb \( D \) and the rubber tubing, etc., to the stopcock \( G \) are filled with cooled, freshly boiled distilled water containing 1 per cent of sulphuric acid ("acid distilled water"), and \( F \) and \( G \) are closed. Fifteen ml. of liquid zinc amalgam are placed in the funnel, and the cooled sample is transferred to the funnel using about 75 ml. of "acid distilled water." Several grams of A.R. sodium bicarbonate (preferably in the form of two tablets) are added, and stopper \( A \) is inserted with cork \( C \) removed. When the gas evolution has ceased, a further few grams of A.R. sodium bicarbonate are added through \( B \). When effervescence ceases, cork \( C \) is immediately replaced and the whole apparatus vigorously shaken for 5 minutes. The funnel is then supported in a stand, \( G \) and \( F \) are opened, and the amalgam is allowed to flow into \( D \); this is best accomplished by alternatively squeezing and releasing the tube \( E \) with the fingers. When the last particles of amalgam have dropped into the flask, \( G \) and \( F \) are closed, and bulb \( D \) is disconnected for convenience whilst titrating. Stopper \( C \) is removed, and 5 ml. of saturated potassium thiocyanate solution added through \( B \) by means of a pipette. Stopper \( A \) is removed, and both tube and stopper are washed into the funnel with "acid distilled water." The solution is then titrated in the funnel with the ferric ammonium sulphate solution (2). It is important to add the latter solution very rapidly until the first appearance of a wine-red colour. Stopcock \( G \) is then opened, and tube \( E \) squeezed several times to force its liquid into the funnel; this will cause the red colour to disappear. The titration is then completed by adding the ferric solution drop by drop to the end point.

The ferric ammonium sulphate solution is approximately 0.07N and is prepared by dissolving ca. 80 g. of the A.R. salt in a mixture of 300 ml. of water and 10 ml. of concentrated sulphuric acid; potassium permanganate solution is added dropwise as long as the pink colour disappears (if at all), and the solution is then diluted to 1 litre. The solution is standardised, after reduction with zinc amalgam in the above apparatus, by titration against standard 0.1N-potassium permanganate.

The zinc amalgam is prepared by washing 15 g. of pure, fine-mesh zinc powder (e.g., A.R.) with dilute sulphuric acid, and then heating for 1 hour on the water-bath with 300 g. of mercury plus 5 ml. of 1 : 4 sulphuric acid. (Caution. Mercury vapour is highly poisonous; the operation must therefore be per-
formed in a fume cupboard provided with a good draught.) The whole is allowed to cool, the amalgam washed several times with dilute sulphuric acid, and the liquid portion separated from the solid by means of a separating-funnel. The solid is reserved for another preparation of the amalgam. The liquid amalgam is preserved under dilute sulphuric acid; reaction with the latter is very slow, and the same sample of amalgam may be employed for several reductions.

Notes. 1. This method is of particular value for the determination of titanium in pigments and similar products. Calcium sulphate does not interfere with the subsequent reduction because its precipitation is prevented by the high concentration of sulphuric acid. Barium sulphate should be removed by filtration before the reduction of the titanium. If two determinations are carried out, and in one case the reduced solution be titrated with the ferric solution and potassium thiocyanate, and in the other case by standard 0.1N-potassium permanganate (this gives Ti + Fe), the method may be employed for the determination of iron and titanium in admixture.

2. For the most accurate results it is best to insert the three-holed rubber stopper referred to above, and to conduct the titration in an atmosphere of carbon dioxide.

3. It is advisable to run a blank to determine how much ferric solution is required to give an end point in a volume of 3 per cent sulphuric acid equal in volume to that of the final solution and containing 5 ml. of saturated potassium thiocyanate solution.

III. 96. Determination of tungsten.—This element is not reduced to any definite valency stage in the Jones reducer. Lead amalgam reduces tungsten as tungstate to the tervalent condition \((W_2O_7)\) in strong hydrochloric acid at 50° C. in an atmosphere of carbon dioxide (K. Someya, 1925). This is titrated with standard 0.1N-potassium permanganate in the presence of concentrated manganous sulphate solution; it is thereby oxidised to the \(WO_3\) stage, when 3 equivalents of \(KMnO_4\) are equivalent to 1 mol. of \(WO_3\).

The lead amalgam is prepared by washing pure lead with concentrated hydrochloric acid (to remove the film of oxide), and then heating with pure mercury in a casserole until a homogeneous liquid is produced. This process should be carried out in a fume cupboard provided with a very efficient draught. The amalgam is allowed to cool, washed with cold distilled water, and the solid removed in a separating-funnel by appropriately manipulating the tap.
Vanadous salts are more powerful reducing agents than titanous salts, but less powerful than the corresponding chromous salts. Thus the standard potential of the couple $V^{++} + e = V^{+}$ is $-0.20$ volt vs. the standard hydrogen electrode: the comparable value for the analogous couple $Cr^{+++} + e = Cr^{++}$ is $-0.40$ volt. The introduction of vanadous salts to volumetric analysis proper is due to A. S. Russell (1926), who prepared a solution of vanadous sulphate by reducing aqueous vanadic sulphate with liquid zinc amalgam; he claimed that the solution in $10N$-sulphuric acid is stable for about an hour in an open burette. It is, however, an established fact that the vanadous ion is so very easily oxidised by air ($4V^{++} + O_2 + 4H^+ = 4V^{+++} + 2H_2O$, etc.) that the solution must be stored and delivered from the burette under an inert gas, which is usually hydrogen; furthermore, the solution being titrated must be scrupulously freed from dissolved oxygen.

The most satisfactory method for preparing and storing a solution of vanadous salt consists in the reduction of a solution of a vanadyl salt by amalgamated zinc in the apparatus illustrated in Fig. III, 97, 1.* The advantages of this apparatus are: (i) it is easily constructed, (ii) the solution is reduced and stored in the same vessel, (iii) a solution containing the vanadium ion entirely in the $+2$ state is obtained, and (iv) both the storage vessel and the burette are easily removed for cleaning. The apparatus consists of a 500-ml. Pyrex round-bottomed flask which is connected by means of a ground-glass joint (securely held by two small coil springs) to the delivery tube; the latter is attached by a short length of thick-walled rubber tubing (closed by a screw clip) to the burette. The ground-glass joint in the

* This is a slightly modified form of that described by J. J. Lingane and R. L. Pecsko (1948) for chromous salts.
mouth of the flask is connected to the burette at its upper end and also to a source of pure hydrogen. The hydrogen is obtained from a small Kipp generator and is freed from oxygen by passage through a vessel containing vanados sulphate solution in ca. N-sulphuric acid and some amalgamated zinc; in practice, it is found that very little hydrogen is required. To prevent small particles of zinc entering the solution to be titrated, a small glass "mushroom" is placed at the bottom of the storage flask immediately below the amalgamated zinc and, as a further precaution, a little purified glass wool is inserted just above the stopcock of the burette. The storage flask is supported on a rubber-covered ring and the burette by two burette clamps, one near the top and the other just below the 50-ml mark. The apparatus is mounted on a stand with a heavy base, and is portable. Both the storage flask and the burette are easily removed for recharging and/or cleaning.

It is important to use pure reagents, as impurities tend to act as catalysts in the otherwise slow reaction:

\[
2V^{++} + 2H^+ = 2V^{+++} + H_2, \text{ etc.}
\]

The zinc used must be very pure; zinc wool of high purity is best, but if this is not available A.R. granulated zinc may be employed. It is amalgamated by stirring for several minutes with a solution of A.R. mercuric chloride in ca. 0.1N-hydrochloric acid (sufficient for 2–3 per cent amalgamation) and then washing well with distilled water. The reservoir is half-filled with the amalgamated zinc (about 100 g. of zinc wool are required for this purpose; if granulated zinc is used, 400–500 g. will be necessary).

It is convenient to prepare and reduce a 0.05M solution of vanadyl sulphate. A stock solution is prepared by dissolving 9·95 g. of the purest commercial vanadyl sulphate VOSO₄.2H₂O in water, filtering if necessary through a sintered-glass crucible (porosity No.3), transferring to a litre volumetric flask and adding sufficient concentrated sulphuric acid (27·8 ml.) to give a solution which is N with respect to this acid. About 200–300 ml. of this solution is placed in the storage vessel, i.e., sufficient to just cover the amalgamated zinc wool; the stopcock connected to the Kipp generator is closed and the glass stopcocks at the two ends of the burette are opened. The large volume of hydrogen evolved in the subsequent reduction will displace the air from the apparatus, and the possible entrance of the vanadium solution into the Kipp apparatus is prevented. If the reservoir is gently shaken, the reduction is usually complete in about 20 minutes. The colour of the solution passes from deep blue (VO⁺⁺), through green (V⁺⁺⁺) to pale violet (V⁺⁺⁺). Reduction is complete when the solution has a uniform pale violet colour. After an hour or two, the stopcock connected to the Kipp generator is opened and that to the burette is closed. The resulting solution of vanados sulphate is stable for 3–4 days; beyond this period a yellow-green precipitate appears and the solution commences to acquire a yellow or brown colour. Owing to the ease and rapidity of reduction and the facility with which the storage vessel can be emptied and recharged, the comparative instability is no serious

* Zinc wool of high purity is manufactured by The Lead Wool Company Ltd., Snodland, Kent, England.
disadvantage. A solution of vanadous sulphate can readily be prepared, when required, from the stock solution of vanadyl sulphate.

A solution of vanadous chloride in \( N \)-hydrochloric acid may be similarly prepared from the commercial vanadyl chloride (dry solid or concentrated solution).

For practice in the use of vanadous sulphate, the student may carry out titrations with potassium permanganate and with a ferric salt. The end points for these two determinations may be detected visually, but for other titrations potentiometric methods are usually necessary (see Chapter VI; a suitable titration vessel is described in Section III, 98).

**Titration against standard potassium permanganate solution.** Place 50 ml. of standard 0·1N potassium permanganate solution in a 350-ml. conical flask provided with a two-holed rubber stopper, and add 100 ml. of 10 per cent sulphuric acid (10 ml. of concentrated sulphuric acid in 100 ml. of water). Insert an inlet tube for nitrogen into one hole of the stopper and leave the other (larger, 0·5 cm.) hole open. Pass oxygen-free nitrogen into the solution for 15 minutes, and then reduce the flow of gas considerably. Insert the tip of the burette into the hole in the stopper and run in the vanadous sulphate solution slowly and with shaking until the colour of the potassium permanganate solution changes suddenly to pale yellow (vanadate). Repeat the titration. Calculate the normality of the vanadous sulphate solution.

\[
10\text{VOSO}_4 + 6\text{KMnO}_4 + 6\text{H}_2\text{O} = 10\text{HVO}_3 + 6\text{MnSO}_4 + 3\text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4
\]

**Titration of ferric iron.** Treat 25 ml. of a 0·1N solution of A.R. ferric ammonium sulphate, contained in a 250-ml. conical flask provided with a rubber stopper having a 1-cm. hole in its centre, with saturated sodium bicarbonate solution until a permanent precipitate of ferric hydroxide is formed, then add 25 ml. in excess, followed by 25 ml. of 0·1M-potassium thiocyanate solution (prepared from the A.R. solid). Add dilute hydrochloric acid (1 : 1) slowly and with swirling of the solution until the colour of the thiocyanate complex appears and a further 0·5 ml. in excess. This treatment will ensure the complete removal of the dissolved oxygen by the carbon dioxide thus evolved. Insert the burette tip through the hole in the stopper and run in the vanadous sulphate solution slowly. The reddish colour of the complex commences to fade about 0·3 ml. before the end point, which is taken as the sudden change from a reddish orange to the clear light green of the vanadium (III) thiocyanate complex.

For purposes of calculation the reaction may be written:

\[
[V(\text{SCN})_2]^{2- - x} + \text{Fe}^{2+} \rightarrow [V(\text{SCN})_2]^{3- - x} + \text{Fe}^{3+}
\]

or as

\[
\text{V}^{++} + \text{Fe}^{+++} \rightarrow \text{V}^{+++} + \text{Fe}^{++}
\]

Compare the normality of the vanadous sulphate solution, computed from the known or determined normality of the ferric solution, with that deduced from the titration against standard potassium permanganate solution.
III, 98. REDUCTIONS WITH CHROMOUS SALTS

Chromous salts are the most powerful reducing agents employed in the form of standard solutions in volumetric analysis: the standard potential of the couple \( \text{Cr}^{++} + e = \text{Cr}^{+++} \) is \(-0.40\) volt vs. the standard hydrogen electrode. Chromous ion is so very easily oxidised by air that the solution must be stored and delivered from the burette under an inert gas (usually oxygen-free hydrogen) and the solution being titrated must be completely freed from dissolved oxygen:

\[
4\text{Cr}^{++} + \text{O}_2 + 4\text{H}^+ = 4\text{Cr}^{+++} + 2\text{H}_2\text{O}
\]

Furthermore, chromous ion is powerful enough a reductant to reduce hydrogen ion:

\[
2\text{Cr}^{++} + 2\text{H}^+ = 2\text{Cr}^{+++} + \text{H}_2
\]

and, in consequence, acid chromous solutions are metastable. The oxidation of chromous ion by hydrogen ion is, however, very slow when the solution in dilute hydrochloric or sulphuric acid is prepared from very pure materials: the oxidation is catalysed by various substances, particularly platinum and other finely-divided metals. It is therefore of great importance to use very pure materials, free from foreign heavy metals, in the preparation of chromous solutions.

The best method for preparing and storing a solution of a chromous salt is the reduction of a chromic solution by amalgamated zinc in the apparatus described under Vanadous Salts (Section III, 97; Fig. III, 97, 1). The solution is reduced and stored in the same vessel. Complete reduction to the chromous state may be achieved, so that by starting with pure potassium dichromate (or any chromic salt of known purity) a solution of any desired normality may be prepared directly: standardisation against copper or potassium dichromate is, however, recommended.

Preparation of 0.1N-chromous sulphate solution. Dissolve 14.711 g. of dry A.R. potassium dichromate in about 250 ml. of water in a litre conical flask and acidify with 13.9 ml. of concentrated sulphuric acid. Place a long-stemmed funnel in the neck of the flask and add slowly in several portions about 40 ml. of pure 30 per cent ("100-volume") hydrogen peroxide. The dichromate is thus reduced to chromic ion. Heat the solution just to boiling until evolution of oxygen ceases (about 15–20 minutes). Cool to room temperature, transfer quantitatively to a litre volumetric flask and dilute to the mark. Rinse out the storage flask (Fig. III, 97, 1), previously charged with about 100 g. of amalgamated pure zinc wool or about 400 g. of amalgamated A.R. granulated zinc (for preparation, see Section III, 97), with two 50-ml. portions of the chromic solution, and then charge it with about 300 ml. of the solution. Close the flask and connect it to the Kipp generator: the hydrogen from the latter should be passed through a vessel containing acid chromous sulphate solution and some amalgamated zinc. It is unnecessary to sweep out the solution or storage flask with hydrogen: the oxygen is very rapidly consumed by the solution itself as it
undergoes reduction, and hence only a small amount of hydrogen is required to keep the solution protected from the air and to replace the solution withdrawn. If the solution just covers the amalgamated zinc, reduction is complete in about 30 minutes; shaking of the flask occasionally to promote contact of the solution with the zinc accelerates the rate of reduction. The reduction is complete when the solution has acquired a uniform pale sky-blue colour without any tinges of green.

A 0·1N solution of chromous chloride in 0·1N-hydrochloric acid may be similarly prepared using the appropriate quantity of hydrochloric acid instead of sulphuric acid.

**Titrations with 0·1N-chromous sulphate solution.** Titrations must be carried out potentiometrically because of the deep green colour of the chromic ion: a simple potentiometer (see Chapter VI) usually suffices because the potential change at the end point is large. The titration vessel may consist of a 200-ml. four-necked flask. The central aperture is fitted with a rubber stopper carrying a long inlet tube to bubble oxygen-free nitrogen through the solution; the other apertures are for the platinum wire electrode (wound as a spiral on a glass tube), a salt bridge, and the burette respectively. The burette tip passes through a large hole in a rubber stopper; the oversize hole serves as the gas exit. The salt bridge may be either 3 per cent agar solution saturated with potassium sulphate or N-sulphuric acid: the outer end of the bridge is placed in a saturated potassium chloride solution in a beaker in which the side arm of a saturated calomel electrode dips. The solution in the titration vessel is freed from oxygen by passing nitrogen through it for at least 15 minutes before the titration.

The normality of the chromous sulphate solution may be checked by titration against pure copper sulphate pentahydrate in a solution containing a large amount of chloride ion. The complex tetrachlorocuprate ion is reduced to a chloro complex of univalent copper (either [CuCl\(_4\)]\(^{-}\) or [CuCl\(_3\)]\(^{-}\) ion):

\[
[CuCl_4]^- + e = [CuCl_2]^- + 2Cl^- \quad (1)
\]

and then to metallic copper:

\[
[CuCl_3]^- + e = Cu + 2Cl^- \quad (2)
\]

The potentiometric titration curve clearly defines both stages of reduction; the change of potential after the completion of reaction (1) is very large and the end point can be located with great precision.

The titration may be carried out as follows. Prepare a 0·1M solution of A.R. copper sulphate pentahydrate. Mix 50 ml. of this solution with 50 ml. of concentrated hydrochloric acid and titrate at room temperature with the chromous sulphate solution under oxygen-free nitrogen. Add the reagent slowly when approaching the second end point, reaction (2), and wait until the potential is steady after each addition. Read off the end point from the potentiometric titration curve, and use this value to calculate the normality of the chromous sulphate solution.

The chromous sulphate solution may also be standardised against pure potassium dichromate by adding a slight excess of ferrous iron to the dichromate solution in N-sulphuric acid and titrating the resulting ferric iron with the chromous solution. Steady potentials are rapidly established; this is not the case when the dichromate solution is
titrated directly with the reagent. The experimental details are as
follows. Dissolve 0.2220 g. of dry A.R. potassium dichromate in ca.
100 ml. of N-sulphuric acid in the titration vessel and, after starting
the flow of oxygen-free nitrogen, add 2 g. of pure ferrous ammonium
sulphate. Pass the nitrogen for 25–30 minutes and then titrate with
the chromous sulphate solution. The titration curve at the equivalence
point is symmetrical, and the end point can be accurately determined
from the maximum value of $\Delta E/\Delta V$. 

\textit{Volumetric Analysis}
OXIDATION AND REDUCTION PROCESSES INVOLVING IODINE—IODIMETRY AND IODOMETRY

III. 99. General discussion.—Iodimetry covers titrations with a standard solution of iodine. Iodometry deals with the titration of iodine liberated in chemical reactions. The normal oxidation potential of the reversible system:

$$I_2 + 2e^- \rightleftharpoons 2I^-$$

is 0.535 volt. This shows that iodine is a much weaker oxidising agent than potassium permanganate, potassium dichromate, and ceric sulphate (compare Table XVI). Strong reducing agents (substances with a much lower oxidation potential), such as stannous chloride, sulphurous acid, hydrogen sulphide, and sodium thiosulphate, react completely and rapidly with iodine even in acid solution. With somewhat weaker reducing agents, e.g., trivalent arsenic, trivalent antimony, and ferrocyanide, complete reaction occurs only when the solution is kept neutral or very faintly acid; under these conditions the oxidation potential of the reducing agent is a minimum, or its reducing power is a maximum. The equations for some of the reactions are given below:

$$Sn^{4+} + I_2 = Sn^{3+} + 2I^-$$
$$SO_3^{--} + I_2 + H_2O = SO_4^{--} + 2H^+ + 2I^-$$
$$H_2S + I_2 = S + 2H^+ + 2I^-$$
$$2S_2O_3^{--} + I_2 = S_4O_6^{--} + 2I^-$$
$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2I^-$$

If a strong oxidising agent is treated in neutral or (more usually) acid solution with a large excess of iodide ion, the latter reacts as a reducing agent and the oxidant will be quantitatively reduced. In such cases, an equivalent amount of iodine is liberated, and is then titrated with a standard solution of a reducing agent, which is usually sodium thiosulphate. Examples of such titrations are illustrated by the following equations:

$$2MnO_4^- + 16H^+ + 10I^- = 2Mn^{3+} + 5I_2 + 8H_2O$$
$$Cr_2O_7^{--} + 14H^+ + 6I^- = 2Cr^{3+} + 3I_2 + 7H_2O$$
$$H_2O_2 + 2H^+ + 2I^- = H_2O + I_2$$
$$BrO_3^- + 6H^+ + 6I^- = Br^- + 3I_2 + 3H_2O$$
$$IO_3^- + 6H^+ + 5I^- = 3I_2 + 3H_2O$$
$$ClO_3^- + 6H^+ + 6I^- = Cl^- + 3I_2 + 3H_2O$$
$$ClO^- + 2H^+ + 2I^- = Cl^- + I_2 + H_2O$$
$$IO_4^- + 8H^+ + 7I^- = I_2 + 4H_2O$$
$$2HNO_3 + 2H^+ + 2I^- = 2NO + I_2 + 2H_2O$$
**Volumetric Analysis**

\[
\begin{align*}
2\text{Ce}^{+++} + 2\text{I}^- &= 2\text{Ce}^{+++} + \text{I}_2 \\
2\text{Cu}^{++} + 4\text{I}^- &= \text{Cu}_2\text{I}_3 + \text{I}_2 \\
\text{Cl}_2 + 2\text{I}^- &= 2\text{Cl}^- + \text{I}_2 \\
\text{Br}_2 + 2\text{I}^- &= 2\text{Br}^- + \text{I}_2
\end{align*}
\]

The normal oxidation potential of the iodine–iodide system is independent of the \(pH\) of the solution so long as the latter is less than about 8; at lower acidities iodine reacts with hydroxyl ions to form iodide and the extremely unstable hypiodite, the latter being transformed rapidly into iodate and iodide by self-oxidation and reduction:

\[
\begin{align*}
\text{I}_2 + 2\text{OH}^- &= \text{I}^- + \text{IO}^- + \text{H}_2\text{O} \\
3\text{IO}^- &= 2\text{I}^- + \text{IO}_3^-
\end{align*}
\]

It has been shown in Section I, 48 that the oxidation potentials of certain substances increase considerably with increasing hydrogen-ion concentration of the solution. This is the case with systems containing permanganate, dichromate, arsenate, antimonate, bromate, etc., i.e., with anions which contain oxygen and therefore require hydrogen for complete reduction. Many weak oxidising anions are completely reduced by iodide ions if their oxidation potentials are raised considerably by the presence in solution of a large amount of acid.

By suitable control of the \(pH\) of the solution, it is sometimes possible to titrate the reduced form of a substance with iodine, and the oxidised form after the addition of iodide with sodium thiosulphate. Thus with the arsenite–arsenate system:

\[
\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} \Leftrightarrow \text{H}_2\text{AsO}_4 + 2\text{H}^+ + 2\text{I}^-
\]

the reaction is completely reversible. At \(pH\) values between 4 and 9, arsenite can be titrated with iodine solution. In strongly acid solutions, however, arsenate is reduced to arsenite and iodine is liberated. Upon titration with sodium thiosulphate solution, the iodine is removed and the reaction proceeds from right to left.

With certain weak oxidising agents, complete reduction with the iodide ion may be difficult; the reaction may be made suitable for quantitative work by one of the following methods:

(i) Increase of the iodide-ion concentration, as for the reaction:

\[
2\text{Fe}^{+++} + 2\text{I}^- \Leftrightarrow 2\text{Fe}^{++} + \text{I}_2
\]

(ii) Increase of the hydrogen-ion concentration if this increases the oxidation potential of the system.

(iii) The iodine may be removed from the sphere of reaction either by boiling and then collecting in an appropriate solvent, or by extracting with an immiscible solvent, such as chloroform, carbon tetrachloride, or carbon disulphide.

(iv) If the reaction is a slow one in an acid medium, it is advisable to replace the air in the titration vessel by carbon dioxide (this is most simply effected by the addition of 2 or 3 half-gram portions of pure sodium bicarbonate). This is because the velocity of the reaction:

\[
4\text{I}^- + 4\text{H}^+ + \text{O}_2 = 2\text{I}_2 + 2\text{H}_2\text{O}
\]

which is extremely slow in a neutral medium, increases with increasing
pH of the solution; it is greatly accelerated by sunlight and by various catalysts as, for example, traces of copper.

In a number of cases, as in the analysis of the higher oxides of manganese and of lead, it is necessary to boil the oxidising agent with hydrochloric acid or hydrobromic acid, and to pass the liberated chlorine or bromine into excess of potassium iodide solution. Direct boiling of the sample with an acid iodide solution is not advisable, since the latter is a much stronger reducing agent than chloride or bromide and will react with ferric iron, which is a common impurity in these oxides.

\[
\begin{align*}
\text{MnO}_2 + 4\text{H}^+ + 4\text{Cl}^- & = \text{Mn}^{2+} + \text{Cl}_2 + 2\text{Cl}^- + 2\text{H}_2\text{O} \\
\text{Cl}_2 + 2\text{I}^- & = 2\text{Cl}^- + \text{I}_2 \\
2\text{Fe}^{3+} + 2\text{I}^- & \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_2
\end{align*}
\]

It seems appropriate to refer at this point to the uses of a standard solution containing potassium iodide and potassium iodate. This solution is quite stable and yields iodine when treated with acid:

\[
\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ = 3\text{I}_2 + 3\text{H}_2\text{O}
\]

The standard solution is prepared by dissolving a weighed amount of pure potassium iodate in a solution containing a slight excess of pure potassium iodide, and diluting to a definite volume. This solution has two important uses. The first is as a source of a known quantity of iodine in titrations (compare Section III, 102A); it must be added to a solution containing strong acid; it cannot be employed in a medium which is neutral or possesses a low acidity.

The second use is in the determination of the acid content of solutions iodometrically or in the standardisation of solutions of strong acids. It is evident from the above equation that the amount of iodine liberated is equivalent to the acid content of the solution. Thus if, say, 25 ml. of an approximately 0·1N solution of a strong acid is treated with a slight excess of potassium iodate (say, 30 ml. of 0·1N-potassium iodate solution, Section III, 102A) and a slight excess of potassium iodide solution (say, 10 ml. of a 10 per cent solution), and the liberated iodine titrated with standard 0·1N-sodium thiosulphate with the aid of starch as an indicator, the normality of the acid may be readily evaluated.

III, 100. Detection of the end point.—A solution of iodine in aqueous iodide has an intense yellow to brown colour. One drop of 0·1N-iodine solution imparts a perceptible pale yellow colour to 100 ml. of water, so that in otherwise colourless solutions iodine can serve as its own indicator. The test is made much more sensitive by the use of a solution of starch as indicator. Starch reacts with iodine in the presence of iodide to form an intensely blue-coloured adsorption complex containing both iodine and iodide, which is visible at very low iodine concentrations. Thus 100 ml. of water containing 0·05–0·1 g. of potassium iodide and a few ml. of 0·5–1 per cent starch solution becomes distinctly blue upon the addition of 1 drop of 0·1N-iodine. The sensitivity of the starch reaction corresponds to an iodine concentration of 1–2 × 10\(^{-5}\) N at about 20° C. in the presence of a small amount of iodide (> 0·001N). The reaction is less sensitive in the absence of iodide, and also decreases in sensitivity with increasing temperature of the solution; thus at 50° C. it is about ten times less sensitive than at 25° C.
The great merit of starch is that it is inexpensive. It possesses the following disadvantages: (i) insolubility in cold water; (ii) instability of suspensions in water; (iii) it gives a water-insoluble complex with iodine, the formation of which precludes the addition of the indicator early in the titration (for this reason, in titrations of iodine, the starch solution should not be added until just prior to the end point when the colour begins to fade); and (iv) there is a "drift" end point, which is marked when the solutions are dilute.

Most of the disadvantages of starch as an indicator are absent in sodium starch glycollate (S. Peat, 1947). This is a non-hygroscopic powder, readily soluble in hot water to give a faintly opalescent solution, which is stable for many months; it does not form a water-insoluble complex with iodine, and hence the indicator may be added at any stage of the reaction. With excess of iodine (e.g., at the beginning of a titration with sodium thiosulphate) the colour of the solution containing 1 ml. of the indicator (0.1 per cent aqueous solution) is green; as the iodine concentration diminishes the colour changes to blue, which becomes intense just before the end point is reached. The end point is very sharp and reproducible and there is no "drift" in dilute solution. It must be understood that throughout this book when starch is recommended as an indicator, it may be replaced with advantage by sodium starch glycollate.

Carbon tetrachloride has been used in certain reactions instead of starch solution. One litre of water at 25° C. will dissolve 0.335 g. of iodine, but the same volume of carbon tetrachloride will dissolve about 28.5 g. Iodine is therefore about eighty-five times as soluble in carbon tetrachloride as it is in water (compare distribution coefficient in Section I, 71), and the carbon tetrachloride solution is highly coloured. When a little carbon tetrachloride is added to an aqueous solution containing iodine and the solution well shaken, the great part of the iodine will dissolve in the carbon tetrachloride; the latter will fall to the bottom since it is immiscible with water, and the colour of the organic layer will be much deeper than that of the original aqueous solution. The reddish-violet colour of iodine in carbon tetrachloride is visible in very low concentrations of iodine; thus on shaking 5 ml. of carbon tetrachloride with 50 ml. of 2 × 10⁻⁵ N-iodine, a distinct violet coloration is produced in the organic layer. This enables many iodometric determinations to be carried out with comparative ease. The titrations are performed in 250-ml. glass-stoppered bottles or flasks with accurately ground stoppers. After adding the excess of potassium iodide solution and 5–10 ml. of carbon tetrachloride to the reaction mixture, the titration with sodium thiosulphate is commenced. At first the presence of iodine in the aqueous solution will be apparent, and gentle rotation of the liquid causes sufficient mixing. Towards the end of the titration the bottle or flask is stoppered and shaken after each addition of sodium thiosulphate solution; the end point is reached when the carbon tetrachloride just becomes colourless. Equally satisfactory results can be obtained with chloroform.

The end point can also be determined potentiometrically (Section I, 51 and Chapter VI).

Preparation and use of starch solution. Make a paste of 1 g. of soluble starch with a little water, and pour the paste, with constant stirring, into 100 ml. of boiling water, and boil for 1 minute. Allow the solution
to cool, and add 3 g. of potassium iodide. This solution may be pre-
served for a long period if kept under a layer of toluene in a stoppered
bottle.*

If soluble starch is not available, grind 1 g. of ordinary starch with a
little cold water, pour the paste slowly into 100 ml. of boiling water,
and boil the solution for 2 minutes. Cool by placing into cold water,
and filter the cold solution. This solution cannot safely be kept for
more than about a day.

Only freshly prepared or properly preserved starch solution should be
used. Two ml. of a 1 per cent solution per 100 ml. of the solution to be
titrated is a satisfactory amount; the same volume of starch solution
should always be added in a titration. In the titration of iodine, starch
must not be added until just before the end point is reached. Apart
from the fact that the fading of the iodine colour is a good indication of
the approach of the end point, if the starch solution is added when the
iodine concentration is high, some iodine may remain adsorbed even
at the end point. The indicator blank is negligibly small in iodimetric
and iodometric titrations of 0·1N-solutions; with more dilute solutions,
it must be determined in a liquid having the same composition as the
solution titrated has at the end point.

Starch solution cannot be employed in alcoholic solution, nor can it
be used in a strongly acid medium because hydrolysis of the starch
occurs.

Preparation and use of sodium starch glycollate indicator.† Sodium starch
glycollate, prepared as described below, dissolves slowly in cold but
rapidly in hot water. It is best dissolved by mixing, say, 5·0 g. of
the finely powdered solid with 1-2 ml. of ethyl alcohol, adding 100 ml.
of cold water, and boiling for a few minutes with vigorous stirring: a
faintly opalescent solution results. This 5 per cent stock solution is
diluted to 0·1 per cent strength as required. The most convenient
concentration for use as an indicator is 1 mg./ml., i.e., 1 ml. of the 0·1
per cent aqueous solution is added to the solution being titrated.

Preparation of sodium starch glycollate.‡ Triturate 10 g. of potato starch
into a cream with cold water and vigorously stir the cream into boiling water:
the total volume of the water should be 160 ml. Continue the stirring at the
boiling point for 30 minutes, and allow the dispersion to cool to room tem-
perature. Introduce 30 ml. of 50 per cent sodium hydroxide solution, and stir for
1 hour at the laboratory temperature. Warm the alkaline solution to 50° C.
and add, during 30 minutes, a warm solution (at 50° C.) of 5 g. of sodium
monochloroacetate in 20 ml. of water. Continue the mechanical stirring of
the viscous solution for 3 hours, and then allow to stand overnight at the
laboratory temperature. Neutralise with dilute acetic acid. Dialyse the
neutral solution for three days in a "cellophane" bag against running
water. Precipitate the sodium starch glycollate by the addition of excess of
ethyl alcohol; a little sodium chloride (<0·1 per cent) assists the
precipitation. The precipitate may be further purified, if desired, by extraction in a
Soxhlet apparatus with water-ethyl alcohol (10 : 90 by volume); the product

* Alternatively, the addition of 0·1 g. of thymol to 100 ml. of boiling water before
mixing with 1 g. of starch produces a starch solution which keeps for several months.
† The following account is based upon information kindly supplied (1950) by Professor
S. Peat, D.Sc., F.R.S.
‡ A "sodium starch glycollate" is marketed by British Drug Houses, Ltd., Poole,
Dorset. Commercial specimens must generally be used in higher concentration, e.g.,
1 ml. of 1 per cent solution.
Volmer's Analysis

is finally washed successively with absolute alcohol and anhydrous ether, and dried in a vacuum desiccator. It contains on average one glycollate group per ten glucose residues.

In iodimetry and iodometry the following solutions *inter alia* are used: iodine, sodium thiosulphate, sodium arsenite, potassium iodate, potassium bromate, and chloramine-T. All of these will be discussed in the ensuing pages.

**III. 101. Preparation of 0.1N-sodium thiosulphate.—Discussion.**

Sodium thiosulphate \( \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \) is readily obtainable in a state of high purity, but there is always some uncertainty as to the exact water content because of the efflorescent nature of the salt and for other reasons. The substance is therefore unsuitable as a primary standard. It is a reducing agent by virtue of the reaction:

\[
2\text{S}_2\text{O}_3^- \rightarrow \text{S}_4\text{O}_6^- + 2e
\]

the equivalent weight of sodium thiosulphate pentahydrate is its molecular weight, or 248.20.* An approximately 0.1N solution is prepared by dissolving about 25 g. of A.R. crystallised sodium thiosulphate in 1 litre of water in a volumetric flask. The solution is standardised by any of the methods described below.

Before dealing with these, it is necessary to refer briefly to the stability of thiosulphate solutions. Solutions prepared with conductivity (equilibrium) water are perfectly stable. However, ordinary distilled water usually contains an excess of carbon dioxide; this may cause a slow decomposition to take place with the formation of sulphur:

\[
\text{S}_4\text{O}_6^- + \text{H}^+ \rightarrow \text{HSO}_3^- + \text{S}
\]

Moreover, decomposition may also be caused by bacterial action (*Thiobacillus thioparus*), particularly if the solution has been standing for some time. For these reasons, the following recommendations are made:

(i) Prepare the solution with recently boiled distilled water.

(ii) Add 1 ml. of chloroform or 10 mg. of mercuric iodide or 1.0 g. of mercuric cyanide per litre; these compounds improve the keeping qualities of the solution. (The addition of alkalis, sodium carbonate or borax, is not recommended since these tend to accelerate the decomposition:

\[
\text{S}_4\text{O}_6^- + 2\text{O}_2 + \text{H}_2\text{O} = 2\text{SO}_4^- - + 2\text{H}^+
\]

(iii) Avoid exposure to light, as this tends to hasten the decomposition.

The standardisation of thiosulphate solutions may be effected with potassium iodate, potassium bromate, potassium dichromate, copper, iodine, potassium permanganate, or ceric sulphate. Owing to the volatility of iodine and the difficulty of preparation of perfectly

* The same result is deduced from the equations:

\[
\text{I}_2 + 2e = 2\text{I}^-
\]

and

\[
2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}
\]

Alternatively, sodium thiosulphate may be regarded as interacting with weak oxidising agents in accordance with the equation:

\[
2\text{Na}_2\text{S}_2\text{O}_3 + \text{O} + \text{H}_2\text{O} = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaOH}
\]

This leads to the same result, viz., the equivalent weight is 1 mol.
pure iodine, this method is not a suitable one for beginners. If, how­
ever, a standard solution of iodine (see Sections III, 103, 104) is
available, this may be used for the standardisation of thiosulphate
solutions.

Procedure. Weigh out 25 g. of A.R. sodium thiosulphate crystals,
Na₂S₂O₃·5H₂O, dissolve in boiled-out distilled water, and make up to
1 litre in a volumetric flask with boiled-out water. If the solution is
to be kept for more than a few days, add 1·0 g. of mercuric cyanide or
0·01 g. of mercuric iodide or 1 ml. of chloroform.

Anhydrous sodium thiosulphate as a primary standard. Anhydrous sodium
thiosulphate is stable at 120° C. for prolonged periods and is
not very hygroscopic. It may be used as a primary standard. An­
ydrous sodium thiosulphate of A.R. quality is marketed;* this may
contain about 1 per cent of water, and should be dried to constant
weight at 100–120° C. before use.

Anhydrous sodium thiosulphate may be prepared from the A.R.
pentahydrate crystals by either of the following methods:

(1) Dehydration in a current of air. Place 40–50 g. of A.R. sodium
thiosulphate pentahydrate in a 100-ml. wide-necked (bolt-head) flask
fitted with a three-holed cork carrying a thermometer and inlet tube
reaching to within 1 cm. of the bottom of the flask and a short tube
extending just below the cork. Mount the flask in an air-bath † and
heat; maintain the contents of the flask at 100–115° C. whilst drawing a
stream of air (water-pump) through the liquid. The contents of the
flask solidify in less than an hour. Allow to cool, remove the solid from
the flask with the aid of a stout glass rod (caution !), powder in a glass
mortar, dry at 110–120° C. for 2 hours, and allow to cool in a desiccator
over anhydrous calcium chloride.

(2) Dehydration in an open beaker. Place 50 g. of A.R. sodium thio­
sulphate pentahydrate in a 100-ml. beaker mounted in an air-bath.
Clamp a thermometer so that its bulb is near the bottom of the beaker.
Fit up a glass stirrer at an angle of 45° and adjust it so that, when the
crystals have just melted, half of the blade is in the liquid and half
outside it; this will materially assist in increasing the speed of dehydra­
tion and also prevent the formation of a solid cake of the anhydrous
salt. Maintain the temperature inside the beaker at 100–115° C. whilst
stirring mechanically. The contents of the beaker solidify in less than
an hour and may be readily removed. Powder the solid, dry at 110–
120° C. for 2–3 hours, and allow to cool in a desiccator over anhydrous
calcium chloride. The method may be adapted to large-scale prepara­
tion, if required.

The purity of the product (as determined by titration with potassium
iodate, Section III, 102) exceeds 99·9 per cent.

III, 102. Standardisation of sodium thiosulphate solutions.—A.
With potassium iodate. A.R. potassium iodate has a purity of at least
99·9 per cent: it can be dried at 120° C. This reacts with potassium
iodide in acid solution to liberate iodine:

\[ \text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{SO}_4 = 3\text{K}_2\text{SO}_4 + 3\text{I}_2 + 3\text{H}_2\text{O} \]

* For example, by Merck and Co. Inc., Rahway, N.J., U.S.A., by Mallinckrodt
Chemical Works, 70–74 Gold Street, New York, N.Y., and by J. T. Baker Chemical Co.,
Phillipsburg, N.J., U.S.A.
† See, for example, Fig. II, 5, 3, in the author's Text Book of Practical Organic
Its equivalent weight as an oxidising agent is \( \frac{1}{3} \) mol. or 214.02/6; a 0.1N solution therefore contains 3.567 g. of potassium iodate per litre.

Weigh out accurately 0.14-0.15 g. of pure dry potassium iodate, dissolve it in 25 ml. of cold, boiled-out distilled water, add 2 g. of iodate-free potassium iodide* and 5 ml. of 2N-sulphuric acid (1). Titrate the liberated iodine with the thiosulphate solution with constant stirring. When the colour of the liquid has become a pale yellow, dilute to ca. 200 ml. with distilled water, add 2 ml. of starch solution, and continue the titration until the colour changes from blue to colourless. Repeat with two other similar portions of potassium iodate.

Calculate the normality of the sodium thiosulphate solution.

\[
1 \text{ ml. } N\text{-Na}_2\text{S}_2\text{O}_3 = 0.03567 \text{ g. KIO}_3
\]

**Note.** 1. Potassium iodate has a small equivalent weight (35.67) so that the error in weighing 0.14-0.15 g. may be appreciable. In this case it is better to weigh out accurately 3.567 g. of the A.R. salt (if a slightly different weight is used, the exact normality is calculated), dissolve it in water, and make up to 1 litre in a volumetric flask. Twenty-five ml. of this solution are treated with excess of pure potassium iodide (1 g. of the solid or 10 ml. of 10 per cent solution), followed by 3 ml. of 2N-sulphuric acid, and the liberated iodine is titrated as detailed above. The titrations are repeated until two agree within 0.1 ml.; not more than three titrations should be necessary. The normality of the sodium thiosulphate solution is then calculated (see Section III, 4A).

**B. With potassium bromate.** Potassium bromate is very similar in properties to potassium iodate; its only advantage over the latter is that it is less expensive. A.R. potassium bromate has a purity of at least 99.9 per cent. It may be dried at 120-150°C, and its aqueous solution is stable. The substance reacts with potassium iodide in acid solution in accordance with the equation:

\[
\text{KBrO}_3 + 6\text{KI} + 6\text{HCl} = \text{KBr} + 6\text{KCl} + 3\text{I}_2 + 3\text{H}_2\text{O}
\]

The equivalent weight as an oxidising agent is \( \frac{1}{6} \) mol.; a 0.1N-solution therefore contains 167.02/60 or 2.784 g. of potassium bromate per litre.

Weigh out accurately 0.11-0.12 g. of pure dry potassium bromate (1). Dissolve it in 35 ml. of boiled-out distilled water, add 2 g. of iodate-free potassium iodide and 5 ml. of 4N-hydrochloric acid (2). Titrate with the sodium thiosulphate solution until most of the liberated iodine has reacted, dilute with 150 ml. of distilled water, then add 2 ml. of freshly prepared starch solution, and complete the titration. Repeat the determination with two further similar samples of potassium bromate.

Calculate the normality of the sodium thiosulphate solution.

\[
1 \text{ ml. } N\text{-Na}_2\text{S}_2\text{O}_3 = 0.02784 \text{ g. KBrO}_3
\]

**Notes.** 1. It is better to prepare a 0.1N solution by weighing out 2.784 g. of A.R. potassium bromate, dissolving it in water, and making up to 1 litre in a volumetric flask (compare **Note** 1 under **A**). Twenty-five ml. of this solution are treated with excess of pure potassium iodide (1.5 g. of the solid or 15 ml. of the 10 per cent solution), followed by 4-5 ml. of 4N-hydrochloric acid.

* The absence of iodate is indicated by adding dilute sulphuric acid when no immediate yellow coloration should be obtained. If starch is added, no immediate blue coloration should be produced.
acid, and the liberated iodine titrated as detailed above. The titrations are repeated until two agree within 0·1 ml.; not more than three titrations should be necessary. The normality of the sodium thiosulphate solution is then calculated.

2. A higher acidity is required than for potassium iodate solutions. The reaction is somewhat slower; the addition of a few drops of 3 per cent ammonium molybdate solution considerably increases the velocity of the reaction.

C. With potassium dichromate. Potassium dichromate is reduced by an acid solution of potassium iodide to a green chromic salt, and an equivalent weight of iodine is set free:

$$\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{KI} + 14\text{HCl} = 8\text{KCl} + 2\text{CrCl}_3 + 3\text{I}_2 + 7\text{H}_2\text{O}$$

This reaction is subject to a number of errors: (1) it is not instantaneous, and (2) the hydriodic acid (from excess of iodide and acid) is readily oxidised by air, especially in the presence of chromic salts. It is accordingly best to pass a current of carbon dioxide through the reaction flask before and during the titration (a more convenient but less efficient method is to add some solid sodium bicarbonate to the acid solution, and to keep the flask covered as much as possible), and to allow 5 minutes for its completion.

Place 100 ml. of cold, recently boiled distilled water in a 500-ml. conical, preferably glass-stoppered, flask, add 3 g. of iodate-free potassium iodide and 2 g. of pure sodium bicarbonate, and shake until the salts dissolve. Add 6 ml. of concentrated hydrochloric acid slowly whilst gently rotating the flask in order to mix the liquids; run in 25 ml. of standard 0·1N-potassium dichromate (1), mix the solutions well, and wash the sides of the flask with a little boiled-out water from the wash bottle. Stopper the flask (or cover it with a small watch glass), and allow to stand in the dark for 5 minutes in order to complete the reaction. Rinse the stopper or watch glass, and dilute the solution with 300 ml. of cold, boiled-out water. Titrate the liberated iodine with the sodium thiosulphate solution contained in a burette, whilst constantly rotating the liquid so as to thoroughly mix the solutions. When most of the iodine has reacted as indicated by the solution acquiring a yellowish-green colour, add 2 ml. of starch solution and rinse down the sides of the flask; the colour should change to a shade of blue. Continue the addition of the thiosulphate solution dropwise, and swirling the liquid constantly, until 1 drop changes the colour from greenish-blue to light green. The end point is sharp, and is readily observed in a good light against a white background. Carry out a blank determination, substituting distilled water for the potassium dichromate solution; if the potassium iodide is iodate-free, this should be negligible. Repeat with two other 25-ml. portions of the dichromate solution. Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ ml. } N\text{-Na}_2\text{S}_2\text{O}_3 = 0·04904 \text{ g. } \text{K}_2\text{Cr}_2\text{O}_7$$

Note. 1. If preferred, about 0·2 g. of A.R. potassium dichromate may be accurately weighed out, dissolved in 50 ml. of cold, boiled-out water, and the titration carried out as detailed above.

The following alternative procedure utilises a trace of copper sulphate as a catalyst to increase the speed of the reaction; in consequence, a
weaker acid (acetic acid) may be employed and the extent of any aerial oxidation of hydriodic acid reduced. Place 25 ml. of 0.1N-potassium dichromate in a 250-ml. conical flask, add 5.0 ml. of glacial acetic acid, 5 ml. of 0.001M-copper sulphate, and wash the sides of the flask with distilled water. Add 30 ml. of 10 per cent potassium iodide solution, and titrate the iodine as liberated with the approximately 0.1N-thiosulphate solution, introducing a little starch indicator towards the end. The titration may be completed in 3-4 minutes after the addition of the potassium iodide solution. Subtract 0.05 ml. to allow for the iodine liberated by the copper sulphate catalyst. Repeat the titration with two other 25-ml. portions of the dichromate solution.

D. With copper. This method is not recommended except where the thiosulphate solution is to be used for the determination of copper. A.R. copper turnings (prepared from electrolytic copper) have a purity of over 99.9 per cent.*

Weigh out accurately about 0.25 g. of pure copper turnings into a 250-300-ml. conical flask, and dissolve it in a mixture of 3 ml. of concentrated nitric acid and 6 ml. of water. Dilute to 25 ml. with water, heat the solution to boiling, add 1.0 g. of urea and boil the solution for 1-2 minutes. The urea completely eliminates nitrous acid and oxides of nitrogen, which interfere with the determination.† Cool the solution, and add 6N-ammonium hydroxide solution slowly until a slight permanent precipitate of cupric hydroxide just forms. Add 5 ml. of glacial acetic acid to the almost neutral solution. Cool the solution, and add 2 g. of potassium iodide dissolved in 30 ml. of water (or 20 ml. of a 10 per cent solution), cover the conical flask with a watch glass, and allow to stand for 1 minute. Titrate the liberated iodine with the thiosulphate solution, added from a burette, until the brown colour due to iodine has changed to light yellow. Add 2 ml. of starch solution, and continue the titration with the thiosulphate, stirring constantly, until 1 drop changes the colour from blue to yellowish-white.‡ The cuprous iodide is always coloured by adsorbed "starch iodide," and is not a pure white at the end point. Repeat the determination with two other 0.25-g. portions of copper.

When starch alone is employed as indicator, the iodine is not completely available for reaction with the sodium thiosulphate, and hence the strength of the thiosulphate solution determined by means of copper is slightly higher (ca. 3 per cent) than that standardised against potassium iodate or iodine. It is for this reason that the method was not recommended above except where the thiosulphate solution is subsequently to be used for the determination of copper.

H. W. Foote (1938) has shown that the iodine adsorbed by the cuprous

* The Bureau of Analyzed Samples, Ltd., or Middlesbrough, England, supply copper turnings of 99.90 per cent purity (a "British Chemical Standard ").

† Nitrite and nitric oxide when present even in minute quantities interfere. Thus nitrite in acid solution reacts in accordance with the equation:

$$2NO_2^- + 2I^- + 4H^+ = 2NO + I_2 + 2H_2O$$

The nitric oxide is oxidised by air to nitrogen peroxide, which reacts with the iodide to form more nitric oxide and iodine; the cycle is then repeated. For this reason, if a trace of nitric oxide is present in the solution, no permanent end point is obtained upon titration with thiosulphate solution in the presence of starch. The colour returns rapidly upon the removal of the iodine.

‡ The end point is rendered sharper by adding 1 or 2 drops of 0.1N-silver nitrate; the yellowish colour of silver iodide neutralises the purplish tinge of cuprous iodide.
iodide is liberated and made available to the thiosulphate if a soluble thiocyanate is added to the solution just before the end point is reached in the usual titration. Under these conditions, the total iodine liberated is closely equivalent to the copper, and the end point is sharp, the precipitate turning almost white. This simple modification permits the use of pure copper in the standardisation of thiosulphate solutions for general use. The experimental procedure is exactly as above. The thiosulphate solution is added until the yellow-brown colour due to iodine is nearly discharged, 2 ml. of starch solution is introduced, and titration is continued until near the end point (i.e., until the blue colour commences to fade). About 1·5-2·0 g. of A.R. ammonium thiocyanate is then added (to liberate the adsorbed iodine), and titration is continued until the blue colour is just discharged.

The principal reaction is:

$$2\text{Cu}^{+} + 4\text{I}^- \rightleftharpoons \text{Cu}_2\text{I}_2 + \text{I}_2$$

It proceeds from left to right because of the insolubility of the cuprous iodide under the experimental conditions employed.

Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ ml. } N\cdot\text{Na}_2\text{S}_2\text{O}_3 = 0\cdot06357 \text{ g. Cu}$$

E. With pure iodine. Pure iodine is prepared as described in Section II, 12B under Sublimation. This method has the advantage of giving a direct value, but suffers from the drawbacks that it is necessary to prepare pure dry iodine and the difficulty of weighing out accurately the volatile iodine. The weighing of the iodine is usually carried out in some form of weighing-bottle containing a concentrated solution of potassium iodide; the solution of iodine in potassium iodide has a lower vapour pressure, thus reducing the volatility.

Select two or three small weighing-bottles fitted with well-ground stoppers and of such size that they will pass completely through the neck of a 350- or 500-ml. conical flask. Into one of these weigh out 2-2·5 g. of iodate-free potassium iodide and 0·5 ml. of water; stopper the weighing-bottle and weigh accurately. Remove the stopper, add 0·4-0·5 g. of pure iodine, quickly replace the stopper, and weigh again; the difference between the two weighings gives the weight of iodine. Place the weighing-bottle in the neck of the conical flask held in an inclined position and containing 200 ml. of water and about 1 g. of pure potassium iodide. Allow the bottle to slide to the bottom of the flask, but just as it falls remove the stopper and allow it to fall also. No iodine is thus lost. If the contents of the weighing-bottle are washed into the water, a slight loss of iodine may occur. Titrate the solution, containing a known weight of iodine, with the sodium thiosulphate solution from a burette. When the liquid is pale yellow in colour, add 2 ml. of starch solution, and continue the titration dropwise until the blue colour is just destroyed. Repeat the determination with two other similar weighing-bottles and 0·4-0·5 g. of iodine.

Calculate the normality of the sodium thiosulphate solution.

$$1 \text{ ml. } N\cdot\text{Na}_2\text{S}_2\text{O}_3 = 0\cdot12692 \text{ g. I}$$

F. With a standard solution of iodine. If a solution of iodine which has been standardised against arsénious oxide (Section III, 104A) is
available, this may be employed in the standardisation of a sodium thiosulphate solution. The procedure is identical with that given under E above.

Calculate the normality of the sodium thiosulphate solution as based upon that of the iodine solution (compare Section III, 4A).

G. With potassium permanganate. This method utilises a secondary standard, and is the least trustworthy of all described. Reasonably satisfactory results can be obtained if the experimental conditions given below are strictly followed. Upon adding potassium permanganate solution to an acid solution containing potassium iodide, the following reaction occurs:

\[2\text{KMnO}_4 + 10\text{KI} + 16\text{HCl} = 12\text{KCl} + 2\text{MnCl}_2 + 5\text{I}_2 + 8\text{H}_2\text{O}\]

Measure out 25 ml. of standard 0·1N-potassium permanganate into a 350-ml. conical, preferably glass-stoppered, flask containing a solution of 6 g. of potassium iodide in 50 ml. of water and 2 ml. of concentrated hydrochloric acid. Allow to stand in the dark for 10 minutes. Titrate the iodine that has been set free with the sodium thiosulphate solution until the solution has a faint straw colour, add 2 ml. of the starch solution, and continue the titration until the blue colour is just destroyed. Carry out a blank determination, but substitute 25 ml. of water for the 25 ml. of the potassium permanganate solution; subtract the volume of thiosulphate solution required in the blank run from that consumed in the other titration. Repeat the determination with two other 25-ml. portions of the permanganate solution.

Calculate the normality of the sodium thiosulphate solution.

\[1\text{ml. } N-Na_2S_2O_3 = 0.03161 \text{ g. KMnO}_4\]

H. With ceric sulphate. This method for standardising sodium thiosulphate solutions makes use of a secondary standard, but gives satisfactory results provided the experimental conditions given below are rigidly adhered to; this is due to the fact that ceric sulphate solution contains free acid, which may otherwise lead to appreciable errors.

For 0·1N-ceric sulphate (Sections III, 74–75), use a solution containing 0·5–0·7 g. of sodium thiosulphate pentahydrate or 25 ml. of the ca. 0·1N-sodium thiosulphate solution, 0·3–0·4 g. of pure potassium iodide, 20 ml. of 0·2 per cent starch solution, dilute to 250 ml., and titrate with the ceric sulphate solution to the starch–iodine end point.

The reaction is:

\[2\text{Ce}^{+++} + 2\text{I}^- = 2\text{Ce}^{+++} + \text{I}_2\]

\[\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} = \text{S}_4\text{O}_6^{2-} + 2\text{I}^-\]

Calculate the normality of the sodium thiosulphate solution.

\[1\text{ml. } N-Na_2S_2O_3 = 0.3323 \text{ g. Ce(SO}_4)_2\]

III. 103. Preparation of 0·1N-iodine solution.—Discussion. 0·335 Gram of iodine dissolves in 1 litre of water at 25°C. In addition to this small solubility, aqueous solutions of iodine have an appreciable vapour pressure of iodine, and therefore decrease slightly in concentration on account of volatilisation when handled. Both difficulties are overcome by dissolving the iodine in an aqueous solution of potassium
iodide. Iodine dissolves readily in aqueous potassium iodide, the
more concentrated the solution, the greater is the solubility of the
iodine. The increased solubility is due to the formation of a tri-
iodide ion:

\[
I_2 + I^- \rightleftharpoons I_3^-
\]

The resultant solution has a much lower vapour pressure than a
solution of iodine in pure water, consequently the loss by volatilisation
is considerably diminished. Nevertheless, the vapour pressure is still
appreciable so that precautions should always be taken to keep vessels
containing iodine closed except during the actual titrations. When an
iodide solution of iodine is titrated with a reductant, the free iodine
reacts with the reducing agent, this displaces the equilibrium to the
left, and eventually all the tri-iodide is decomposed; the solution
therefore behaves as though it were a solution of free iodine.

Iodine solution attacks rubber, hence it should always be used with
burettes fitted with glass taps. Since iodine and iodides are com­
paratively expensive, all residual liquids or precipitates containing iodine in
any form should be returned to the bottle marked “Iodine Residues.”

For the preparation of standard iodine solutions, A.R. or resublimed
iodine and iodate-free (e.g., A.R.) potassium iodide should be employed.
The solution may be standardised against pure arsenious oxide or pure
anhydrous sodium thiosulphate, or with a sodium thiosulphate
solution which has been recently standardised against potassium iodate.
For work of the highest accuracy purposely purified iodine may be
weighed out directly, but in view of the volatility of the solid, this
method is not recommended for beginners nor, indeed, is it necessary
for most ordinary purposes. It is given here for the sake of
completeness.

The equation:

\[
I_2 + 2e^- \rightleftharpoons 2I^-
\]

indicates that the equivalent weight is equal to the atomic weight, or
126.92.*

Procedure. Preparation of 0.1N-iodine. Method A. Dissolve 20 g. of
iodate-free potassium iodide (e.g., A.R.) in 30–40 ml. of water in a
glass-stoppered 1-litre flask. Weigh out about 12.7 g. of A.R. or re­
sublimed iodine on a watch glass on a rough balance (never on an
analytical balance on account of the iodine vapour), and transfer it by
means of a small dry funnel into the concentrated potassium iodide
solution. Insert the glass stopper into the flask, and shake in the cold
until all the iodine has dissolved. Allow the solution to acquire room
temperature, and make up to the mark with distilled water.
The iodine solution is best preserved in small glass-stoppered bottles.
These should be filled completely and kept in a cool, dark place.

Method B. Purify re-sublimed or A.R. iodine as described in Section
II, 12B. Secure a large weighing-bottle provided with a well-fitting
ground-glass stopper. Place 20 g. of pure potassium iodide and 5 ml.
of water into it; the solid will dissolve completely on gentle shaking.
When the bottle and contents have acquired room temperature, weigh
them accurately to 0.1 mg. Weigh out 6.0–6.5 g. of the purified iodine

* This also follows from the hypothetical equation:

\[
I_2 + H_2O = 2HI + O
\]
on a rough balance and introduce it carefully without splashing into the weighing-bottle. Allow to stand (say, for 20 minutes) in order to attain the room temperature; and weigh again to the nearest 0-1 mg. Immediately after the weighing transfer the solution quantitatively to a glass-stoppered 500-ml. volumetric flask, and make up to the mark with distilled water. Stopper the flask, and store it in a dark place.

Calculate the normality of the iodine solution from the weight of pure iodine employed. A 0·1N-solution contains 12·692 g. of iodine per litre.

III, 104. Standardisation of iodine solutions.*—A. With arsenious oxide. Discussion. A.R. Arsenious oxide of 99·9 per cent purity can be obtained commercially; the U.S. Bureau of Standards supply a product of 99·99 per cent guaranteed purity.† This substance therefore provides an excellent primary standard for the standardisation of iodine solutions. The reaction between arsenious oxide and iodine is a reversible one:

\[
H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_2AsO_4 + 2H^+ + 2I^- \]

and proceeds quantitatively from left to right if the hydrogen iodide is removed from the solution as fast as it is formed. This may be done by the addition of sodium bicarbonate; sodium carbonate and sodium hydroxide cannot be used, since they react with the iodine, forming iodide, hypoiodite, and iodate. Actually it has been shown that the complete oxidation of the arsenite occurs when the pH of the solution lies between 4 and 6, the best value being 6-5, which is very close to the neutral point. Buffer solutions (Section I, 20) are employed to maintain the correct pH. A 0·12N solution of sodium bicarbonate saturated with carbon dioxide (carbonic acid) has a pH of 7; a solution saturated with both borax and boric acid has a pH of about 6·2, whilst a \( Na_2HPO_4 \cdot NaH_2PO_4 \) solution is almost neutral. Any of these three buffer solutions is suitable, but the first-named is generally employed as already stated.

Procedure. Weigh out accurately about 2·5 g. of finely powdered A.R. arsenious oxide (I), transfer to a 400-ml. beaker, and dissolve it in a concentrated solution of sodium hydroxide, prepared from 2 g. of iron-free sodium hydroxide (e.g., A.R.) and 20 ml. of water. Dilute to about 200 ml., and neutralise the solution with N-hydrochloric acid, using a strip of litmus paper as indicator.§ When the solution is faintly acid, remove the litmus paper by means of a stirring-rod and carefully rinse both the rod and the paper. Transfer the contents of the beaker quantitatively to a 500-ml. volumetric flask, add 2 g. of

* Prepared by Method A, Section III, 108.
† Arsenious oxide of 99·95 per cent assay value is obtainable from the Mallinckrodt Chemical Works, U.S.A. If there is any doubt as to the purity of the arsenious oxide, it may be purified by dissolving in hot dilute hydrochloric acid (1 : 2), filtering, and cooling the filtrate. The supernatant liquor is poured off, the crystals washed with water, dried at 105–110° C. for 1–2 hours, and then sublimed (Section II, 12B). The sublimate may be dried for 12–24 hours in a desiccator over concentrated sulphuric acid. Pure arsenious oxide is not appreciably hygroscopic and, except for work of the highest accuracy, it is unnecessary to dry it before use.
§ The reaction is sometimes written:

\[
As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons AsO_4 + 4HI
\]

This equation shows that the equivalent weight of arsenious oxide in this reaction is 1 mol., or 197·82/4 = 49·46.

§ Alternatively, a drop of phenolphthalein may be used as indicator.
pure sodium bicarbonate, and, when all the salt has dissolved, dilute to the mark. Shake well (2).

Measure out from a burette (this is advisable owing to the poisonous properties of the solution) 25 ml. of the arsenite solution into a 250-ml. conical flask (3), add 25–50 ml. of water, 5 g. of sodium bicarbonate, and 2 ml. of starch solution. Swirl the solution carefully until the bicarbonate has dissolved. Then titrate slowly with the iodine solution, contained in a burette, to the first blue colour.

Alternatively, the arsenite solution may be placed in the burette, and titrated against 25 ml. of the iodine solution contained in a conical flask. When the solution has a pale yellow colour, add 2 ml. of starch solution, and continue the titration slowly until the blue colour is just destroyed.

For either method, further titrations should be carried out until individual titrations agree within 0·1 ml. Not more than three titrations should be necessary.

Calculate the normality of the iodine solution. A 0·1N-solution of arsenious oxide contains 4·946 g. As₂O₃ per litre.

Notes. 1. If an exactly 0·1N solution is required, this is obtained by weighing out exactly 2·473 g. of arsenious oxide.

2. For the preparation of sodium arsenite solution with a Na₂HPO₄/NaH₂PO₄ buffer mixture, proceed as follows (Washburn, 1908). Weigh out accurately about 2·47 g. of pure dry arsenious oxide into a 500-ml. volumetric flask, dissolve it in a concentrated solution containing 6 g. of pure sodium hydroxide, add 5 ml. of pure syrupy phosphoric acid (0·15 mol.), and dilute to the mark. This solution will preserve its titration value indefinitely.

3. If it is desired to base the standardisation directly upon arsenious oxide without the intermediate use of a volumetric flask, proceed as follows. Weigh out accurately about 0·2 g. of pure arsenious oxide into a conical flask, dissolve it in 10 ml. of N-sodium hydroxide, and add a small excess of dilute sulphuric acid (say, 12–15 ml. of N acid). Then add carefully a solution of 5 g. of sodium bicarbonate in 50 ml. of water, followed by 2 ml. of starch solution. Titrate slowly with the iodine solution to the first blue colour. Repeat with two other similar quantities of arsenious oxide.

Calculate the normality of the iodine solution.

B. With standard sodium thiosulphate solution. Sodium thiosulphate solution, which has been recently standardised, preferably against pure potassium iodate, is employed. Transfer 25 ml. of the iodine solution to a 250-ml. conical flask, dilute to 100 ml., and add the standard thiosulphate solution from a burette until the solution has a pale-yellow colour. Add 2 ml. of starch solution, and continue the addition of the thiosulphate solution slowly until the solution is just colourless. Repeat the titration with two further 25-ml. portions of the iodine solution. The titrations should agree within 0·1 ml.

From the known normality of the sodium thiosulphate solution, calculate the normality of the iodine solution (compare Section III, 4A).

C. With anhydrous sodium thiosulphate. Dry a sample of pure anhydrous sodium thiosulphate (commercial A.R. product or, preferably, prepared from the A.R. pentahydrate, Section III, 101) at 110–120°C to constant weight. The equivalent and molecular weight is 158·12.

Weigh out accurately 0·40–0·45 g. of pure, dry anhydrous sodium
thiosulphate, and dissolve it in 25–50 ml. of cold, boiled-out distilled water. Add the starch indicator, and run in the iodine solution with continuous stirring or swirling until a permanent blue colour is obtained. Repeat the titration with two other similar portions of anhydrous sodium thiosulphate.

Calculate the normality of the iodine solution.

\[ 1 \text{ ml. } N-I_2 = 0.1581 \text{ g. } Na_2S_2O_3 \]

Alternatively, weigh out accurately 7.906 g. of the anhydrous salt (if a slightly different weight is used, the exact normality is calculated), dissolve it in boiled-out distilled water, and make up to 500 ml. with boiled-out water in a volumetric flask. Either titrate 25 ml. of the 0.1N-sodium thiosulphate solution with the iodine as above or place the thiosulphate solution in the burette and titrate 25 ml. of the iodine solution as detailed under B.

ANALYSES INVOLVING THE USE OF STANDARD SODIUM THIOSULPHATE SOLUTION, STANDARD IODINE SOLUTION, OR STANDARD SODIUM ARSENITE SOLUTION

III, 105. Determination of copper in crystallised copper sulphate. For practice in this estimation, the student may determine the percentage of copper in A.R. copper sulphate, CuSO_4·5H_2O.

Procedure. Weigh out accurately about 3.0 g. of the salt, dissolve it in water, and make up to 250 ml. in a volumetric flask. Shake well. Pipette 50 ml. of this solution into a 250-ml. conical flask. Shake well. Pipette 50 ml. of this solution into a 250-ml. conical flask, add 1 g. of potassium iodide (or 10 ml. of a 10 per cent solution) (1), and titrate the liberated iodine with standard 0.1N-sodium thiosulphate (Section III, 102, Procedure 1J) (2). Repeat the titration with two other 50-ml. portions of the copper sulphate solution.

The reaction is:

\[ 2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4 \]

from which it follows that:

\[ 2CuSO_4 = I_2 = 2Na_2S_2O_3 \]

or

\[ 1 \text{ ml. } N-Na_2S_2O_3 = 0.06357 \text{ g. Cu} \]

Calculate the percentage of copper in crystallised copper sulphate.

Notes. 1. If in a similar determination, free mineral acid is present, a few drops of dilute sodium carbonate solution must be added until a faint permanent precipitate remains, and this is removed by means of a drop or two of acetic acid. The potassium iodide is then added and the titration continued. For accurate results, the solution should have a pH of 4–5.5.

2. It has been pointed out in Section III, 102D that this simple procedure may be in error by as much as 3 per cent owing to the adsorption of the iodine by the cuprous iodide. This also leads to difficulty in detecting the exact end point. Accurate results are obtained and the end point is readily detected by the following simple modification. After the addition of the potassium iodide solution, run in standard 0.1N-sodium thiosulphate until the brown colour of the iodine fades, then add 1 ml. of starch solution, and continue the addition of the thiosulphate solution until the blue colour commences to fade. Then add about 1 g. of A.R. potassium or ammonium
thiocyanate, preferably as a 10 per cent aqueous solution: the blue colour will instantly become more intense. Complete the titration as quickly as possible. The precipitate possesses a pale flesh colour, and a distinct permanent end point is readily obtained.

**III. 106. Determination of copper in an ore.—Discussion.** Of the common elements which are usually associated with copper ores, those that interfere with the iodometric estimation are iron, arsenic, and antimony. Ferric iron is reduced by iodide:

\[ 2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2 \]

but by the addition of excess of fluoride, the ferric iron is converted into the complex \([\text{FeF}_6]^{3-}\), which yields so small a concentration of ferric ions that it has no oxidising action upon the iodide. Arsenic and antimony in the trivalent form react with iodine, but in consequence of the oxidising medium usually employed to bring the sample into solution they will be present in the quinquevalent form. Arsenic and antimonic compounds will not oxidise iodide in a solution having a \(pH\) greater than about 3·2. By the use of excess of ammonium bi-fluoride, \(\text{NH}_4\text{HF}_2\), which acts as a buffer, the \(pH\) of the solution can be maintained above 3·2; under these conditions the reduction of the cupric ion proceeds to completion. The concentration of the fluoride should be 1·0-1·6 M.

**Procedure.** Weigh out accurately 0·5-1·0 g. of the finely powdered copper ore * into a 250-ml. beaker, add 10-15 ml. of concentrated nitric acid, and heat until the ore is well disintegrated and all the copper is in solution. Evaporate to a volume of 5 ml. (e.g., on an electric hot-plate). Add 10 ml. of concentrated hydrochloric acid and 10 ml. of 1 : 1-sulphuric acid, and evaporate to dense white fumes. To complete the oxidation of arsenic, etc., add cautiously 20 ml. of water and 10 ml. of saturated bromine water, and boil the solution until all the bromine is expelled. Filter off the residue on a small quantitative filter-paper, (1), and collect the filtrate in a 250-ml. conical flask. Wash the residue with hot 1 per cent nitric acid until the washings are colourless. Concentrate the filtrate to about 30 ml. (place a short funnel in the neck of the flask), add 0·5 g. of urea to the hot solution, and heat to boiling for 1 minute; this removes any nitrous acid or oxides of nitrogen which may be present. To the cold solution add ammonia solution (1 : 1) dropwise until the solution smells slightly of ammonia. This will precipitate all the iron as hydroxide; an excess of ammonia solution should be avoided. Add 2·0 g. of ammonium bi-fluoride \(\text{NH}_4\text{HF}_2\) (2) and shake until all the ferric hydroxide has dissolved. Now add 3 g. of A.R. potassium iodide dissolved in 5-10 ml. of water, and titrate at once with standard 0·1N-sodium thiosulphate, which has been standardised against pure copper (Section III, 102, Procedure D), adding 2 ml. of starch solution when the brown colour of the iodine decreases in intensity. Continue the addition of the thiosulphate solution until the blue colour becomes faint. Then add 20 ml. of 10 per cent aqueous ammonium or potassium thiocyanate solution, and complete the titration without delay. Repeat the determination with another sample of the ore.

Calculate the percentage of copper in the copper ore.

* Ridsdale's "Copper pyrites, No. 26" (one of the Analysed Samples for Students) is suitable.
Notes. 1. If the residue is small in amount or light coloured, the filtration may be omitted. The subsequent washing with 1 per cent nitric acid and treatment with urea is then unnecessary.

2. About 1 g. of ammonium bi-fluoride should be added for each 0·1 g. of iron present.

III, 107. Determination of manganese dioxide in pyrolusite. — Discussion. All higher oxides of the heavy metals which evolve chlorine upon treatment with concentrated hydrochloric acid may be determined with accuracy by passing the chlorine into excess of potassium iodide solution, and titrating the liberated iodine with standard sodium thiosulphate or sodium arsenite solution. It is essential to be certain that all the chlorine reacts with the potassium iodide solution. With pyrolusite, the following reactions occur:

\[
\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \\
2\text{KI} + \text{Cl}_2 = 2\text{KCl} + \text{I}_2
\]

Procedure. A distillation apparatus, such as is portrayed diagrammatically in Fig. III, 107, 1 or Fig. III, 107, 2, is employed. The apparatus fitted with ground-glass joints is to be preferred, since chlorine attacks rubber.

The apparatus in Fig. III, 107, 1, consists of a distillation flask of about 200 ml. capacity, connected to two U (Péligot) tubes containing potassium iodide solution. In Fig. III, 107, 2, a 250–300-ml. flask is provided with two ground-glass joints at A and B; the tube from B passes into a small conical flask containing potassium iodide solution; C is a small tube containing glass beads moistened with potassium iodide solution; the rest of the apparatus is self-explanatory. Weigh out accurately about 0·2 g. of the finely powdered mineral * into a small weighing-tube (1 cm. wide and 2 cm. long is a convenient size), and introduce the tube and contents into the distillation flask; connect up

* Ridsdale's "Pyrolusite (Mn) Ore, No. 18" (one of the Analyzed Samples for Students) or the Bureau of Analyzed Samples "Manganese Ore, No. 176" (one of the British Chemical Standards) is suitable.
Quantitative Inorganic Analysis

the apparatus as shown in the figure. Introduce 100 ml. of water containing 3·6 g. of iodate-free (e.g., A.R.) potassium iodide into the absorption apparatus, which should be immersed in cold water. Place 25 ml. of concentrated hydrochloric acid into the separating-funnel, and add it to the contents of the flask; meanwhile maintain a very slow stream of carbon dioxide through the apparatus. Heat the mixture very gently so that chlorine is slowly evolved. Increase the temperature gradually to the boiling point, and finally pass a slow current of carbon dioxide through the boiling solution until all the chlorine has been expelled (about 15 minutes). Immediately before the heating is stopped, increase the current of carbon dioxide in order to prevent the solution in the absorption vessels from passing back into the flask. Disconnect the absorption vessels. With the apparatus of Fig. III, 107, 1, the contents of the U-tubes are quantitatively transferred to a conical flask; with the apparatus of Fig. III, 107, 2, the tubes and beads are well rinsed with water and removed from the flask. Titrate the liberated iodine at once with standard 0·1N-sodium thiosulphate in the usual manner. If desired, the solution may be made up to 100 ml. in a volumetric flask, and 50-ml. portions titrated with the sodium thiosulphate solution; if this procedure is adopted, the weight of the mineral may be increased to 0·3–0·4 g.

Calculate the percentage of MnO₂ in the mineral.

1 ml. N-Na₂S₂O₃ = 0·04347 g. MnO₂

Note. Red lead Pb₃O₄ and lead dioxide PbO₂ may be estimated in a similar manner (compare Section III, 57, Note).

III, 108. Determination of chlorates and of bromates.—Discussion. Chlorates and bromates may be determined by the distillation process described in the previous Section for pyrolusite. The process of distillation may be avoided in these and similar cases * by mere digestion with hydrochloric acid and potassium iodide solution at an elevated temperature; decomposition is quantitative.

KClO₃ + 6HCl = KCl + 3Cl₂ + 3H₂O
3Cl₂ + 6KI = 6KCl + 3I₂
Na₂S₂O₃ + I = KClO₃/6 = KBrO₃/6

A strong bottle ("pressure bottle") with a very accurately ground stopper is necessary. Generally, the ordinary stoppered bottle of commerce is not sufficiently tight, and it is better to re-grind the stopper with a little very fine emery and water. It must then be tested by securing the stopper tightly and immersing in hot water; if any bubbles of air pass through the stopper, the bottle is useless. The stopper may be secured by means of fine copper wire threaded through a piece of

* For example, chromates and dichromates. These yield the green chromic chloride and an equivalent quantity of iodine:

2K₂CrO₇ + 6KI + 10HCl = 10KCl + 2CrCl₃ + 3I₂ + 8H₂O
K₂Cr₂O₇ + 6KI + 14HCl = 8KCl + 2CrCl₃ + 3I₂ + 7H₂O

Here it is necessary to dilute the solution very considerably in order to prevent the green colour of the chromic salt from masking the blue colour of the starch in the subsequent titration with standard sodium thiosulphate solution.

1 ml. N-Na₂S₂O₃ = 0·06474 g. K₂Cr₂O₇ = 0·04904 g. K₄Cr₂O₇
rubber tubing securely fixed to the neck of the bottle, or by means of a special screw clamp (Fig. III, 108, 1) *

For practice, the student may determine the percentage of ClO$_3$ (or of BrO$_3$) in potassium chlorate (or potassium bromate), preferably of A.R. quality.

Procedure. Weigh out accurately 0.25–0.30 g. of the finely powdered potassium chlorate into a pressure bottle, add 7 g. of iodate-free potassium iodide dissolved in a small volume of water, and displace the air from the bottle by means of carbon dioxide from a Kipp's apparatus or from a cylinder. Add 25 ml. of concentrated hydrochloric acid, insert the stopper, fasten it down securely, and wrap the bottle in a thick duster. Immerse the whole in cold water in a water-bath, heat the water gradually to boiling, and continue the boiling for 1 hour. Allow the water to cool, and when quite cold, remove the bottle, open it, transfer the contents quantitatively into a 250-ml. volumetric flask, and make up to the mark. Shake well. Titrate 50-ml. portions with standard 0.1N-sodium thiosulphate, using starch as indicator.

Calculate the percentage of ClO$_3$ in the sample of potassium chlorate.

\[
1 \text{ ml. } N\text{-Na}_2\text{S}_2\text{O}_3 = 0.11391 \text{ g. ClO}_3 = 0.02043 \text{ g. KClO}_3
\]

**III, 109. Volumetric determination of lead.**—Discussion. The lead is precipitated as the chromate with potassium chromate or dichromate solution in a medium buffered with a mixture of acetic acid and sodium or ammonium acetate. The precipitate is washed with water, dissolved in dilute hydrochloric acid, treated with potassium iodide solution, and the liberated iodine titrated with a standard solution of sodium thiosulphate.

\[
Pb(C_2H_3O_2)_2 + K_2CrO_4 = PbCrO_4 + 2K-C_2H_3O_2
\]
\[
PbCrO_4 + 2HCl = H_2CrO_4 + PbCl_2
\]
\[
2H_2CrO_4 + 6KI + 12HCl = 2CrCl_3 + 6KCl + 3I_2 + 8H_2O
\]

Thus \( Pb = 3I \) or

\[
1 \text{ ml. } N\text{-I} = 1 \text{ ml. } N\text{-Na}_2\text{S}_2\text{O}_3 = 0.06907 \text{ g. Pb}
\]

Another method, which is sometimes used, consists in adding excess of 0.1N-potassium dichromate to the solution buffered with alkali acetate, boiling for 2–3 minutes, filtering the precipitate on a sintered-glass or porous-porcelain crucible, washing the precipitate well with cold water, and determining the excess of dichromate in the cooled filtrate either iodometrically by the addition of excess of potassium iodide and titration with standard thiosulphate solution or with standard ferrous ammonium sulphate solution.

For practice, the student may determine the percentage of lead in lead nitrate, preferably of A.R. purity.

* Such bottles may be purchased, for example, from A. Gallenkamp and Co., Ltd., London, E.C.2, England, or from the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.
Quantitative Inorganic Analysis

**Procedure.** Weigh out accurately about 0.3 g. of A.R. lead nitrate, dissolve it in excess of dilute acetic acid (1:4), and add 2 g. of sodium acetate; * dilute to 150 ml. Heat the solution to boiling, and add from a pipette 10 ml. of hot 4 per cent potassium chromate solution. Boil gently for 5–10 minutes, filter the lead chromate through a sintered-glass or porous-porcelain crucible, and wash several times with dilute sodium acetate solution. Transfer the precipitate quantitatively to a 250-ml. conical flask, dissolve it in dilute hydrochloric acid (1:1), add 20 ml. of 10 per cent potassium iodide solution and stir gently. Titrate at once with standard 0.1 N-sodium thiosulphate until the iodine colour has nearly disappeared, add 2 ml. of starch solution, and continue the titration until the colour of the solution changes to a clear green. Dilution facilitates the detection of the end point.

Calculate the percentage of lead in the sample of lead nitrate.

III. 110. Analysis of hydrogen peroxide.—Discussion. Hydrogen peroxide reacts with iodide in acid solution in accordance with the equation:

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{I}^- = \text{I}_2 + 2\text{H}_2\text{O}
\]

The reaction velocity is comparatively slow, but increases with increasing concentration of acid. The addition of 3 drops of a neutral 20 per cent ammonium molybdate solution renders the reaction almost instantaneous, but as it also accelerates the atmospheric oxidation of the hydriodic acid, the titration is best conducted in an atmosphere of carbon dioxide.

The iodometric method has the advantage over the permanganate method (Section III, 55) that it is less affected by stabilisers which are sometimes added to commercial hydrogen peroxide solutions. These preservatives are often boric acid, salicylic acid, and glycerol, and render the results obtained by the permanganate procedure less accurate.

**Procedure.** Dilute the hydrogen peroxide solution to 2-volume strength (ca. 0.6 per cent H₂O₂). Thus, if a “10-volume” hydrogen peroxide is used, transfer 20 ml. by means of a burette or pipette to a 100-ml. volumetric flask, and make up to the mark. Shake well. Remove 10 ml. of this diluted solution, and add it gradually and with constant stirring to a solution of 2 g. of pure potassium iodide in 200 ml. of 2N-sulphuric acid (1:20) contained in a stoppered bottle. Allow the mixture to stand for 15 minutes, and titrate the liberated iodine with standard 0.1 N-sodium thiosulphate, adding 2 ml. of starch solution when the colour of the iodine has been nearly discharged. Run a blank determination at the same time.

Better results are obtained by transferring 10 ml. of the diluted hydrogen peroxide solution to a conical flask, and adding 180 ml. of 2N (1:20) sulphuric acid. Pass a slow stream of carbon dioxide through the flask, add 20 ml. of 10 per cent potassium iodide solution, followed by 3 drops of 20 per cent ammonium molybdate solution. Titrate the liberated iodine immediately with standard 0.1 N-sodium thiosulphate in the usual way.

Repeat the titration with two other 10-ml. portions of the peroxide solution.

* The addition of alkali acetate is essential only when potassium dichromate (e.g. 10 ml. of the saturated solution) is used for precipitation.
Calculate the weight of H₂O₂ in 1000 ml. of the original solution.

\[ 1 \text{ ml. } N \cdot \text{Na}_2\text{S}_2\text{O}_3 = 0.01701 \text{ g. } \text{H}_2\text{O}_2 \]

Note. The above method is available for all per-salts.

**III. 111. Determination of the available chlorine in bleaching powder.**

_Discussion._ Bleaching powder consists essentially of a mixture of calcium hypochlorite Ca(OCl)₂ and the basic chloride CaCl₂Ca(OH)₂H₂O; some free slaked lime is usually present. The active constituent is the hypochlorite, which is responsible for the bleaching action. Upon treating bleaching powder with acid, chlorine is liberated.

\[
\text{Ca(OCl)}_2 + 4\text{HCl} = \text{CaCl}_2 + 2\text{Cl}_2 + 2\text{H}_2\text{O}
\]

The **available chlorine** refers to the chlorine liberated by the action of dilute acids, and is expressed as the percentage by weight of the bleaching powder. The bleaching powder of commerce contains 36–38 per cent of available chlorine.

Two methods are in common use for the determination of the available chlorine. In the first, the bleaching-powder solution or suspension is treated with an excess of a solution of potassium iodide, and strongly acidified with acetic acid:

\[
\text{Ca(OCl)}_2 + 4\text{KI} + 4\text{H⋅C}_2\text{H}_5\text{O}_2 = \text{CaCl}_2 + 4\text{K⋅C}_2\text{H}_5\text{O}_2 + 2\text{I}_2 + 2\text{H}_2\text{O}
\]

The liberated iodine is titrated with standard sodium thiosulphate solution. The solution should not be acidified with hydrochloric acid, for the little calcium chlorate which is usually present, by virtue of the decomposition of the hypochlorite, will react slowly with the potassium iodide and liberate iodine:

\[
\text{HClO}_3 + 6\text{KI} + 5\text{HCl} = 6\text{KCl} + 3\text{I}_2 + 3\text{H}_2\text{O}
\]

In the second method, the bleaching-powder solution or suspension is titrated against standard 0.1N-sodium arsenite. No internal indicator is at present available for the detection of the end point, since hypochlorite destroys most organic dyes. An external indicator, potassium iodide–starch paper, is employed. As long as excess of hypochlorite is present, a drop of the solution being titrated will turn iodide–starch paper blue; at the end point, a drop of the solution will no longer produce a blue stain. The external indicator may be dispensed with by adding excess of the standard arsenite solution, and titrating back with standard iodine solution, using starch as indicator.

\[
\text{Ca(OCl)}_2 + \text{As}_2\text{O}_3 = \text{CaCl}_2 + \text{As}_2\text{O}_5
\]

The potassium iodide–starch paper may be purchased, or it can be prepared as follows. Boil 1 g. of starch with 100 ml. of water, filter the solution, and add 0.1–0.2 g. of pure potassium iodide to the filtrate. Dip strips of filter-paper into the solution, and dry them on a porcelain or glass plate at 40–50°C.

**Procedure A (iodometric method).** Weigh out accurately about 5 g. of the bleaching powder into a clean glass mortar. Add a little water, and rub the mixture to a smooth paste. Add a little more water, triturate with the pestle, allow the mixture to settle, and pour off the milky liquid into a 500-ml. volumetric flask. Grind the residue with a little more water, and repeat the operation until the whole of the sample
Quantitative Inorganic Analysis

has been transferred to the flask either in solution or in a state of very fine suspension, and the mortar washed quite clean. The flask is then filled to the mark with distilled water, well shaken, and 50 ml. of the turbid liquid immediately withdrawn with a pipette. This is transferred to a 250-ml. conical flask, 25 ml. of water added, followed by 2 g. of iodate-free potassium iodide (or 20 ml. of a 10 per cent solution) and 10 ml. of glacial acetic acid. Titrate the liberated iodine with standard 0.1N-sodium thiosulphate; add 2 ml. of starch solution when the solution has a pale-yellow colour, and continue the titration dropwise until the blue colour just disappears. Repeat the determination with two other 50-ml. portions of the well-mixed suspension.

Calculate the available chlorine in the bleaching powder.

1 ml. \( N{-Na}_2S_2O_3 \) = 0.03546 g. Cl

Procedure B (arsenite method). Prepare a bleaching-powder solution or suspension as is described in Procedure A. Transfer 50 ml. of the well-mixed suspension to a 250-ml. beaker, and titrate with the standard 0.1N-sodium arsenite (Section III, 104A), delivered from a burette, until a drop of the mixture removed with a glass rod and brought into contact with potassium iodide–starch paper gives no blue stain. The first titration will be approximate. In subsequent titrations, add the arsenite solution until within 1 ml. of the previously determined end point, and remove test drops only during the completion of the titration.

The use of the external indicator may be avoided by adding excess (say, 75 ml.) of the standard sodium arsenite solution, and titrating back the excess with standard 0.1N-iodine, using starch as indicator.

Calculate the percentage of available chlorine in the sample of bleaching powder.

1 ml. \( N{-As}_2O_3 \) = 0.03546 g. Cl

III, 112. Determination of hypochlorites.—This problem arises in the analysis of sodium hypochlorite solution and of "high-test hypochlorite" (H.T.H.). The latter substance, marketed in the U.S.A., consists of calcium hypochlorite of 75–100 per cent purity; it is more stable than ordinary bleaching powder, keeps well, is almost non-hygrosopic, and gives a practically clear aqueous solution.

Both the iodometric and sodium arsenite methods described in the previous Section may be used, and need therefore not be repeated here.

III, 113. Determination of antimony.—Discussion. Antimonious oxide reacts with iodine in a similar way to arsenious oxide (Section III, 104), and the antimony may be determined by titration with a standard solution of iodine:

\[
Sb_2O_3 + 2I_2 + 2H_2O \rightleftharpoons Sb_4O_6 + 4HI
\]

The hydriodic acid must be removed as formed by the addition of excess of sodium bicarbonate solution. To prevent the precipitation of antimonious hydroxide when an acid solution is diluted or neutralised, some tartrate is added, which forms a soluble complex salt, for example:

\[
\begin{align*}
SbCl_3 + KH\cdot C_4H_4O_6 + 3NaHCO_3 & \rightarrow K(SbO)C_4H_4O_6 + 3NaCl + 2H_2O + 3CO_2 \\
K(SbO)C_4H_4O_6 + I_2 + 4NaHCO_3 & \rightarrow KNa\cdot C_4H_4O_6 + NaH_2SbO_4 + 2NaI + H_2O + 4CO_2
\end{align*}
\]
This method is satisfactory for tartar emetic, antimony oxide, and certain other antimony compounds, but fails when applied to alloys in which antimony is not the principal constituent (5-20 per cent antimony). The potassium bromate method (Sections III, 135, 137) or the permanganate method (Section III, 117) may then be used, and is, in general, more satisfactory for the volumetric estimation of antimony.

For practice, the student may determine the percentage of antimony in tartar emetic K(SbO)C₆H₄O₆·0.5H₂O or in the anhydrous A.R. potassium antimonyl tartrate.

Procedure (antimony in tartar emetic). Weigh out accurately about 2 g. of the finely powdered A.R. tartar emetic (or 2·5 g of the hydrated compound), dissolve it in water, and make up to 25 ml. in a volumetric flask. Shake well. Transfer 50 ml. of the solution to a 250-ml. conical flask by means of a burette (a pipette should NOT be used, for antimony salts are nearly as poisonous as those of arsenic), add 20 ml. of a cold saturated solution of pure sodium bicarbonate (about 10 ml. are required to about 0.1 g. of Sb₂O₅) and 2 ml. of starch solution. Titrate with standard 0·1N-iodine until the blue colour just appears. The titration must be carried out immediately after the sodium bicarbonate solution is added, otherwise a portion of the metal is precipitated as antimonious hydroxide, which reacts extremely slowly with the iodine. Repeat the determination with two other 50-ml. volumes of the solution.

Calculate the percentage of antimony in the sample used.

1 ml. \( N\cdot I = 0\cdot06088 \) g. Sb

III, 114. Determination of antimony in antimonious oxide and in antimonates.—Here the reaction is the reverse of that for the determination of antimonious compounds:

\[
\text{Sb}_2\text{O}_5 + 4\text{H}^+ + 4\text{I}^- \rightarrow \text{Sb}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O}
\]

The antimonious oxide or antimonate is treated with concentrated hydrochloric acid and an at least five-fold excess of potassium iodide in an apparatus similar to that used in Section III, 107, and the iodine liberated is collected in potassium iodide solution. The free iodine in the distillate is then titrated with a standard solution of 0·1N-sodium thiosulphate.

1 ml. \( N\cdot\text{Na}_2\text{S}_2\text{O}_3 = 1 \) ml. \( N\cdot I = 0\cdot08088 \) g. Sb₂O₅

III, 115. Determination of arsenic in arsenic oxide and in arsenates.—The reaction is the reverse of that employed in the standardisation of iodine with sodium arsenite solution (Section III, 104A):

\[
\text{As}_2\text{O}_5 + 4\text{H}^+ + 4\text{I}^- \rightarrow \text{As}_2\text{O}_3 + 2\text{I}_2 + 2\text{H}_2\text{O}
\]

For the determination of arsenic in arsenic pentoxide or in, say, commercial lead arsenate, shake an amount of the material equivalent to about 0·15 g. As₂O₅ (e.g., 0·5 g. of lead arsenate) in a glass-stoppered bottle with 30 ml. of concentrated hydrochloric acid, add 0·5 g. of potassium iodide, and after 15 minutes titrate the liberated iodine with standard 0·1N-sodium thiosulphate, using starch as indicator. It is desirable, and for very small quantities of arsenates it is essential, to work in an atmosphere of carbon dioxide in order to avoid the liberation of iodine by exposure to the air. A "blank" should be run simul-
Quantitative Inorganic Analysis

Simultaneously with the iodide and acid under the same conditions, and the resulting thiosulphate titre deducted as a correction.

$$1 \text{ ml. } N-Na_2S_2O_3 = 1 \text{ ml. } N-I = 0.05746 \text{ g. } As_2O_3$$

Note. For those arsenates which do not yield an insoluble salt with sulphuric acid, 12N-sulphuric acid gives good results.

III, 116. Determination of tin. —Discussion. The method depends upon the oxidation of stannous chloride to stannic chloride by means of iodine solution in the presence of concentrated hydrochloric acid:

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI$$

A small amount of sulphuric acid is not objectionable, but nitric acid must be absent. Very few substances, particularly arsenic and antimony, ordinarily met with in analysis for tin interfere: foreign substances must not be present in such concentrations that they affect the action of the starch indicator. The determination must, however, be conducted in a non-oxidising atmosphere; this is achieved by maintaining an atmosphere of carbon dioxide from a Kipp’s apparatus or from a cylinder.

If the tin is present in the stannic state, it must be reduced by warming with pure (e.g., A.R.) antimony (powdered), iron, lead, aluminium, or nickel. When a coil of sheet nickel is employed in the reduction, a large excess of hydrochloric acid must be present in order to prevent the precipitation of antimony.

Attention is directed to the fact that it has been shown that the iodimetric titration of stannous tin is subject to a variable error due to the presence of dissolved oxygen in the iodine solution. The error may be as high as 1 per cent for 0.1N-iodine and 10 per cent for 0.01N-iodine. It is accordingly recommended that for the determinations of tin described below the iodine solution be prepared in a carbon dioxide atmosphere with boiled-out distilled water which has been allowed to cool in carbon dioxide. The solution should be stored in the self-filling apparatus shown in Fig. II, 25, 1, or Fig. II, 25, 2, under carbon dioxide, the air in the burette and storage bottle being, of course, first displaced by carbon dioxide. It is found that iodine does not appreciably attack red rubber “pressure-tubing,” but black lightly vulcanised tubing is unsatisfactory.

For practice, the student may determine the tin in, and hence the purity of, A.R. stannous chloride $SnCl_2.2H_2O$, and also the tin in an alloy.

Procedure A (tin in stannous chloride). Weigh out accurately about 2 g. of A.R. stannous chloride, dissolve it in 150 ml. of concentrated hydrochloric acid, transfer to a 250-ml. volumetric flask, and make up to the mark with air-free distilled water. No appreciable oxidation of the tin occurs in this process. Transfer 50 ml. of the solution to a 250-ml. conical flask, dilute with 50 ml. of air-free water, and add 2 ml. of starch solution. Pass a current of carbon dioxide over the surface of the liquid, and titrate with standard 0.1N-iodine to the first appearance of a blue colour. Repeat the titration with two other 50-ml. portions of the solution.

Calculate the percentage of tin in the salt used, and therefrom its $SnCl_2.2H_2O$ content.

$$1 \text{ ml. } N-I = 0.05935 \text{ g. } Sn$$
Procedure B (tin in an alloy). Dissolve 0.2-2.0 g., accurately weighed, of the finely divided alloy,* according to the percentage of tin present, in concentrated hydrochloric acid, transfer the solution quantitatively to a 350-ml. or 500-ml. wide-mouthed conical flask, add 50 ml. of concentrated hydrochloric acid, and dilute the solution to 200 ml. Add about 1 g. of finely powdered pure antimony, e.g., A.R. \((3\text{SnCl}_4 + 2\text{Sb} = 3\text{SnCl}_3 + 2\text{SbCl}_3)\) or 1 g. of A.R. iron wire \((\text{SnCl}_4 + \text{Fe} = \text{FeCl}_3 + \text{SnCl}_3)\) or 1 g. of aluminium turnings \((3\text{SnCl}_4 + 2\text{Al} = 3\text{SnCl}_2 + 2\text{AlCl}_3)\). Insert a three-hole rubber stopper, carrying in one hole a gas-inlet tube extending to the bottom of the flask, in the second hole a vertical condenser tube 15-20 cm. in length, and in the third a small stopper. Pass a slow stream of carbon dioxide through the flask, gradually heat to boiling, and continue the gentle ebullition for 30 minutes. Cool (preferably in ice) to about 10°C whilst a more rapid stream of carbon dioxide is passed through. When the solution is cold, continue the current of the gas, remove the stopper in the third hole, add 2 ml. of starch solution from a pipette, and insert the tip of a burette containing standard 0.1N-iodine. Titrate to the first permanent blue colour.

The iodine solution may be standardised against arsenious oxide or, better, against A.R. tin which has been dissolved and treated as in the above method.

Calculate the percentage of tin in the alloy.

III, 117. Determination of antimony and tin in type metal.—Discussion. The method given below combines the excellent permanganate method for the determination of antimony:

\[4\text{MnO}_4^- + 5\text{Sb}_2\text{O}_3 + 12\text{H}^+ = 4\text{Mn}^{++} + 5\text{Sb}_2\text{O}_5 + 6\text{H}_2\text{O}\]

or

\[\text{Sb}_2\text{O}_3 + 2\text{O} = \text{Sb}_2\text{O}_5\]

and the iodimetric method for tin given in the previous Section.

Procedure. Determination of antimony. Weigh out accurately 1 g. of the finely divided alloy † (or an amount corresponding to approximately 0.1 g. of antimony), dissolve it in 20-30 ml. of concentrated sulphuric acid (according to the amount of lead present), allow to cool, dilute very carefully to 100 ml., and allow to stand. Decant the clear liquid from the lead sulphate formed into a wide-mouthed 350- or 500-ml. conical flask, and boil for 5 minutes to expel sulphur dioxide. Boil the lead sulphate with the appropriate volume of concentrated hydrochloric acid ‡ and an equal volume of water. When the lead sulphate is completely in solution, wash back quantitatively into the main antimony solution, disregarding any lead salt which may now be re-precipitated. Titrate the solution at 40-60°C with standard 0.1N-potassium permanganate, added slowly to prevent loss of chlorine, and when the end point has almost been reached add a few drops of methyl orange, and continue the titration until the colour of the indicator is discharged (compare Section III, 135).

* Ridsdale’s “White Metal, No. 6b” (one of the Analysed Samples for Students) or the Bureau of Analysed Samples “White Metal, No. 178” is suitable. About 0.2 g. should be used.
† The Bureau of Analysed Samples “White Metal, No. 177” (one of the British Chemical Standards) is suitable for this estimation. About 1 g. should be used.
‡ Conc. H₂SO₄ ml. . 0 10 20 30
Conc. HCl ml. . 30-50 30-55 15-20 10-15 (W. Pugh, 1933).

These volumes apply to a final volume of 200 ml.
The potassium permanganate solution may be standardised against arsenious oxide or sodium oxalate in the usual way. It is better, however, to use finely powdered A.R. antimony* or anhydrous A.R. potassium antimonyl tartrate. The standard antimony solution may be prepared by dissolving about 3-0 g. of pure antimony, accurately weighed, in 30 ml. of concentrated sulphuric acid, diluting it, boiling off traces of sulphur dioxide, and making up to 500 ml. in a volumetric flask with 125 ml. of concentrated hydrochloric acid and water.

In the analysis of lead–tin alloys, the ratio of hydrochloric to sulphuric acid is important for the attainment of correct results; too little hydrochloric acid leads to the precipitation of a basic antimony salt, whilst too much may cause reduction of the permanganate by chloride ions, with the liberation of chlorine, and the end point becomes barely perceptible.

**Determination of tin.** After the titration of the antimony by the permanganate solution is complete, add sufficient concentrated hydrochloric acid to bring this to 20 per cent by volume of the entire solution, and add 1 g. of finely powdered pure antimony or 1 g. of A.R. iron wire. Insert a three-holed rubber stopper, and proceed exactly as described for the determination of tin in Section III, 116, Procedure B.

Calculate the percentages of antimony and of tin in the alloy.

**III, 118. Determination of sulphurous acid and of sulphites.**—

**Discussion.** The iodimetric estimation is based upon the equation:

\[
H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI
\]

For accurate results, the following experimental conditions must be observed:

(i) the solutions shall be very dilute;
(ii) the sulphite must be added slowly and with constant stirring to the iodine solution, and not conversely; and
(iii) exposure of the sulphite to the air be minimised.

Under these conditions the following possible errors are almost entirely avoided:

(a) loss of sulphur dioxide by volatilisation;
(b) precipitation of sulphur by the "total" reaction

\[
3H_2SO_3 = 2H_2SO_4 + S + H_2O
\]

which is catalysed by hydriodic acid, and also by the reaction

\[
H_2SO_3 + 4HI = 2I_2 + S + 3H_2O
\]

and

(c) oxidation of sulphite to sulphate.

In determinations of sulphurous acid and sulphites, excess of standard 0.1N-iodine is diluted with several volumes of water, acidified with hydrochloric or sulphuric acid, and a known volume of the sulphite or sulphurous acid solution is added slowly and with constant stirring from a burette, with the jet close to the surface of the liquid. The excess of iodine is then titrated with standard 0.1N-sodium thiosulphate. Solid

---

* A.R. antimony can be obtained from the Mallinckrodt Chemical Works, U.S.A., or from the J. T. Baker Chemical Works, Phillipsburg, U.S.A.
soluble sulphites are finely powdered and added directly to the excess of the iodine solution. Insoluble sulphites (e.g., calcium sulphite) react very slowly, and must be in a very fine state of division.

For practice, the student may determine the percentage of Na₂SO₃·7H₂O in the ordinary or A.R. crystallised product.

Procedure. Weigh out accurately about 0.25 g. of crystallised sodium sulphite (1), and add it to a 350-ml. conical flask containing 25 ml. of standard 0.1N-iodine, 5 ml. of 2N-hydrochloric acid, and 150 ml. of water. Swirl or stir the liquid until all the solid has reacted, and titrate the excess of iodine with standard 0.1N-sodium thiosulphate using starch as indicator. Repeat the determination with two other 0.25-g. portions of the sulphite.

Calculate the percentage of Na₂SO₃·7H₂O in the sample employed.

1 ml. N-I = 0.03203 g. SO₂ = 0.1261 g. Na₂SO₃·7H₂O

Note. 1. Alternatively, weigh out accurately about 2.5 g. of crystallised sodium sulphite, dissolve it in boiled-out water, and make the solution up to 250 ml. in a volumetric flask with boiled-out water. Shake well. Use 25 ml. for each titration.

III, 119. Determination of hydrogen sulphide and sulphisides.—

Discussion. The iodimetric method utilises the reversible reaction

\[ \text{H}_2\text{S} + \text{I}_2 \rightleftharpoons 2\text{HI} + \text{S} \]

For reasonably satisfactory results, the sulphide solution must be dilute (concentration not greater than 0.04 per cent or 0.02N), and the sulphide solution added to excess of acidified 0.01N- or 0.1N-iodine and not conversely. Loss of hydrogen sulphide is thus avoided, and side reactions are almost entirely eliminated. (With solutions more concentrated than about 0.02N, the precipitated sulphur encloses a portion of the iodine, and this escapes the subsequent titration with the standard sodium thiosulphate solution.) The excess of iodine is then titrated against standard thiosulphate solution, using starch as indicator.

1 ml. N-I = 0.01703 g. H₂S

Excellent results are obtained by the following method, which is of wider applicability. When excess of standard sodium arsenite solution is treated with hydrogen sulphide solution and then acidified with hydrochloric acid, arsenious sulphide is precipitated:

\[ \text{As}_2\text{O}_3 + 3\text{H}_2\text{S} = \text{As}_2\text{S}_3 + 3\text{H}_2\text{O} \]

The excess of arsenious acid is determined with 0.1N-iodine and starch (compare Section III, 104A).

Procedure. Prepare a saturated solution of hydrogen sulphide by bubbling the gas through distilled water. Place 50 ml. of standard 0.1N-sodium arsenite into a 250-ml. volumetric flask, add 20 ml. of the hydrogen sulphide water, mix well, and add sufficient hydrochloric acid to render the solution distinctly acid. A yellow precipitate of arsenious sulphide is formed, but the liquid itself is colourless. Make up to the mark with distilled water, and shake thoroughly. Filter the mixture through a dry filter-paper into a dry vessel. Remove 100 ml.
Quantitative Inorganic Analysis

of the filtrate, neutralise it with sodium bicarbonate, and titrate with standard 0.1N-iodine and starch to the first blue colour. The quantity of residual arsenious acid is thus determined, and is deducted from the original 50 ml. employed.

Calculate the concentration of the hydrogen sulphide in the solution.

\[ 1 \text{ ml. } N-\text{As}_2\text{O}_3 = 0.02556 \text{ g. } H_2S \]

III, 120. Determination of ferricyanides.—Discussion. The reaction between ferricyanides and potassium iodide is a reversible one:

\[ 2K_3[Fe(CN)_6] + 2KI \rightleftharpoons 2K_4[Fe(CN)_6] + I_2 \]

but proceeds quantitatively from left to right in a slightly acid medium in the presence of a zinc salt. The very sparingly soluble potassium zinc ferrocyanide is formed:

\[ 2K_4[Fe(CN)_6] + 3ZnSO_4 = K_2Zn_3[Fe(CN)_6]_2 + 3K_2SO_4 \]

and the ferrocyanide ions are thus removed from the sphere of action.

For practice, the student may determine the purity of potassium ferricyanide, preferably of A.R. grade.

Procedure. Weigh out accurately about 10 g. of the potassium ferricyanide and dissolve it in 250 ml. of water in a volumetric flask. Pipette 25 ml. of this solution into a 250-ml. conical flask, add about 20 ml. of 10 per cent potassium iodide solution, 2 ml. of 2N-sulphuric or hydrochloric acid, and 15 ml. of a solution containing 2·0 g. of crystallised zinc sulphate. Titrate the liberated iodine immediately with standard 0.1N-sodium thiosulphate and starch; add the starch solution (2 ml.) after the colour has faded to a pale yellow. The titration is complete when the blue colour has just disappeared. When great accuracy is required, the process should be conducted in an atmosphere of carbon dioxide. Repeat the titration with two other 25-ml. portions of the solution.

Calculate the purity of the salt.

\[ 1 \text{ ml. } N-\text{Na}_2\text{S}_2\text{O}_3 = 0.3293 \text{ g. } K_3[Fe(CN)_6] \]

III, 121. Determination of ferric iron (iodometric method).—The reaction:

\[ 2Fe^{+++} + 2I^- \rightleftharpoons 2Fe^{++} + I_2 \]

is quantitative to the right-hand side if the iodine is removed by titration with sodium thiosulphate solution, but is normally too slow to be of practical utility. The addition of a little cuprous iodide, however, acts as a catalyst and so accelerates the reaction that titration may be carried out forthwith. The cuprous iodide is prepared as follows. About 1 ml. of N-copper sulphate solution is treated with an excess of 10 per cent potassium iodide solution (2–3 ml.) and the free iodine is discharged by the addition of aqueous sodium thiosulphate in the presence of starch solution. The precipitate is first thoroughly washed by decantation, and then shaken with 20 ml. of water; about 1 ml. of the suspension thus obtained is used for a titration.

The ferric solution, slightly acid with hydrochloric acid and containing about 0·15 g. of Fe, is treated with 1 ml. of the cuprous iodide suspension and sufficient 10 per cent potassium iodide solution, to give
a concentration of ca. 2 per cent, and shaken well. After 3–5 minutes the whole is titrated with standard 0·1\(N\)-sodium thiosulphate to the disappearance of the blue starch colour. The end point is fairly definite and permanent, although the starch coloration re-appears more rapidly than in the copper-thiosulphate titration (Sections III, 105–108).

\[
1 \text{ ml. } N\cdot\text{Na}_{2}\text{S}_{2}\text{O}_{3} = 0.05584 \text{ g. Fe}
\]

Note. If A.R. ferric alum is employed, the method will serve as a useful check for the standardisation of thiosulphate solutions.
Oxidations with Potassium Iodate

III, 122. General discussion.—A glance at the table of standard oxidation potentials (Table XVI, Section I, 46) reveals the fact that both potassium iodate and potassium bromate are stronger oxidising agents than iodine. The reaction between potassium iodate and reducing agents, such as potassium iodide or arsenious oxide, in weakly acidic solutions, say 0·1-2·0N-hydrochloric acid, stops at the stage when the iodate is reduced to iodine:

\[
\text{KIO}_3 + 5\text{KI} + 6\text{HCl} = 6\text{KCl} + 3\text{I}_2 + 3\text{H}_2\text{O}
\]

Actually the iodate is first reduced to iodide, and the latter is subsequently converted into free iodine. This can readily be shown by carrying out the oxidation of reducing substances in weak acid solutions (0·1–2N-hydrochloric acid) containing mercuric sulphate; here the iodide is converted into the fairly stable complex ion \([\text{HgI}_4]^{2-}\) as fast as it is formed, and the reaction is accordingly arrested at the iodide stage. An example is:

\[
4\text{KIO}_3 + 12\text{H}_3\text{AsO}_3 + 6\text{H}_2\text{SO}_4 (\text{+ HCl}) = \text{K}_2\text{SO}_4 + \text{K}_2[\text{HgI}_4] + 12\text{H}_2\text{AsO}_4 (\text{+ HCl})
\]

In more concentrated hydrochloric acid solutions (exceeding 4N) L. W. Andrews (1903) has shown that the iodate is reduced ultimately to iodine monochloride—the substance therefore acts as a very much more powerful oxidising agent. Examples are:*

\[
\text{KIO}_3 + 2\text{KI} + 6\text{HCl} = 3\text{KCl} + 3\text{ICl} + 3\text{H}_2\text{O}
\]

\[
\text{KIO}_3 + 2\text{H}_3\text{AsO}_3 + 2\text{HCl} = 2\text{H}_3\text{AsO}_4 + \text{KCl} + \text{ICl} + \text{H}_2\text{O}
\]

\[
\text{KIO}_3 + 2\text{I}_2 + 6\text{HCl} = \text{KCl} + 5\text{ICl} + 3\text{H}_2\text{O}
\]

In these reactions the iodine which is initially liberated is converted into iodine chloride. Now both iodine and iodine chloride are brownish-yellow in aqueous solution, but in organic solvents, such as carbon tetrachloride or chloroform, iodine is purple whilst iodine chloride remains yellow. The point at which the last trace of iodine disappears may be determined by the change in colour from purple to yellow when a few ml. of carbon tetrachloride or chloroform are shaken up in the solution during the titration (compare Section I, 71, and Section III, 100).

The use of potassium iodate in the presence of high concentrations of hydrochloric acid forms the basis of the Andrews procedure for the determination of reducing agents. It has been applied by G. S. Jamieson (1926)† and others to numerous quantitative determinations. Essentially, all methods depend upon the reaction:

\[
\text{I}^- - 2e = \text{I}^+
\]

* These equations give the final products only.
† G. S. Jamieson, Volumetric Iodide Methods, 1926 (Chemical Catalog Co., N.Y.); see also W. Böttger and R. E. Oesper, Newer Methods of Volumetric Chemical Analysis, 1938, p. 69 (Van Nostrand).
and conditions are so chosen as to stabilise the iodine cation. In the Andrews procedure, the experimental conditions are such that iodine chloride (ICl $\rightleftharpoons$ I$^+$ + Cl$^-$)* is stable and its hydrolysis is repressed:

\[ \text{HCl} + \text{HIO} \rightarrow \text{ICl} + \text{H}_2\text{O} \text{(or H}^+ + \text{HIO} \rightarrow \text{I}^+ + \text{H}_2\text{O)} \]

Let us write down the ionic equations for the various stages in the reduction of iodate under the Andrews’ conditions:

\[ \text{IO}_3^- + 6\text{H}^+ + 6\text{e} = \text{I}^- + 3\text{H}_2\text{O} \]

or

\[ 10\text{IO}_3^- + 60\text{H}^+ + 60\text{e} = 10\text{I}^- + 30\text{H}_2\text{O} \]

or

\[ 2\text{IO}_3^- + 12\text{H}^+ + 10\text{I}^- = 6\text{I}_2 + 6\text{H}_2\text{O} \]

or

\[ 3\text{IO}_3^- + 18\text{H}^+ + 6\text{I}_2 = 15\text{I}^+ + 9\text{H}_2\text{O} \]

Upon addition, we have:

\[ 15\text{IO}_3^- + 90\text{H}^+ + 60\text{e} = 15\text{I}^+ + 45\text{H}_2\text{O} \]

or

\[ \text{IO}_3^- + 6\text{H}^+ + 4\text{e} = \text{I}^+ + 3\text{H}_2\text{O} \]

Hence under these particular conditions the equivalent weight of potassium iodate is KIO$_3$/4, or a 0.1N solution of potassium iodate will contain KIO$_3$/4 $\times$ 10, or 214.02/40, or 5.3505 g. per litre.†

Other methods for stabilising the iodine cation have been used, and give, in most instances, equally satisfactory results. The most important of these is that due to R. Lang (1922 →), in which cyanide ions are used; in the latter case the acidity should be slightly greater than N, and may be provided by either hydrochloric or sulphuric acid. Here iodine cyanide gives the necessary stability:

\[ \text{I}^+ + \text{CN}^- \rightleftharpoons \text{ICN} \]

The similarity between the Andrews’ hydrochloric acid method and Lang’s cyanide method may be illustrated by the stoichiometric equations for the determination of iodides:

\[ \text{HIO}_3 + 2\text{HI} + 3\text{HCl} = 3\text{ICl} + 3\text{H}_2\text{O} \]

\[ \text{HIO}_3 + 2\text{HI} + 3\text{HCN} = 3\text{ICN} + 3\text{H}_2\text{O} \]

In view of the highly poisonous character of hydrogen cyanide, flasks with long and narrow necks must be used in all processes employing the “iodine cyanide” method. Only the “iodine chloride” procedure will, however, be described in this book.‡

Potassium iodate, as already pointed out in Section III, 102A, is available commercially in a high state of purity, is anhydrous, can be dried at 120° C., and is stable in solution. The A.R. product has an

* The following reaction may occur:

\[ \text{I}^+ + 2\text{Cl}^- \rightleftharpoons \text{ICl}_2^- \]

† The same result can be deduced from the hypothetical equation

\[ \text{KIO}_3 + 2\text{HCl} = \text{KCl} + \text{ICl} + \text{H}_2\text{O} + 2\text{O} \]

‡ For details of Lang’s cyanide method, see W. Böttger and R. E. Oesper, Newer Methods of Volumetric Chemical Analysis, 1938, p. 76 (Van Nostrand and Co. or Chapman and Hall), and F. Sutton and A. D. Mitchell, A Systematic Handbook of Volumetric Analysis, 1936 (J. and A. Churchill).
assay value of better than 99.9 per cent. The titrations are carried out in glass-stoppered bottles or flasks of 250 or 300 ml. capacity in the presence of a high concentration of hydrochloric acid, otherwise hydrolysis of the iodine monochloride is liable to occur. The solution to be titrated should contain so much hydrochloric acid that, even after all the titrating solution has been added, the acidity is at least 4N; that is, at least one-third, and preferably one-half, of the solution should consist of concentrated acid. The end point is detected by the loss of the last trace of purple (violet) colour from a layer of 5 ml. of chloroform or carbon tetrachloride when shaken with the liquid. When a titration has actually been completed, there is no return of the iodine colour even after keeping the solution for a day. Iodate titrations can be made in the presence of filter-paper, alcohol, formaldehyde, saturated organic acids, as well as many other kinds of organic matter.

The use of carbon tetrachloride or chloroform as an indicator for the disappearance of the last trace of iodine gives good results, but a glass-stoppered bottle or flask must be employed, since the reaction mixture must be shaken near the end point. The titration may be carried out in an open beaker (say, of 400-ml. capacity) or in a conical flask in the presence of an irreversible indicator, such as Amaranth, Brilliant Ponceau 5R, or Naphthol Blue Black * (G. F. Smith, 1942). The indicators are employed in 0.2 per cent aqueous solution, and about 0.5 ml. is utilised per titration; the indicator blank is equivalent to 0.05 ml. of 0.1N-potassium iodate per 1 ml. of indicator and is therefore negligible. The indicators are irreversible and are destroyed at the completion of the reaction. The tendency of the indicators to fade as the equivalence point is reached is counteracted by delaying their addition until most of the iodine has disappeared from the solution upon the introduction of the standard iodate solution; the addition of a drop or two of indicator just before the end point is recommended. Amaranth or Brilliant Ponceau 5R may replace carbon tetrachloride or chloroform in the determinations described in Sections III, 125-134.

No really satisfactory reversible redox indicators are yet available, although p-ethoxychrysoidine (0.1 per cent solution in alcohol) is promising for the determination of trivalent arsenic; † the indicator blank is equivalent to about 0.2 ml. of 0.1N-potassium iodate. The indicator is added after the colour of the iodine commences to fade; near the end point the colour changes to deep purple, and the titration is then carried out slowly until the colour changes to orange.

III, 123. Preparation of 0.1N (0.025M)-potassium iodate.—Dry some A.R. potassium iodate at 120° C. for 1 hour and allow it to cool in a desiccator. Weigh out exactly 5.351 g. of the finely powdered potassium iodate on a watch glass, and transfer it by means of a clean camel-hair brush directly into a dry 1-litre volumetric flask. Add about 400-500 ml. of water, and gently rotate the flask until the salt is completely dissolved. Make up to the mark with distilled water. Shake well. The solution will keep indefinitely.

* Amaranth (British Colour Index, No. 184); Brilliant Ponceau 5R (B.C.I., No. 185) and Naphthol Blue Black (B.C.I., No. 246) of indicator quality may be obtained, for example, from the G. Frederick Smith Chemical Co., 867 McKinley Avenue, Columbus, Ohio, U.S.A., or from Eimer and Amend, 635 Greenwich Street, New York, 14, N.Y., or from Fisher Scientific Co., 717 Forbes Street, Pittsburgh 19, Pa., U.S.A. The action of Naphthol Blue Black is somewhat slow at the end point.

† Private communication from R. Belcher, F.R.I.C.
It must be emphasised again that the solution is 0·1N only for the reaction:

\[ \text{IO}_3^- + 6\text{H}^+ + 4e^- = \text{I}^- + 3\text{H}_2\text{O} \]

**Analyses Involving the Use of Potassium Iodate Solutions**

**III, 124. Determination of iodides.**—This estimation is based upon the reaction:

\[ \text{IO}_3^- + 6\text{H}^+ + 2\text{I}^- = 3\text{I}^- + 3\text{H}_2\text{O} \]

or, e.g., \[ \text{KIO}_3 + 6\text{HCl} + 2\text{KI} = \text{3KCl} + 3\text{ICl} + 3\text{H}_2\text{O} \]

Thus 1 ml. 0·025M-KIO\(_3\) = 0·006347 g. I\(^-\) (since KIO\(_3\) = 2I\(^-\)).

For practice, the student may determine the percentage of iodine in potassium iodide.

**Procedure.** Weigh out accurately about 2·0 g. of potassium iodide, and dissolve it in 250 ml. of water in a standard flask. Shake well. Transfer 25 ml. of this solution by means of a pipette into a stoppered reagent bottle of about 250-ml. capacity,\(^*\) and add 25 ml. of water, 60 ml. of concentrated hydrochloric acid together with about 5 ml. of carbon tetrachloride or chloroform. Cool to room temperature. Run in the standard 0·1N-potassium iodate from a burette until the solution, which at first is strongly coloured with iodine, becomes pale brown. The bottle is then stoppered and vigorously shaken, and the solvent layer acquires the purple colour due to iodine. Continue to add small volumes of the iodate solution, shaking vigorously after each addition, until the organic layer is only very faintly violet. Continue the addition drop-wise, with shaking after each drop, until the solvent loses the last trace of violet and has only a very pale-yellow colour (due to iodine chloride). The end point is very sharp and, after a little experience, is rarely overshot. If this should occur, a small volume of the iodide solution is added from a graduated pipette, and the end point re-determined. Repeat the titration with two other 25-ml. portions of the iodide solution.

Calculate the percentage of iodine in the sample of potassium iodide.

**Note.** Iodine is similarly determined:

\[ \text{IO}_3^- + 6\text{H}^+ + 2\text{I}_2 = 5\text{I}^- + 2\text{H}_2\text{O} \]

or, e.g., \[ \text{KIO}_3 + 6\text{HCl} + 2\text{I}_2 = \text{KCl} + 5\text{ICl} + 3\text{H}_2\text{O} \]

Hence 1 ml. 0·025M-KIO\(_3\) = 0·01279 g. I

since \[ \text{KIO}_3 = 2\text{I}_2 \]

A mixture of iodine and iodide is estimated by first titrating the iodine with standard sodium thiosulphate solution, and then determining the iodine + iodide in a fresh portion with potassium iodate.

\(^*\) A 250-ml measuring-flask with a short neck and a well-fitting ground-glass stopper may also be used. The colour of the organic layer is readily seen by inverting the flask so that the layer of indicator collects in the neck.

Alternatively, in this and all subsequent titrations with 0·1N-potassium iodate, a 250- or 300-ml. conical flask may be used and the carbon tetrachloride or chloroform indicator replaced by 0·5 ml. of Amaranth or Brilliant Ponceau 6R indicator, which is added after most of the iodine colour has disappeared from the reaction mixture (for details, see Section III, 122).
III, 125. Determination of arsenic or of antimony.—Discussion. The determination of arsenic in arsenious compounds is based upon the following reactions:

\[ \text{KIO}_3 + \text{As}_2\text{O}_3 + 2\text{HCl} = \text{KCl} + \text{As}_2\text{O}_5 + \text{ICl} + \text{H}_2\text{O} \]

i.e., \[ \text{IO}_3^- + \text{As}_2\text{O}_3 + 2\text{H}^+ = \text{I}^+ + \text{As}_2\text{O}_5 + \text{H}_2\text{O} \]

or \[ \text{KIO}_3 + 2\text{AsCl}_3 + 5\text{H}_2\text{O} = \text{KCl} + 2\text{H}_3\text{AsO}_4 + \text{ICl} + 4\text{HCl} \]

Similar reactions occur with antimonial compounds. The determination of antimony in the presence of tartrate is not very satisfactory with an immiscible solvent as indicator; Amaranth (Section III, 122), however, gives excellent results.

Thus 1 ml. 0·025M-\text{KIO}_3 = 0·003746 g. As = 0·006088 g. Sb.

Iron and copper do not interfere with these estimations.

For practice, the student may determine the percentage of \text{As}_2\text{O}_3 in commercial arsenious oxide or in the A.R. product.

Procedure. Weigh out accurately about 1·1 g. of arsenious oxide, dissolve this in a small quantity of warm 10 per cent sodium hydroxide solution, and make up to 250 ml. in a volumetric flask. Shake well. Transfer 25 ml. of this solution to a 250-ml. stoppered reagent bottle, add 25 ml. of concentrated hydrochloric acid and 5 ml. of carbon tetrachloride. Titrate with the standard 0·1N-potassium iodate, as detailed in Section III, 124, until the iodine colour in the organic layer has disappeared. Allow to stand for 10 minutes, and observe whether the carbon tetrachloride shows any purple colour. If no colour is seen, the titration is complete. The acidity of the entire mixture at the end of the titration should not be less than 3\text{N} and not more than 5\text{N}; with too high acidity the reaction takes place very slowly. Repeat the titration with two other 25-ml. portions of the solution.

Calculate the percentage of \text{As}_2\text{O}_3 in the sample.

As an additional exercise, the student may employ an irreversible indicator (Section III, 122); with Amaranth the colour change at the equivalence point is from red to pale yellow; the colour change for Brilliant Ponceau 5R is orange to colourless.

III, 126. Determination of copper.—Discussion. The copper is precipitated as cuprous thiocyanate, and then titrated with standard potassium iodate solution in the presence of strong hydrochloric acid and a carbon tetrachloride or chloroform indicator. The reaction proceeds according to the following equation:

\[ 7\text{KIO}_3 + 2\text{Cu}(\text{CNS})_2 + 14\text{HCl} = 7\text{KCl} + 4\text{CuSO}_4 + 7\text{ICl} + 4\text{HCN} + 5\text{H}_2\text{O} \]

Thus \[ 7\text{KIO}_3 = 4\text{Cu} \]

or \[ 1 \text{ ml. } 0·025\text{M-}\text{KIO}_3 = 0·0009077 \text{ g. Cu} \]

The method may be applied to ores and certain alloys of copper; the nitric acid employed for bringing the substance into solution must be expelled by evaporating with concentrated sulphuric acid to copious fuming.

For practice, the student may determine the percentage of copper in crystallised copper sulphate, preferably of A.R. grade. About 0·02 g. of copper is a suitable quantity for titration with 0·025M-potassium iodate.
**Volumetric Analysis**

**Procedure.** Weigh out accurately about 0·8 g. of crystallised copper sulphate CuSO₄·5H₂O, dissolve it in water, add 5 ml. of N-sulphuric acid, and make up to 250 ml. in a volumetric flask. Shake well. Transfer 25 ml. to a conical flask, add 10–15 ml. of freshly prepared saturated sulphurous acid solution, heat to boiling and add 10 per cent ammonium thioyanate solution, slowly and with constant stirring, from a burette until further addition produces no change in colour, and add 3–4 ml. in excess (5–10 ml. in all). Allow the precipitate to settle for 10–15 minutes, filter through a quantitative filter-paper or through a Gooch crucible with asbestos. Wash with a cold 1 per cent ammonium sulphate solution until free from thiocyanate. Transfer the washed precipitate with the filter-paper or with the asbestos quantitatively into a 250-ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of chloroform or carbon tetrachloride. Add the 0·1N-potassium iodate rapidly whilst rotating the bottle in order to keep the contents mixed. When the iodine has just disappeared from the solution, insert the stopper and shake thoroughly. The organic layer will be strongly coloured. From this point, continue the titration slowly, shaking the closed bottle after each addition of the iodate solution until the iodine colour has disappeared from the carbon tetrachloride or chloroform layer; this marks the end point. Repeat with two other 25-ml. portions of the solution.

Calculate the percentage of copper in the sample used.

**III, 127. Determination of mercury.**—Discussion. The mercury is precipitated as mercurous chloride. The latter reacts with potassium iodate solution under the usual conditions in accordance with the equation:

\[ \text{KIO}_3 + 2\text{Hg}_2\text{Cl}_2 + 6\text{HCl} = \text{KCl} + 4\text{HgCl}_2 + \text{I}_2 + 3\text{H}_2\text{O} \]

Thus

\[ \text{KIO}_3 = 4\text{Hg} = 2\text{Hg}_2\text{Cl}_2 \]

and

1 ml. 0·025M-KIO₃ = 0·02006 g. Hg = 0·02361 g. Hg₂Cl₂

For practice, the student may determine the percentage of mercury in mercuric chloride, preferably of A.R. quality.

**Procedure.** Weigh out accurately about 2·5 g. of finely powdered mercuric chloride, and dissolve it in 100 ml. of water in a measuring flask. Shake well. Transfer 25 ml. of the solution to a conical flask, add 25 ml. of water, 2 ml. of N-hydrochloric acid, and excess of 50 per cent phosphorous acid solution. Stir thoroughly and allow to stand for 12 hours or more. Filter the precipitated mercurous chloride through a quantitative filter-paper or through a Gooch crucible with asbestos, and wash the precipitate moderately with cold water. Transfer the precipitate with the filter-paper or asbestos quantitatively to a 250-ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of carbon tetrachloride or chloroform. Titrate the mixture with standard 0·1N-potassium iodate in the usual manner (Section III, 124).

Calculate the percentage of mercury in the sample.

**III, 128. Determination of tin.**—Discussion. Potassium iodate solution reacts quantitatively with stannous chloride in the presence of concentrated hydrochloric acid in accordance with the equation:

\[ \text{KIO}_3 + 2\text{SnCl}_2 + 6\text{HCl} = \text{KCl} + 2\text{SnCl}_4 + \text{I}_2 + 3\text{H}_2\text{O} \]

or

\[ \text{IO}_3^- + 2\text{Sn}^{++} + 6\text{H}^+ = 2\text{Sn}^{+++} + \text{I}^- + 3\text{H}_2\text{O} \]

Thus \[ \text{KIO}_3 = 2\text{Sn}, \] or 1 ml. 0·025M-KIO₃ = 0·005935 g. Sn
This method possesses several advantages. The end point is very sharp. Extreme precautions need not be taken to prevent atmospheric oxidation if the bulk of the iodate solution is added rapidly at first; the titration can then be completed at leisure. The method cannot be applied in the presence of antimony, cuprous and ferrous salts, or precipitated metals; these interfering substances can, however, be simply removed.

For practice, the student may determine the percentage of tin in hydrated stannous chloride, preferably of A.R. grade.

**Procedure.** Weigh out accurately about 1.5 g. of crystallised stannous chloride SnCl₂·2H₂O, dissolve it in concentrated hydrochloric acid, and make up to 250 ml. in a volumetric flask. Shake thoroughly. Remove 25 ml. of the solution to a 250-ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of carbon tetrachloride or chloroform. Add standard 0.1N-potassium iodate rapidly at first, whilst shaking the bottle to give the contents a gentle rotary motion, until the iodine colour, which gradually appears, has increased to the maximum intensity, then insert the stopper, and shake the solution thoroughly. Continue the titration slowly, shaking after each addition, until the organic layer is no longer violet. Repeat the titration with two other 25-ml. portions of the solution.

Calculate the percentage of tin in the sample.

**III, 129. Determination of peroxides (lead, barium, and manganese dioxide).—Discussion.** The method employed is an indirect one. Excess of potassium iodide solution, which has been standardised against potassium iodate (Section III, 124), is added to a weighed amount of the dioxide, and the mixture is titrated in the usual manner with standard potassium iodate solution, using chloroform or carbon tetrachloride as indicator. The reactions which occur are:

\[
\text{2MO}_2^- + 2\text{KI} + 8\text{HCl} = 2\text{MCl}_2 + 2\text{KCl} + 2\text{H}_2\text{O} + \text{I}_2
\]

\(\text{KIO}_3 + 2\text{KI} + 6\text{HCl} = 3\text{KCl} + 3\text{Cl}_2 + 3\text{H}_2\text{O}\)

Now \(\text{MO}_2 = \text{KI}\), so that when the excess of iodide is determined by titration with the iodate, the percentage of \(\text{MO}_2\) in the sample can be readily calculated. Any organic matter which may be present does not interfere with the estimation.

For practice, the student may determine the percentage of PbO₂ in the commercial dioxide.

**Procedure.** Weigh out accurately about 0.4 g. of lead dioxide into a 250-ml. reagent bottle; it may be washed into the bottle with a little water. Add 25 ml. of 0.1N-potassium iodide and a volume of concentrated hydrochloric acid equal to the volume of liquid already in the bottle. Insert the stopper, and shake until all the lead dioxide has dissolved. Titrate the excess of potassium iodide with standard 0.1N-potassium iodate as described in Section III, 124. Titrate the potassium iodide solution against the standard potassium iodate solution, and thence compute the amount of potassium iodide which has reacted with the lead dioxide.

Calculate the percentage of PbO₂ in the sample.
III, 180. Determination of hydrogen peroxide.—Discussion. The method depends upon the interaction of dilute hydrogen peroxide solution with excess of standard sodium arsenite solution in the presence of sodium hydroxide:

$$\text{As}_2\text{O}_3 + 2\text{H}_2\text{O}_2 = \text{As}_2\text{O}_6 + 2\text{H}_2\text{O}$$

The excess of sodium arsenite is then determined by titration with potassium iodate as detailed in Section III, 125:

$$\text{KIO}_3 + \text{As}_2\text{O}_3 + 2\text{HCl} = \text{KCl} + \text{As}_2\text{O}_6 + \text{HCl} + \text{H}_2\text{O}$$

or

$$\text{IO}_3^- + \text{As}_2\text{O}_3 + 2\text{H}^+ = \text{I}^- + \text{As}_2\text{O}_6 + \text{H}_2\text{O}$$

The amount of arsenite, found by titration, is deducted from that originally taken. Since $\text{As}_2\text{O}_3 = 2\text{H}_2\text{O}_2$, the percentage of hydrogen peroxide in the original solution can be readily calculated. This method, like that of Section III, 110, is not influenced by the presence of organic preservatives.

Procedure. Dilute 25 ml. of “20 volume” hydrogen peroxide to 250 ml. in a volumetric flask. Place 50 ml. of 0.1N-sodium arsenite (Section III, 104A) and 10 ml. of 10 per cent sodium hydroxide solution into a 250-ml. reagent bottle, and add 25 ml. of the diluted hydrogen peroxide solution slowly from a burette whilst the contents of the bottle are gently rotated. Allow the mixture to stand for 2 minutes, and cautiously add 50 ml. of concentrated hydrochloric acid. Insert the glass stopper and, whilst holding it down firmly, shake the bottle vigorously. Release the stopper carefully so as to allow the excess of carbon dioxide (producing a positive pressure) to escape without losing any of the solution. Add 5 ml. of chloroform or of carbon tetrachloride, and titrate the unoxidised arsenious acid with standard 0.025$\text{M}$-potassium iodate. Repeat the titration with two other 25-ml. portions of the diluted hydrogen peroxide solution.

Titrate 25 ml. of the arsenite solution against the standard potassium iodate solution (Section III, 125). Calculate the volume of the arsenite solution which has reacted with the hydrogen peroxide, and thence the percentage of $\text{H}_2\text{O}_2$ in the original solution.

$$1\text{ml. N-As}_2\text{O}_3 = 0.01701\text{g. H}_2\text{O}_2$$

III, 131. Determination of hydrazine.—Discussion. Hydrazine reacts with potassium iodate under the usual Andrews conditions thus:

$$\text{KIO}_3 + \text{N}_2\text{H}_4 + 2\text{HCl} = \text{KCl} + \text{N}_2 + \text{IO}^- + 3\text{H}_2\text{O}$$

or

$$\text{IO}_3^- + \text{N}_2\text{H}_4 + 2\text{H}^+ = \text{I}^- + \text{N}_2 + 3\text{H}_2\text{O}$$

Thus

$$\text{KIO}_3 = \text{N}_2\text{H}_4$$

or

$$1\text{ml. 0.025M-KIO}_3 = 0.0008013\text{g. N}_2\text{H}_4 = 0.003253\text{g. N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$$

As an exercise, the student may determine the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ content of hydrazine sulphate, preferably of A.R. quality.

Procedure. Weigh out accurately 0.08-0.1 g. of hydrazine sulphate into a 250-ml. reagent bottle, add a mixture of 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of chloroform or carbon tetrachloride. Run in the standard 0.025M-potassium iodate slowly from a burette, with shaking between the additions, until the organic layer is just decolorised.

Calculate the percentage of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ in the sample.
III, 132. Determination of thallium.—Discussion. Thallous salts are oxidised by potassium iodate under the Andrews conditions in accordance with the following equation:

$$KIO_3 + 2TlCl + 6HCl = KCl + 2TlCl_3 + ICl + 3H_2O$$

i.e.,

$$IO_3^- + 2Tl^+ + 6H^+ = I^+ + 2Tl^{+++} + 3H_2O$$

Thus

$$KIO_3 = 2Tl$$

or

$$1 \text{ ml. } 0.025M-KIO_3 = 0.01022 \text{ g. Tl}$$

Procedure. Place 20 ml. of the solution containing 0.25–0.3 g. of thallium (e.g., as thallous nitrate) into a 250-ml. reagent bottle, add 60 ml. of concentrated hydrochloric acid and 5 ml. of chloroform or carbon tetrachloride. Titrate with standard 0.025M-potassium iodate in the usual manner (Section III, 124) until the violet colour of the organic layer just vanishes.

Calculate the thallium content of the solution.

III, 133. Determination of iron.—Discussion. Ferrous iron in hydrochloric acid solution is much less stable than in a sulphuric acid solution, and consequently the results of determinations by titration with 0.1N-potassium iodate under the usual conditions are unsatisfactory, due largely to the oxidation of the ferrous salt by oxygen in the air. If, however, excess of iodine chloride solution is added to the ferrous salt solution before the hydrochloric acid, the ferrous iron is oxidised by the iodine monochloride, and the liberated iodine may be titrated with standard potassium iodate solution:

$$2Fe^{++} + 2ICl + HCl = 2Fe^{+++} + I_2 + 2Cl^- + HCl$$

$$2I_2 + KIO_3 + 6HCl = KCl + 5ICI + 3H_2O$$

The solution to be titrated with potassium iodate must contain sufficient hydrochloric acid to prevent the hydrolysis of the iodine monochloride which is formed: at least 50 per cent concentrated hydrochloric acid by volume must be present at the end of the titration.

For the most accurate results, the potassium iodate solution should be standardised against pure iron, preferably after dissolution in hydrochloric acid and passage through a silver reductor (Section II, 39C).

Procedure. For practice in the determination, the student may titrate 0.1N-ferrous ammonium sulphate with 0.1N-potassium iodate.

Prepare the iodine monochloride solution by dissolving 5.00 g. of A.R. potassium iodide and 3.22 g. of A.R. potassium iodate in 37.5 ml. of water, and adding 37.5 ml. of concentrated hydrochloric acid and 5 ml. of carbon tetrachloride. If the carbon tetrachloride layer does not have a faint pink colour after shaking vigorously, add a little potassium iodide solution until the presence of a little iodine is observed in the carbon tetrachloride; if the colour of the latter is more than a faint pink, add a little potassium iodate solution to convert some of the iodine into iodine monochloride.

To 25 ml. of the 0.1N-ferrous solution add 6 ml. of the iodine monochloride solution, 60 ml. of concentrated hydrochloric acid, and 5 ml. of chloroform or carbon tetrachloride. When cold, titrate with the 0.1N-potassium iodate in the usual manner.

Alternatively, replaced the immiscible solvent by 0.5 ml. of Amaranth.
Volumetric Analysis

indicator (introduced after most of the iodine colour has disappeared); the colour change at the equivalence point is from red to colourless.

Titrate the 0.1N-ferrous ammonium sulphate solution with standard 0.1N-potassium permanganate or 0.1N-ceric sulphate, and compare the result with that obtained by the potassium iodate method.

III, 134. Determination of vanadium with potassium iodate.—Discussion. Vanadates are reduced by iodides in strongly acid (hydrochloric) solution in an atmosphere of carbon dioxide to the quadrivalent condition:

\[ 2\text{H}_3\text{VO}_4 + 2\text{HI} + 4\text{HCl} = 2\text{VOCl}_2 + \text{I}_2 + 6\text{H}_2\text{O} \]

The liberated iodine and the excess of iodide is determined by titration with standard potassium iodate solution; the hydrochloric acid concentration must not be allowed to fall below 7N in order to prevent re-oxidation of the vanadium compound by iodine chloride.

\begin{align*}
\text{HIO}_3 + 2\text{I}_2 + 5\text{HCl} & = 5\text{ICl} + 3\text{H}_2\text{O} \\
\text{HIO}_3 + 2\text{HI} + 3\text{HCl} & = 3\text{ICl} + 3\text{H}_2\text{O}
\end{align*}

The total result of the reaction is:

\[ 4\text{H}_3\text{VO}_4 + 4\text{HI} + \text{HIO}_3 + 13\text{HCl} = 4\text{VOCl}_2 + 5\text{ICl} + 15\text{H}_2\text{O} \]

and it can easily be shown that

\[ 1\text{ ml. 0.026M-KIO}_3 = 0.005095\text{ g. V} \]

This method is applicable in the presence of arsenate, phosphate, or ferric iron, and also in the presence of tungstic acid, which may be held in solution by adding phosphoric acid.

Procedure. Place 25 ml. of the solution containing 0.05–0.10 g. of vanadium (as vanadate) in a 250-ml. glass-stoppered reagent bottle, and pass a rapid current of carbon dioxide for 2–3 minutes into the bottle, but not through the solution. Then add sufficient concentrated hydrochloric acid through a funnel to make the solution 6-8N during the titration. Introduce a known volume (excess) of approximately 0.05M-potassium iodide, which has been titrated against the standard iodate solution (Section III, 124). Mix the contents of the bottle, allow to stand for 1–2 minutes, add 5 ml. of carbon tetrachloride, and then titrate as rapidly as possible with standard 0.025M-potassium iodate until no more iodine colour can be detected in the organic layer. Add concentrated hydrochloric acid as needed during the titration so that the concentration does not fall below 7N.

Calculate the concentration of vanadium in the solution.
OXIDATIONS WITH POTASSIUM BROMATE

III. 135. General discussion.—Potassium bromate is a powerful oxidising agent in acid solution (Table XVI, Section I, 46). Reducing agents convert it smoothly into the bromide:

\[ \text{BrO}_3^- + 6\text{H}^+ + 6e^- = \text{Br}^- + 3\text{H}_2\text{O} \]

The equivalent weight is therefore \( \frac{1}{6} \) mol. (KBrO\(_3\)/6), or 167.02/6, or 27.84, and a 0.1N solution contains 2.784 g. potassium bromate per litre.* At the end of the titration free bromine appears:

\[ \text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ = 3\text{Br}_2 + 3\text{H}_2\text{O} \]

The presence of free bromine, and consequently the end point, can be detected by its yellow colour, but it is better to use indicators such as methyl orange, methyl red, or indigo carmine (reaction mixture preferably at 80–90° C.) or Brilliant Ponceau 5R, Bordeaux, or Naphthol Blue Black (reaction mixture at the laboratory temperature). These indicators have their usual colour in acid solution, but are destroyed by the first excess of bromine. With all irreversible oxidation indicators the destruction of the indicator is often premature to a slight extent: a little additional indicator is usually required near the end point. The quantity of bromate solution consumed by the indicator is exceedingly small, and the "blank" can be neglected for 0.1N solutions. Direct titrations with bromate solution in the presence of irreversible dyestuff indicators are usually made in hydrochloric acid solution, the concentration of which should be at least 1.5–2N. At the end of the titration some chlorine may appear by virtue of the reaction:

\[ 10\text{Cl}^- + 2\text{BrO}_3^- + 12\text{H}^+ = 5\text{Cl}_2 + \text{Br}_2 + 6\text{H}_2\text{O} \]

this immediately bleaches the indicator.

The titrations should be carried out slowly so that the indicator change, which is a time reaction, may be readily detected. If the determinations are to be executed rapidly, the volume of the bromate solution to be used must be known approximately, since ordinarily with irreversible dyestuff indicators there is no simple way of ascertaining when the end point is close at hand. With the highly coloured indicators (Brilliant Ponceau 5R, Bordeaux, or Naphthol Blue Black), the colour fades as the end point is approached (owing to local excesses of bromate) and another drop of indicator can be added. At the end point the indicator is irreversibly destroyed and the solution becomes colourless or almost so. If the fading of the indicator is confused with the equivalence point, another drop of the indicator may be added. If the indicator has faded, the additional drop will colour the solution; if the end point has been reached, the additional drop of indicator will be destroyed by the slight excess of bromate present in the solution.

* The same result can be obtained by considering the hypothetical equation:

\[ \text{HBrO}_3 = \text{HBr} + 30 \]

i.e., 1 mol. of potassium bromate supplies 6 equivalents of oxygen.

368
The introduction of reversible redox indicators for determinations of trivalent arsenic and trivalent antimony has considerably simplified the procedure: those at present available are α-naphthoflavone and p-ethoxychrysoidine. The addition of a little tartaric acid is recommended when antimony (III) is titrated with bromate in the presence of p-ethoxychrysoidine.

Examples of determinations utilising direct titration with standard bromate solutions are expressed by the following equations:

\[
\begin{align*}
KBrO_3 + 3H_2AsO_3 (+ HCl) &= KBr + 3H_2AsO_4 (+ HCl) \\
KBrO_3 + 3SbCl_3 + 6HCl &= KBr + 3SbCl_5 + 3H_2O \\
KBrO_3 + 3SnCl_2 + 6HCl &= KBr + 3SnCl_4 + 3H_2O \\
2KBrO_3 + 3N_2H_4 (+ HCl) &= 2KBr + 3N_2 + 6H_2O (+ HCl) \\
KBrO_3 + NH_2OH (+ HCl) &= KBr + HNO_3 + H_2O (+ HC1) \\
KBrO_3 + 6K_4[Fe(CN)]_6 + 6HCl &= KBr + 6K_3[Fe(CN)]_6 + 6KCl + 3H_2O \\
\end{align*}
\]

Various substances cannot be oxidised directly with potassium bromate, but react quantitatively with an excess of bromine. Acid solutions of bromine of exactly known concentration are readily obtainable from a standard potassium bromate solution by adding acid and an excess of bromide:

\[
BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O
\]

In this reaction 1 mol. of bromate yields six atoms of bromine, hence the equivalent weight is \( KBrO_3/6 \), identical with that of potassium bromate alone. Bromine is very volatile, and hence such operations should be conducted at as low a temperature as possible and in reagent bottles fitted with ground-glass stoppers. The excess of bromine may be determined iodometrically by the addition of excess of potassium iodide and titration of the liberated iodine with standard thiosulphate solution:

\[
2KI + Br_2 = 2KBr + I_2
\]

Potassium bromate is readily available in a high state of purity; the A.R. product has an assay value of at least 99.9 per cent. The substance can be dried at 120–150°C., is anhydrous, and the aqueous solution keeps indefinitely. It can therefore be employed as a primary standard. Its only disadvantage is that the equivalent weight is comparatively small.

**III, 136. Preparation of 0.1N-potassium bromate.**—Dry some finely powdered A.R. potassium bromate for 1–2 hours at 120°C., and allow to cool in a desiccator. Weigh out accurately 2.784 g. of the pure potassium bromate, and dissolve it in 1 litre of water in a volumetric flask.

**Analyses Involving the Use of Standard Potassium Bromate Solutions**

**III, 137. Determination of antimony or of arsenic.**—Discussion. The antimony or the arsenic must be present in the trivalent condition. The reaction of trivalent arsenic or antimony with potassium bromate may be written:

\[
2KBrO_3 + 3M_2O_8 + 2HCl = 2KCl + 3M_2O_6 + 2HBr \quad (M = As \text{ or } Sb)
\]
Hence

\[ 370 \]

The presence of tin and of considerable quantities of iron and copper interfere with the determinations.

For practice in the use of potassium bromate solution, the student may:
(a) titrate standard 0·1N-sodium arsenite with the standard potassium bromate and (b) determine the percentage of antimony in tartar emetic.

Procedure. Titration of standard sodium arsenite solution. Method A (with irreversible indicator). Place 25 ml. of standard 0·1N-sodium arsenite (Section III, 48, Procedure A, Note 1, and Section III, 104A) into a 250-ml. conical flask, add 25 ml. of water, 15 ml. of concentrated hydrochloric acid, and 2 drops of methyl red or, preferably, of Naphthol Blue Black (0·1 per cent aqueous solution), Brilliant Ponceau 5R (0·2 per cent aqueous solution), or Bordeaux (0·1 per cent aqueous solution) indicators.* Titrate slowly with the standard 0·1N-potassium bromate with constant swirling of the solution. As the end point approaches, add the bromate solution dropwise with intervals of 2–3 seconds between the drops until the solution is colourless or very pale yellow. If the colour of the indicator fades, add another drop of indicator. (The immediate discharge of the colour indicates that the equivalence point has been passed and the titration is of little value.) Repeat the titration with two other 25-ml. portions of the arsenite solution: individual titrations should not differ by more than 0·1 ml.

Compare the volume of potassium bromate solution used with the calculated value.

Method B (with reversible indicator). Place 25 ml. of standard sodium arsenite solution in a 250-ml. conical flask, add 10 ml. of 10 per cent potassium bromide solution, 6 ml. of concentrated hydrochloric acid, 10 ml. of water, and 1 ml. of \( \alpha \)-naphthoflavone indicator (1). Titrate with standard 0·1N-potassium bromate until the colourless liquid is coloured a persistent orange by one drop of the bromate solution. It is sometimes advantageous to add a further drop of indicator near the end point. Repeat the titration. Compare the volume of potassium bromate solution used with that found in Method A.

Carry out another titration substituting \( \alpha \)-naphthoflavone by 2 drops of \( p \)-ethoxychrysoidine indicator (2). As the end point is approached, add the bromate solution slowly, since the disappearance of the red colour is not instantaneous. At the equivalence point there is a sharp change from red (pink) to very pale yellow. Repeat the titration.

Notes. 1. It is important that the \( \alpha \)-naphthoflavone be pure; it should be a white, crystalline solid of m. p. 155–156\(^\circ\) C. and be easily soluble in warm ethyl alcohol. The \( \alpha \)-naphthoflavone indicator is prepared by dissolving 0·1 g. of the pure compound in 100 ml. of ethanol.
2. The \( p \)-ethoxychrysoidine indicator is prepared by dissolving 0·2 g. of the solid in 100 ml. of water or ethanol.

* Naphthol Blue Black (British Colour Index, No. 246), Brilliant Ponceau 5R (B.C.I., No. 185), and Bordeaux (B.C.I., No. 88) of indicator quality may be obtained, for example, from the G. Frederick Smith Chemical Co., 867 McKinley Avenue, Columbus, Ohio, U.S.A., or from Eimer and Amend, 635 Greenwich Street, New York 14, N.Y., or from Fisher Scientific Company, 717 Forbes Street, Pittsburgh 19, Pa., U.S.A.
Volumetric Analysis

Procedure. **Antimony in tartar emetic. Method A** (with irreversible indicator). Weigh out accurately about 4 g. of finely powdered A.R. potassium antimonyl tartrate or 5 g. of tartar emetic, dissolve it in water, and make up to 250 ml. in a volumetric flask. Transfer 25 ml. of this solution to a 250-ml. conical flask, add 25 ml. of water, 10 ml. of concentrated hydrochloric acid, and 2 drops of methyl red or, preferably, of Naphthol Blue Black, Brilliant Ponceau 8R, or Bordeaux indicators. Introduce the standard 0·1N-potassium bromate with constant swirling of the solution until the colour of the indicator commences to fade, add a further drop of indicator, and continue the addition of the bromate solution dropwise with intervals of 2–3 seconds between the drops until the colour of the solution is just discharged. Repeat the titration with two further 25-ml. portions of the solution.

Calculate the percentage of antimony in the sample.

**Method B** (with reversible indicator). Transfer 25 ml. of the solution of potassium antimonyl tartrate, prepared as in Method A, to a 250-ml. conical flask, add 5 ml. of concentrated hydrochloric acid, 10 ml. of 10 per cent potassium bromide solution, 25 ml. of water, and 1 ml. of alpha-naphthoflavone indicator. Titrate with the standard 0·1N-potassium bromate until the colour of the solution changes sharply from colourless to orange. Repeat the titration with another 25-ml. portion of the solution.

Alternatively, proceed as above but use 2 drops of p-ethoxychrysoidine indicator. Add the 0·1N-potassium bromate slowly near the equivalence point, since the colour change red (pink) to very pale yellow is not instantaneous.

Calculate the percentage of antimony in the sample.

**III, 138. Determination of metals by means of 8-hydroxyquinoline ("oxine").—Discussion.** Various metals (e.g., aluminium, iron, copper, zinc, cadmium, nickel, cobalt, manganese, and magnesium) under specified conditions of pH yield well-defined crystalline precipitates with 8-hydroxyquinoline. These precipitates have the general formula $M(C_{8}H_{8}ON)_{n}$, where $n$ is the valency of the metal $M$ (see, however, Section I, 620). Upon treatment of the oxinates with dilute hydrochloric acid, the oxine is liberated. Oxine reacts with 4 equivalents of bromine to give 5 : 7-dibromo-8-hydroxyquinoline (R. Berg, 1926):

$$C_{8}H_{7}ON + 2Br_{2} = C_{8}H_{8}ONBr_{2} + 2HBr$$

Hence 1 mol. of the oxinate of a divalent metal requires 8 equivalents of bromine, whilst that of a trivalent metal requires 12 equivalents. The bromine is derived by the addition of standard 0·1N-potassium bromate and excess of potassium bromide to the acid solution.

$$KBrO_{3} + 5KBr + 6HCl = 6KCl + 3Br_{2} + 3H_{2}O$$

Full experimental details are given below for the determination by the student of aluminium in potash alum and of magnesium in magnesium sulphate.

Of the other elements which may be estimated volumetrically with the aid of 8-hydroxyquinoline iron, copper (Sections III, 106, 126), cadmium (Section III, 38), zinc (Sections III, 145, 38), nickel (Sections III, 42 and IV, 32D), cobalt (Section III, 37), and manganese (Sections III, 60 and VI, 12) may be determined by other more convenient and
Quantitative Inorganic Analysis

less expensive methods. Outlines of the procedures for cadmium, cobalt, nickel, titanium, and zinc will be given.

Procedure A. Determination of aluminium. Prepare a 2 per cent solution of A.R. 8-hydroxyquinoline in 2N-acetic acid; add ammonia solution until a permanent precipitate is just produced, and re-dissolve this by warming.

Weigh out accurately about 3·50 g. of potash alum, preferably of A.R. grade, and dissolve it in 250 ml. of water in a volumetric flask. Shake well. Transfer 25 ml. of the solution, which contains about 0·02 g. of Al, to a conical flask, add 125 ml. of water, and warm to 50–60° C. Then add a 20 per cent excess of the oxine solution (1·001 g. of Al), when the complex Al(C₈H₄ON)₃ will be formed. Complete the precipitation by the addition of a solution of 40 g. of ammonium acetate in the minimum quantity of water, stir the mixture, and allow to cool. Filter the granular precipitate through a coarse-mesh, sintered-glass crucible (or through a porous-porcelain crucible), and wash with hot water (2). Dissolve the complex in warm concentrated hydrochloric acid, collect the solution in a 250-ml. reagent bottle, add a few drops of indicator (0·1 per cent solution of the sodium salt of methyl red or 1 per cent indigo-carmine solution), and 0·5–1 g. of pure potassium bromide. Titrate slowly with standard 0·1N (i.e., M/60) potassium bromate until the colour becomes pure yellow (with either indicator). The exact end point is not easy to detect, and it is better to add a slight excess of standard bromate solution (free bromine is thus present, and is tested for by removing a drop of the liquid on to potassium iodide-starch paper), diluting the solution considerably with 2N-hydrochloric acid (to prevent the precipitation of 5:7-dibromo-8-hydroxyquinoline during the titration), then add (after 5 minutes) 10 ml. of 10 per cent potassium iodide solution, and titrate the liberated iodine with standard 0·1N-sodium thiosulphate, using starch as indicator (3). Repeat the titration with two other 25-ml. portions of the aluminium solution.

From the above discussion, it is evident that Al = 12Br, i.e., to 12,000 ml. of 0·1N-bromate (or 0·1N-thiosulphate), hence

\[ 1 \text{ ml. } \text{N-KBrO}_3 = 0·002249 \text{ g. } \text{Al} \]

Calculate the percentage of aluminium in the sample employed.

Notes. 1. An alcoholic solution cannot be used, since the aluminium complex is slightly soluble in alcohol, nor can this solvent be used for washing the complex.
   2. This will remove the excess of oxine. Complications due to adsorption of iodine will thus be avoided.
   3. A brown additive compound of iodine with the dibromo compound may separate during the titration; this compound usually dissolves during the subsequent titration with thiosulphate, yielding a yellow solution so that the end point with starch may be found in the usual manner. Occasionally, the dark-coloured compound, which contains adsorbed iodine, may not dissolve readily and thus introduce an uncertainty in the end point; this difficulty may be avoided by adding 10 ml. of carbon disulphide before introducing the potassium iodide solution.

Procedure B. Determination of magnesium. Weigh out accurately about 1·0 g. of crystallised magnesium sulphate, preferably of A.R. quality, and dissolve it in 250 ml. of water in a standard flask. Mix thoroughly. Pipette 25 ml. of this solution into a beaker, add 5 g. of ammonium acetate dissolved in 50 ml. of water, and heat to boiling. Add a slight excess of a 2 per cent solution of oxine in 2N-acetic acid,* and then concentrated ammonia solution slowly and with stirring until the liquid is faintly alkaline (e.g., to phenolphthalein paper). Boil the mixture for 1 or 2 minutes until the yellow precipitate becomes crystalline, and allow to settle. The supernatant liquid should be yellow, indicating that an excess of reagent is present. Filter the precipitate through a sintered-glass crucible (porosity No. 3, or through a porous-porcelain crucible), and wash the precipitate thoroughly with hot water (1). Dissolve the precipitate on the filter in 2-3N-hydrochloric acid, and wash the filter with the same acid until the washings are colourless. Transfer the filtrate and washings quantitatively to a reagent bottle or a glass-stoppered flask. Add 1 g. of pure potassium bromide, several drops of indicator (methyl red or indigocarmine), and titrate with standard 0·1N-potassium bromate as described under aluminium (Procedure A). The same difficulty in detecting the end point is experienced here also, and is overcome in a similar way. Repeat the titration with two other 25-ml. portions of the solution.

Calculate the percentage of magnesium in the sample.

\[ 1 \text{ ml. } N\text{-KBrO}_3 = 0.003040 \text{ g. Mg} \]

Note. 1. The magnesium “ oxinate ” is appreciably soluble in hot water, hence washing is discontinued when the colour of the washings changes from a deep yellow to a pale yellow. It is probably better to employ a hot 1-2 per cent ammonia solution as the wash liquid (R. Berg, 1938).

Procedure C. Determination of cadmium. The solution (about 100 ml.; up to 0·1 g. Cd) is treated with sodium carbonate solution until faintly cloudy, and the turbidity is just removed by the addition of dilute acetic acid. The mixture is warmed to 60° C., 3-5 g. of sodium acetate are added (1), and a slight excess of a 2 per cent solution of oxine in alcohol stirred in, the supernatant liquor being then of a golden-yellow colour and the precipitate of Cd(C_9H_5ON)_2.2H_2O a pale yellow. The mixture is heated nearly to boiling, set aside for a few minutes, and then filtered on a sintered-glass or porous-porcelain crucible, washed with hot water (2), dissolved in moderately concentrated hydrochloric acid (say, 4N), and titrated with 0·1N-potassium bromate (Procedure A).

\[ 1 \text{ ml. } N\text{-KBrO}_3 = 0.01405 \text{ g. Cd} \]

Notes. 1. If copper is initially present, precipitation should be carried out in 10 per cent acetic acid solution without the addition of sodium acetate. The copper is thus completely precipitated as Cu(C_6H_5ON)_2† and the cadmium remains in the filtrate, from which it is precipitated by neutralisation and the addition of sodium acetate. Furthermore, precipitation in the presence of potassium cyanide from sodium acetate solutions containing a trace of acetic acid ensures that mercury, if present, remains in solution.

* For details of the preparation of the reagent, see Section 1. 62C.
† For the gravimetric determination of copper, the precipitate is dried at 105–110° C. and weighed as Cu(C_6H_5ON)_2, which contains 18·07 per cent Cu.
Quantitative Inorganic Analysis

2. For the gravimetric determination of cadmium, the precipitate is dried at 130°C and weighed as \( \text{Cd(C}_6\text{H}_5\text{ON)}_2 \), which contains 28.05 per cent Cd.

**Procedure D. Determination of cobalt.** The neutral or weakly acidic (acetic acid) solution* of the cobaltous salt (150 ml.; up to 0.06 g. Co) containing sodium acetate (5 g.) is warmed to 70°C, treated with a slight excess of a 2 per cent alcoholic solution of oxine, and boiled gently until the light-brown amorphous cobalt oxinate \( \text{Co(C}_6\text{H}_5\text{ON)}_2\text{H}_2\text{O} \) becomes crystalline. The latter is allowed to settle, filtered off on a sintered-glass or porous-porcelain crucible, washed with hot water, dissolved in fairly strong hydrochloric acid, and titrated with standard 0.1N-potassium bromate (Procedure A).

\[
1 \text{ ml. } N\text{-KBrO}_3 = 0.007368 \text{ g. Co}
\]

**Procedure E. Determination of nickel.** The solution of the nickelous salt (150 ml.; up to 0.1 g. Ni), containing 3–5 g. of sodium acetate and 8–10 per cent of acetic acid, is warmed to 70°C, treated with excess of 2 per cent alcoholic oxine solution, and then boiled until the precipitate of \( \text{Ni(C}_6\text{H}_5\text{ON)}_2\text{H}_2\text{O} \) becomes granular. The whole is filtered through a sintered-glass or porous-porcelain crucible, the precipitate thoroughly washed with hot water, dissolved in hydrochloric acid, and titrated with 0.1N-potassium bromate (Procedure A).

\[
1 \text{ ml. } N\text{-KBrO}_3 = 0.007335 \text{ g. Ni}
\]

**Note.** This process affords a complete separation from manganese.

**Procedure F. Determination of titanium.** The solution (150 ml.; up to 0.07 g. Ti) is treated with 1 g. of tartaric acid, 0.5 g. of sodium acetate, then with ammonia until barely alkaline to phenolphthalein, and finally with 1.5 ml. of glacial acetic acid. The solution is warmed to 60°C, stirred whilst excess of 2 per cent alcoholic oxine solution is added, and then boiled for 10 minutes to effect granulation of the titanium oxinate, \( \text{TiO(C}_6\text{H}_5\text{ON)}_2\text{H}_2\text{O} \). The latter is then filtered off on a sintered-glass or porous-porcelain crucible, and washed with hot water (1). The precipitate is dissolved in 1:1 hydrochloric acid, and titrated with 0.1N-potassium bromate and 0.1N-sodium thiosulphate (Procedure A).

\[
1 \text{ ml. } N\text{-KBrO}_3 = 0.005988 \text{ g. Ti}
\]

**Note.** 1. The excess of oxine is removed when the washings are colourless. To confirm this (or when in doubt) mix 25 ml. of the filtrate with 10 ml. of concentrated hydrochloric acid, add 2 drops of a 0.2 per cent alcoholic solution of methyl red (or of the aqueous solution of the sodium salt) and a little potassium bromide solution; the addition of 1 drop of 0.1N-potassium bromate should result in decolorisation.

**Procedure G. Determination of zinc.** The solution should contain either (i) 5 g. of sodium or ammonium acetate and 4 g. of acetic acid or (ii) 5 g. of sodium tartrate and 25 ml. of N-sodium hydroxide in 100 ml., and not more than 0.15 g. of zinc. In (i), the solution is warmed to 60°C, treated with a slight excess of a 2 per cent solution of oxine in 2N-acetic acid or in alcohol, boiled for a few minutes, filtered, and washed with hot water (1). In (ii), the solution is treated with a 2 per cent alcoholic solution of oxine in the cold, warmed at

* If mineral acid is present, sodium acetate is added.
60°C, until the precipitate becomes crystalline, and filtered. The well-washed precipitate (I) is dissolved in 2N-hydrochloric acid and titrated with 0.1N-potassium bromate (Procedure A).

1 ml. N-KBrO₃ = 0.008175 g. Zn

Note. 1. For the gravimetric determination of zinc, the precipitate is dried at 130-140°C and weighed as Zn(C₆H₆ON)₂, which contains 18.49 percent Zn.

III. 139. Determination of hydroxylamine.—The method based upon the reduction of ferric solutions in the presence of sulphuric acid, boiling, and subsequent titration in the cold with standard 0.1N-potassium permanganate frequently yields high results unless the experimental conditions are closely controlled:

\[
2\text{NH}_2\text{OH} + 2\text{Fe}_2(\text{SO}_4)_3 = 4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{N}_2\text{O} + \text{H}_2\text{O}
\]

1 ml. N-KMnO₄ = 0.01652 g. NH₂OH

The best results are obtained by oxidation with potassium bromate in the presence of hydrochloric acid:

\[
\text{NH}_2\text{OH} + \text{HBrO}_3 = \text{HNO}_3 + \text{HBr} + \text{H}_2\text{O}
\]

The hydroxylamine solution is treated with a measured volume of 0.1N (i.e., M/60) potassium bromate so as to give 10-30 ml. excess, followed by 40 ml. of 5N-hydrochloric acid. After 15 minutes the excess of bromate is determined by the addition of potassium iodide solution and titration with standard 0.1N-sodium thiosulphate (compare Section III, 138).

1 ml. N-KBrO₃ = 0.005505 g. NH₂OH
OXIDATIONS WITH CHLORAMINE-T

III, 140. General discussion. Preparation and standardisation of 0.1N solution.—Chloramine-T is the sodium derivative of \( N\)-chloro-\( p\)-toluenesulphonamide \( \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NClNa} \), and is obtainable commercially in a high state of purity; it is a by-product in the manufacture of saccharin. The aqueous solution reacts as if it were a hypochlorite, and it has the great advantage that it is far more stable than sodium hypochlorite solution:

\[
\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NClNa} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NH}_2 + \text{NaCl}.
\]

Chloramine-T was introduced as a volumetric reagent by A. Noll (1924) as a cheap substitute for iodine in the determination of trivalent arsenic and antimony. The reagent reacts in dilute acid (3–5 per cent) solution; if the acid is too concentrated, secondary changes occur.

Chloramine-T reacts with potassium iodide in acid solution to liberate iodine:

\[
\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NClNa} + 2\text{KI} + 2\text{HCl} = \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NH}_2 + \text{I}_2 + \text{NaCl} + 2\text{KCl}.
\]

The equivalent weight is therefore \( \frac{1}{2} \) mol., or \( 281.70/2 \), or 140.85. Reaction also occurs quantitatively with arsenious acid:

\[
2\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NClNa} + \text{As}_2\text{O}_3 + 2\text{H}_2\text{O} = 2\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NH}_2 + \text{As}_2\text{O}_5 + 2\text{NaCl}.
\]

Prepare an approximately 0.1N solution of chloramine-T by dissolving 14.5 g. of the purest commercial product in 1 litre of water. It may be standardised by one of two methods.

1. Treat 25 ml. of the chloramine-T solution with 2 ml. of 2N-hydrochloric acid and 10 ml. of 10 per cent potassium iodide solution. Titrate the liberated iodine with standard 0.1N-sodium thiosulphate in the usual way, using 2 ml. of starch as indicator.

2. Add the chloramine-T solution from a burette to 25 ml. of standard 0.1N-arsenious oxide, containing a small crystal of pure potassium iodide and 1 ml. of starch solution, until a permanent blue colour just appears.

ANALYSES INVOLVING THE USE OF STANDARD CHLORAMINE-T SOLUTIONS

III, 141. Determination of antimony.—For practice in this estimation, the student may determine the percentage of antimony in tartar emetic or in A.R. potassium antimony tartrate.

Weigh out accurately about 0.35 g. of tartar emetic or of A.R. potassium antimonyt tartrate, and dissolve it in 100 ml. of water in a conical flask. Add 0.2 g. of tartaric acid, 1 g. of sodium bicarbonate, 2 ml. of starch solution, and a small crystal of pure potassium iodide.
Volumetric Analysis

Titrate with the standard 0·1N-chloramine-T to the first permanent blue coloration. Repeat the titration with two similar quantities of the antimony compound.

Calculate the percentage of antimony in the sample.

1 ml. N-chloramine-T = 0·06088 g. Sb

III, 142. Determination of nitrites.—For practice in this estimation, the student may determine the percentage purity of sodium nitrite, preferably of A.R. grade.

Weigh out accurately about 1·5 g. of sodium nitrite, and dissolve it in 500 ml. of boiled-out water in a volumetric flask. Shake thoroughly. Place 50 ml. of the standard chloramine-T solution in a conical flask, and transfer 25 ml. of the nitrite solution to the flask by means of a pipette, keeping the tip of the pipette below the surface of the liquid during the addition. Add a few ml. of dilute acetic acid. The sodium salt is decomposed with the separation of the corresponding free chlor­amine as a white cloud, which rapidly diminishes in intensity. After 2 minutes, add excess of 10 per cent potassium iodide solution, and titrate the liberated iodine with standard 0·1N-sodium thiosulphate, using 2 ml. of starch solution as indicator. To another 50 ml. of the chloramine solution add potassium iodide solution and dilute acid, and titrate with the standard 0·1N-sodium thiosulphate (Section III, 140); the difference between the two titres is a measure of the nitrite. Repeat the titration with two other 25-ml. portions of the nitrite solution.

\[
\text{NaN}_2\text{O}_2 + \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NClNa} + \text{H}_2\text{O} = \text{NaNO}_3 + \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 + \text{NaCl}
\]

Now

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NClNa} = 2\text{Na}_2\text{S}_2\text{O}_3 = \text{NaNO}_2
\]

hence 1 ml. N-Na$_2$S$_2$O$_3$ = 0·02301 g. NO$_2$ = 0·03456 g. NaNO$_2$

Calculate the percentage of NaN$_2$O$_2$ in the sample.

III, 148. Determination of tin.—Discussion. The tin must be present in the stannous condition. Reduction is best effected in hydrochloric acid solution by means of pure aluminium (free from iron), pure zinc turnings, or pure lead foil. During the whole of the titration a continuous current of carbon dioxide should be maintained above the stannous solution, for this is very sensitive to atmospheric oxidation. The reaction between stannous solution and the chloramine-T is:

\[
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NClNa} + \text{SnCl}_2 + 2\text{HCl} = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 + \text{SnCl}_4 + \text{NaCl}
\]

hence 1 ml. N-chloramine-T = 0·05325 g. Sn

For practice, the student may determine the percentage of tin in hydrated stannous chloride.

Procedure. Weigh out accurately about 2·5 g. of crystallised stannous chloride, preferably of A.R. quality, dissolve it in 150 ml. of concentrated hydrochloric acid, transfer to a 250-ml. volumetric flask, and make up to the mark with boiled-out distilled water. Shake well. Transfer 25 ml. of the solution (which contains about 0·15 g. Sn) into a 350- or 500-ml. conical flask, add 30 ml. of concentrated hydrochloric acid and 100 ml. of water, and finally pure lead foil to give a surface of about 24 square inches (or an equivalent quantity of A.R. lead granules).
Insert a three-holed rubber stopper as detailed in Section III, 116, Procedure E, and pass a slow stream of carbon dioxide through the flask. Boil for 80 minutes and then allow to cool; the current of gas is maintained throughout the reduction * and the subsequent titration. Add sufficient sodium hydroxide (14-15 g.), dissolved in air-free water, to reduce the free acid concentration to 3-5 per cent in order to avoid side reactions of the chloramine. Then add a crystal of potassium iodide, 2 ml. of starch solution, and titrate the mixture with standard 0·1N-chloramine-T until the presence of the slightest excess is shown by the liberation of iodine and the appearance of the usual blue colour. Repeat the estimation with another 25-ml. portion of the solution.

Calculate the percentage of tin in the sample.

Note. If experience with a stannic salt is desired, stannic ammonium chloride (ammonium chlorostannate) may be used.

III, 144. Determination of ferrocyanides.—Discussion. Ferrocyanides are quantitatively oxidised by chloramine-T in weakly acid solution (2·5 per cent by volume of hydrochloric acid) :

$$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCINa} + 2\text{H}^+ + 2[\text{Fe(CN)}_6]^-- \rightarrow \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 + \text{NaCl} + 2[\text{Fe(CN)}_6]^--$$

Excess of standard chloramine-T solution is added to the feebly acid solution of the ferrocyanide at 40° C.; the residual chloramine-T is determined by means of excess of standard sodium arsenite solution after the addition of sodium bicarbonate.

For practice, the student may determine the percentage purity of A.R. potassium ferrocyanide $K_4[\text{Fe(CN)}_6]_3\cdot3\text{H}_2\text{O}$.

Procedure. Weigh out accurately about 1 g. of A.R. potassium ferrocyanide, and dissolve it in 100 ml. of distilled water in a glass-stoppered conical flask. Warm to 40° C., and add 2·5 ml. of $N$-hydrochloric acid. Add 50 ml. of standard 0·1N-chloramine-T and mix thoroughly. Then introduce 1·1·5 g. of sodium bicarbonate, shake until dissolved, and add a known volume (excess) of standard 0·1N-sodium arsenite. Determine the excess of the latter by the addition of a crystal of potassium iodide, and 2 ml. of starch solution, followed by titration with the standard chloramine-T solution to the first permanent blue colour. Repeat with a similar quantity of potassium ferrocyanide.

Calculate the percentage purity of the sample.

1 ml. $N$-chloramine-T = 0·3684 g. $K_4[\text{Fe(CN)}_6]_3$.

* The reduction is not really essential in the present instance, but is described in order to illustrate the technique involved in other estimations, e.g., tin in an alloy or in a stannic salt.
MISCELLANEOUS VOLUMETRIC DETERMINATIONS

III, 145. Determination of zinc with standard potassium ferrocyanide solution.—Discussion. Zinc ions in neutral or acid medium react with potassium ferrocyanide solution to form the very sparingly soluble potassium zinc ferrocyanide:

\[ 3\text{Zn}^{2+} + 2\text{K}_4[\text{Fe(CN)}_6] = \text{K}_2\text{Zn}_3[\text{Fe(CN)}_6]_2 + 6\text{K}^+ \]

Formerly the end point of the reaction was determined by means of external indicators, such as uranyl nitrate and ammonium molybdate. The acidified zinc solution was slowly titrated at 60–80°C with the ferrocyanide solution until a drop of the solution, brought into contact with a drop of uranyl nitrate solution on a white spot plate, gave a light-brown colour (due to the formation of uranyl ferrocyanide). In recent years the external indicator has been replaced by the more convenient internal indicator (diphenylamine, diphenylbenzidine, or sodium diphenylamine sulphonate). The latter substances are oxidation-reduction indicators, and are therefore dependent for their action upon the ratio of the concentration of ferricyanide to ferrocyanide in the solution (compare Section I, 50). A 0.05M-potassium ferrocyanide solution, to which 0.3 g. of potassium ferricyanide per litre is added, is employed; the solution is accordingly approximately 0.001M with respect to ferricyanide. The oxidation potential of a ferrocyanide-ferricyanide electrode is given by the equation (Section I, 48):

\[ E = E^0 + 0.0591 \log \left( \frac{[\text{Fe(CN)}_6^{3-}]}{[\text{Fe(CN)}_6^{4-}]} \right) \text{ (at 25°C)} \]

As long as excess of zinc ions remain in solution, the concentration of the ferrocyanide is very small, and the potential is large. As soon as the zinc ions are quantitatively precipitated, however, the next drop of ferrocyanide solution causes a sudden increase in \([\text{Fe(CN)}_6^{3-}]\), and hence a sudden decrease in the oxidation potential. The end point may therefore be detected by any of the three indicators mentioned above. We may also titrate in the reverse manner; the method can therefore be used for the titration of ferrocyanides by means of standard zinc solution.

In this determination it is essential to work, so far as possible, under uniform conditions, if concordant results are to be obtained. The titration must not be carried out too rapidly, and the solution must be thoroughly shaken throughout the titration, otherwise over-titration may easily occur. Nitrates, oxidising agents, lead, copper, cadmium, iron, manganese, nickel, and cobalt must be absent.

*p-Ethoxychrysoidine (0.2 per cent solution in 1:1 sulphuric acid) has been recommended as an indicator for this titration. Excellent results are obtained by potentiometric titration (Chapter VI) in the presence of excess of ammonium sulphate.

Procedure. Preparation of 0.05M-potassium ferrocyanide. Weigh out 21.12 g. of A.R. potassium ferrocyanide \(K_4[\text{Fe(CN)}_6]_3\cdot3\text{H}_2\text{O}\) and 0.3 g. of A.R. potassium ferricyanide, dissolve them in boiled-out water.
or in "equilibrium" conductivity water (Section II, 100), and make up to 1 litre in a volumetric flask.

If the potassium ferrocyanide is pure:

\[
1 \text{ ml. } 0.05M\text{-K}_4[\text{Fe(CN)}_6] = 0.004904 \text{ g. Zn}
\]

**Standardisation of the potassium ferrocyanide solution.** Prepare a 0.1M-zinc solution by weighing out either 1.6345 g. of A.R. zinc or 2.0345 g. of ignited A.R. zinc oxide, dissolving either in dilute sulphuric acid, and making up to 250 ml. in a volumetric flask. If exact weights are not employed, the exact concentrations may be calculated from the weights used.

Pipette 25 ml. of the zinc solution into a 250–350-ml. conical flask, add 50 ml. of water, 25 ml. of 7N-sulphuric acid, 10 g. of ammonium sulphate, and several drops of diphenylbenzidine solution (Section III, 63).* Titrate the cold solution slowly and with vigorous shaking until the colour change from blue-violet to pale green is permanent. Repeat the titration with two other 25-ml. portions of the zinc solution.

Calculate the volume of the potassium ferrocyanide solution equivalent to 0.01 g. of zinc, and compare this with the value deduced from the actual weight of A.R. potassium ferrocyanide used.

For further practice in this estimation, the student may determine the percentage of zinc in crystallised zinc sulphate, preferably of A.R. quality, or of zinc in commercial zinc oxide. The sample must be treated exactly as in the standardisation.

**III. 146. Determination of phosphorus.—Discussion.** The phosphorus must be in the form of orthophosphate. Upon treatment at 20–45° C. with a large excess of ammonium molybdate solution in the presence of nitric acid, ammonium phosphomolybdate \((\text{NH}_4)_3\text{PO}_4\cdot 12\text{MoO}_3\cdot 2\text{HNO}_3\cdot 3\text{H}_2\text{O}\) is precipitated; this is converted into \((\text{NH}_4)_5\text{PO}_4\cdot 12\text{MoO}_3\) or \((\text{NH}_4)_9[\text{PMO}_{12}\text{O}_{40}]\) when suitably washed with dilute potassium nitrate solution. The phosphorus in the washed precipitate may be determined in one of three ways.

A. It may be titrated against standard sodium hydroxide solution with phenolphthalein as indicator. The following reaction is assumed to take place:

\[
(\text{NH}_4)_3\text{PO}_4\cdot 12\text{MoO}_3 + 23\text{NaOH} = 11\text{Na}_2\text{MoO}_4 + (\text{NH}_4)_2\text{MoO}_4 + \text{Na}((\text{NH}_4)\text{HPO}_4 + 11\text{H}_2\text{O})
\]

whence \(1 \text{ ml. } N\text{-NaOH} = 0.001849 \text{ g. P} = 0.003088 \text{ g. } P_2\text{O}_5\)

B. The precipitate is dissolved in dilute ammonia solution, sulphuric acid added, and the resultant solution passed through a Jones reductor (the molybdenum is thus reduced to the tervalent state) into excess of ferric alum solution. The ferrous salt is titrated with standard 0.1N-potassium permanganate.

\[
(\text{NH}_4)_3[\text{PMO}_{12}\text{O}_{40}] + 39\text{H}_2\text{SO}_4 + 18\text{Zn(Hg)} = 6\text{Mo}_5(\text{SO}_4)_3 + 7\text{NH}_4\text{HSO}_4 + \text{H}_3\text{PO}_4 + 18\text{ZnSO}_4 + 36\text{H}_2\text{O}
\]

\[
5\text{Mo}_5(\text{SO}_4)_3 + 6\text{KMnO}_4 + 16\text{H}_2\text{O} = 10\text{H}_2\text{MoO}_4 + 3\text{K}_2\text{SO}_4 + 6\text{MnSO}_4 + 6\text{H}_2\text{SO}_4
\]

\(1 \text{ ml. } N\text{-KMnO}_4 = 0.0008805 \text{ g. P}\)

* If diphenylamine is used, 3 drops of the indicator are added; with more of the indicator, the results are low. The amount appears to be immaterial (up to 10 drops) for diphenylbenzidine.
Volumetric Analysis

since \( P = 12 \text{MoO}_3 \), which is equivalent to 18 atoms or 36 equivalents of oxygen.

The washed precipitate is dissolved in dilute ammonia solution and the molybdenum is precipitated as molybdyl oxinate \( \text{MoO}_3(\text{C}_9\text{H}_6\text{ON})_2 \). The latter may be weighed after drying at 130–140° C., or it may be titrated with standard potassium bromate solution (Section III, 137). Arsenic precipitated with ammonium phosphomolybdate does not affect the results: this constitutes an advantage of this procedure over that of \( A \) and also that of weighing phosphorus as magnesium pyrophosphate (Section IV, 65).

**Procedure.** Prepare the molybdate reagent as follows. Dissolve 100 g. of A.R. molybdic anhydride or 118 g. of A.R. molybdic acid (ca. 85 per cent \( \text{MoO}_3 \)) in a mixture of 400 ml. of water and 80 ml. of concentrated ammonia solution; filter, if necessary. Add the molybdate solution thus obtained slowly and with constant stirring into a solution containing 400 ml. of concentrated nitric acid and 600 ml. of water; the end of the tube carrying the molybdate solution should dip under the surface of the dilute nitric acid. Keep the mixture in a warm place for several days, or until a portion heated to 40–45° C. deposits no yellow precipitate. Decant the solution from any sediment and preserve in glass-stoppered bottles.

For practice in this estimation, the student may determine the percentage of phosphorus in anhydrous sodium phosphate \( \text{Na}_3\text{HPO}_4 \), preferably of A.R. grade: this should be dried for 1 hour at 120° C. and allowed to cool in a desiccator before use. Weigh out accurately 0.2–0.25 g. of anhydrous sodium phosphate, dissolve it in water, and dilute to 250 ml. in a volumetric flask. Shake well. Transfer 25 ml. of the solution into a 250–350-ml. conical flask, dilute to 100 ml., and add 12 g. of pure ammonium nitrate; shake until the solid dissolves. Add 75 ml. of the molybdate reagent, previously warmed to 40–45° C., slowly using a tap funnel or a drawn-out funnel, and shaking continuously. It is important not to heat above 45° C. in order to avoid contamination of the precipitate with molybdic anhydride. Fit the flask with a rubber stopper, shake vigorously for 10 minutes, and allow to stand for 30 minutes. Filter the precipitate through a quantitative filter-paper. Wash the flask and the precipitate with 1 per cent potassium nitrate solution until the filtrate will not decolorise 1 ml. of water containing 1 drop of 0.1N-sodium hydroxide and 1 drop of phenolphthalein; this will require about 100 ml. of the washing liquid. Place the paper and precipitate in the original flask. Complete the determination by either of the following methods.

**A.** Treat the precipitate \( (\text{NH}_4)_3[\text{PMO}_{12}\text{O}_{40}] \) with a slight excess of 0.1N carbonate-free sodium hydroxide (say, 50 ml.). Stopper the flask and shake; if all the precipitate does not dissolve, a further quantity of standard alkali solution must be added. Dilute to approximately 150 ml., add 5 drops of phenolphthalein indicator, and titrate with standard 0.1N-hydrochloric acid until the pink colour is completely discharged. Complete the titration by adding standard alkali until the re-appearance of the pink colour.

Calculate the volume of standard alkali which has reacted with the precipitate, and thence the percentage of phosphorus in the original salt.

**B.** Dissolve the precipitate in 3N-ammonia solution, and add excess
of sulphuric acid until the concentration of the latter is about 2N. Pass the solution at once through a Jones reductor (Section III, 51B) into 50 ml. of A.R. ferric alum solution (100 g. of A.R. crystals, and 25 ml. each of concentrated sulphuric acid and syrupy phosphoric acid in 1 litre). Wash with about 200 ml. of water, and titrate the ferrous salt with standard 0·1N-potassium permanganate. Carry out a blank on the acid, water, and ferric alum solution.

C. Dissolve the washed precipitate \((\text{NH}_4)_3\text{[PMo}_{12}\text{O}_{40}]\) in 6N-ammonia solution (about 20 ml.), add ca. 5 g. of ammonium acetate, dilute to about 200 ml., then add a slight excess of a 5 per cent solution of oxine in acetone, followed by 20–30 ml. of glacial acetic acid. Heat to boiling, stir for 3 minutes, filter through a sintered-glass or porous-porcelain crucible, and wash the precipitate with hot water. Dry the precipitate to constant weight at 130–140° C. The phosphorus content is computed from:

\[
P = 0.006202 \times \text{Weight of MoO}_2\text{C}_5\text{H}_4\text{ON}_2
\]

Alternatively, titrate the molybdyl oxinate with 0·1N-potassium bromate, following the experimental details of Section III, 137.

Calculate the percentage of phosphorus in the original solid.

III. 147. Determination of temporary and permanent hardness of water.—Discussion. Waters are described as “soft” or “hard” according to their action upon soap. A water is said to be “soft” if it gives an immediate lather with soap solution, and “hard” if a lather is obtained with difficulty. Hardness is due almost entirely to the presence of calcium and magnesium ions; these combine with the ions of the soap (usually sodium or potassium salts of oleic, palmitic, or stearic acids) to form insoluble calcium and magnesium compounds. The actual salts present in hard water are the bicarbonates, chlorides, and sulphates of calcium and magnesium.

Upon boiling hard water, the bicarbonates are decomposed with the precipitation of the normal carbonates:

\[
\text{Ca(HCO}_3\text{)}_2 = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2
\]

The hardness due to the presence of alkaline-earth bicarbonates therefore largely disappears on boiling (a little of the resultant carbonate dissolves in the water); this hardness is designated as temporary hardness. The residual hardness, due to the chlorides and sulphates of the alkaline earths and the amount of their carbonates soluble in pure water, cannot be removed by boiling, and is termed permanent hardness. The sum of the temporary and permanent hardness of a water represents the total hardness.

The most accurate method for the estimation of the total hardness is to determine the calcium and magnesium by a gravimetric procedure; the result is expressed in terms of calcium carbonate. Two other procedures, Clark's and the titration method, are in general use, but these do not give identical results. Clark’s method is the older process; accurate results are not obtained if a large quantity of magnesium salts is present, but this is rarely the case in actual practice. It has the advantage, however, that it does measure the soap-consuming power of the water. The titration method gives better results on the whole, since magnesium salts are quantitatively precipitated when it is used.
Hardness is conveniently expressed as parts of CaCO₃ per 100,000 parts of water; if a solution contains \( n \) parts of CaCO₃ in 100,000 parts of water, it possesses \( n \) degrees of hardness. This is the standard employed in France, and will be adopted in this book. In Germany each degree of hardness indicates 1 part of CaO in 100,000 parts of water. The term “English degree of hardness” is sometimes applied to the hardness based upon grains of CaCO₃ per gallon of water (1 Imperial gallon = 70,000 grains). In the United States hardness is given in terms of grains of CaCO₃ per U.S. gallon, which is five-sixths as large as the Imperial gallon. Hence: 1 “French” degree = 0·56 “German” degree = 0·70 “English” degree = 0·585 “U.S.” degree.

When magnesium salts are present, they are expressed in terms of the equivalent amounts of CaCO₃ or of CaO.

Procedure A. Clark’s method. This method must be carried out with care and slowly, especially for waters containing magnesium salts; the experimental conditions must be closely followed. Before commencing the determination, it is advisable to estimate the total solid matter present by evaporating a known volume of the water, and weighing the residue. This gives a useful approximate idea as to how much to use for the soap test. The total hardness for many waters is about one-half the total solids, and the sample may be so diluted, if necessary, as to bring it within the limits mentioned below. Thus if a water contains 50 grains of solids per gallon (i.e., ca. 70 parts per 100,000), take 25 ml. for hardness.

The tedious and time-consuming evaporation of a known volume of water can be avoided by employing the volumetric trial-and-error method. Thus determine whether 50 ml. of the water will produce a lather with 15 ml. of standard soap solution (details are given below); if no lather is produced, try 20 ml. of the soap solution, and continue the process until the approximate volume of soap solution required to produce a permanent lather is ascertained.

Preparation of standard solution of calcium chloride. Weigh out accurately 0·2000 g. of pure calcite (or of A.R. calcium carbonate) and dissolve it in dilute hydrochloric acid, taking care to keep the vessel covered with a clock glass to prevent loss by spurting. Use a platinum dish if available, otherwise employ a Pyrex vessel. When all the solid has dissolved, evaporate to dryness on the water-bath, add a little distilled water, and again evaporate to dryness. Repeat the evaporation several times to ensure complete expulsion of the free acid. Finally, dissolve the residue of calcium chloride in distilled water, and make up to 1 litre in a standard flask. Fifty ml. of this solution correspond to 10 mg. of CaCO₃.

Preparation of standard solution of soap. Method 1. Weigh out 10 g. of soft soap (Sapo mollis, B.P.),* and dissolve it in 1 litre of a mixture of equal volumes of industrial methylated spirit and distilled water.

Method 2. Weigh out 50 g. of oleic acid into a beaker, and add 100 ml. of alcoholic potash, made by dissolving 20 g. of potassium hydroxide (sticks or pellets) in 180 ml. of industrial spirit; continue adding the same solution from a burette until a drop of the oleate just gives a red colour with phenolphthalein spotted on a white plate—about 10 ml. more being required. Make the volume up to 500 ml. by the addition of methylated spirit. 56·25 ml. of the solution thus obtained are

* For elementary work, the so-called “Castile” soap is satisfactory.
diluted with a mixture of industrial methylated spirit (2 vols.) and water (1 vol.) to 1 litre.

In either case, the solution is set aside in a cool place (preferably in an ice-chest) for 24 hours, filtered through a double filter, and standardised against the standard calcium chloride solution as described below. The soap solutions will be a little too concentrated, and are to be diluted to such strength that exactly 14.25 ml. are required to form a permanent lather with 50 ml. of the calcium chloride solution.

Standardisation of the soap solution. Measure out 50 ml. of the standard calcium chloride solution into a glass-stoppered bottle of about 250-ml. capacity. Run in 1 ml. of the soap solution from a burette into the bottle, close the bottle, and shake it vigorously for a short time. If no permanent lather is formed, add another 1 ml., and shake again. Continue the addition of the soap solution, shaking the mixture well after each addition, until a lather is produced which remains for a short time when the bottle is laid upon the bench. The titration is complete when the lather remains upon the surface in an unbroken layer for 5 minutes even when the bottle is rolled half-way round on its side. Towards the end of the titration, the volume of soap solution which is added each time should be decreased, and it should finally not exceed 0.2-0.3 ml. Repeat the titration with another 50 ml. of the standard calcium chloride solution; add the soap solution 1 ml. (or less) at a time, with shaking after each addition, and never in large quantities.

Dilute the soap solution with the calculated volume of the water-methylated spirit mixture such that exactly 14.25 ml. of the final solution are required to produce a lather with 50 ml. of the standard calcium chloride solution.

Determination of the total hardness. Measure out 50 ml. of the water, or, if necessary, a smaller quantity * (usually 25 or 10 ml. together with 25 or 40 ml. of recently boiled and cooled distilled water) into a 250-ml. glass-stoppered bottle. Titrate the water with the soap solution as described under the standardisation. Waters containing much magnesium salts give a false or "ghost" lather after the addition of only a few ml. of soap solution; this, however, disappears entirely on allowing the bottle to remain for several minutes on its side after an extra vigorous shaking. Such water must always be diluted so that not more than 7 ml. of soap solution are required to produce a permanent lather. Repeat the titration.

Ascertain the hardness from Table II; multiply the result by 2 or 5 when 25 or 10 ml. of the water, diluted to 50 ml., have been used. It should be pointed out that some authors prefer to regard the actual titre as the real measure of the hardness, and consider the table of little significance for finding the true amount of CaCO₃.

Determination of permanent hardness. Boil a known volume (say, 100 ml.) of the water gently in an open flask for 30 minutes. Mark the original level of the water in the flask, and add hot distilled water from time to time to make up the loss by evaporation. At the end of 30 minutes, cover the flask loosely and cool to the laboratory temperature, then make up to the original volume by the addition of recently boiled

* A titre of less than 16 ml. of the soap solution should be obtained. The requisite volume of the water is obtained either from an estimation of the total solids or by a preliminary titration with 50 ml. of the water.
and cooled distilled water. Filter through a dry filter, and determine the hardness in the filtrate by titration with standard soap solution.

Determination of temporary hardness. The difference between the total hardness and the permanent hardness gives the temporary hardness of the water.

Procedure B. Titration method. Place 500 ml. of the water, or a smaller volume (250 or 100 ml.) if the water is very hard, into a large evaporating-dish or casserole, add a few drops of methyl orange or, preferably, methyl orange-indigo carmine indicator, and add standard 0·1N-hydrochloric acid from a burette until the end point is reached. It is advisable to add the same amount of indicator to 500 ml. of distilled water. Filter through a dry filter, and determine the hardness in the filtrate by titration with standard soap solution.

**Volumetric Analysis**

**Table II.—Tables of Hardness, Parts in 100,000**

(Calculated for titrations of 50 ml. of water)

<table>
<thead>
<tr>
<th>Ml. of Soap Solution</th>
<th>CaCO₃ per 100,000</th>
<th>Ml. of Soap Solution</th>
<th>CaCO₃ per 100,000</th>
<th>Ml. of Soap Solution</th>
<th>CaCO₃ per 100,000</th>
<th>Ml. of Soap Solution</th>
<th>CaCO₃ per 100,000</th>
<th>Ml. of Soap Solution</th>
<th>CaCO₃ per 100,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·7</td>
<td>0·00</td>
<td>0·7</td>
<td>0·00</td>
<td>0·7</td>
<td>0·00</td>
<td>0·7</td>
<td>0·00</td>
<td>0·7</td>
<td>0·00</td>
</tr>
<tr>
<td>0·8</td>
<td>0·16</td>
<td>0·8</td>
<td>0·16</td>
<td>0·8</td>
<td>0·16</td>
<td>0·8</td>
<td>0·16</td>
<td>0·8</td>
<td>0·16</td>
</tr>
<tr>
<td>0·9</td>
<td>0·32</td>
<td>0·9</td>
<td>0·32</td>
<td>0·9</td>
<td>0·32</td>
<td>0·9</td>
<td>0·32</td>
<td>0·9</td>
<td>0·32</td>
</tr>
<tr>
<td>1·0</td>
<td>0·48</td>
<td>1·0</td>
<td>0·48</td>
<td>1·0</td>
<td>0·48</td>
<td>1·0</td>
<td>0·48</td>
<td>1·0</td>
<td>0·48</td>
</tr>
<tr>
<td>1·1</td>
<td>0·63</td>
<td>1·1</td>
<td>0·63</td>
<td>1·1</td>
<td>0·63</td>
<td>1·1</td>
<td>0·63</td>
<td>1·1</td>
<td>0·63</td>
</tr>
<tr>
<td>1·2</td>
<td>0·79</td>
<td>1·2</td>
<td>0·79</td>
<td>1·2</td>
<td>0·79</td>
<td>1·2</td>
<td>0·79</td>
<td>1·2</td>
<td>0·79</td>
</tr>
<tr>
<td>1·3</td>
<td>0·95</td>
<td>1·3</td>
<td>0·95</td>
<td>1·3</td>
<td>0·95</td>
<td>1·3</td>
<td>0·95</td>
<td>1·3</td>
<td>0·95</td>
</tr>
<tr>
<td>1·4</td>
<td>1·11</td>
<td>1·4</td>
<td>1·11</td>
<td>1·4</td>
<td>1·11</td>
<td>1·4</td>
<td>1·11</td>
<td>1·4</td>
<td>1·11</td>
</tr>
<tr>
<td>1·5</td>
<td>1·27</td>
<td>1·5</td>
<td>1·27</td>
<td>1·5</td>
<td>1·27</td>
<td>1·5</td>
<td>1·27</td>
<td>1·5</td>
<td>1·27</td>
</tr>
<tr>
<td>1·6</td>
<td>1·43</td>
<td>1·6</td>
<td>1·43</td>
<td>1·6</td>
<td>1·43</td>
<td>1·6</td>
<td>1·43</td>
<td>1·6</td>
<td>1·43</td>
</tr>
<tr>
<td>1·7</td>
<td>1·60</td>
<td>1·7</td>
<td>1·60</td>
<td>1·7</td>
<td>1·60</td>
<td>1·7</td>
<td>1·60</td>
<td>1·7</td>
<td>1·60</td>
</tr>
<tr>
<td>1·8</td>
<td>1·69</td>
<td>1·8</td>
<td>1·69</td>
<td>1·8</td>
<td>1·69</td>
<td>1·8</td>
<td>1·69</td>
<td>1·8</td>
<td>1·69</td>
</tr>
<tr>
<td>1·9</td>
<td>1·82</td>
<td>1·9</td>
<td>1·82</td>
<td>1·9</td>
<td>1·82</td>
<td>1·9</td>
<td>1·82</td>
<td>1·9</td>
<td>1·82</td>
</tr>
<tr>
<td>2·0</td>
<td>1·95</td>
<td>2·0</td>
<td>1·95</td>
<td>2·0</td>
<td>1·95</td>
<td>2·0</td>
<td>1·95</td>
<td>2·0</td>
<td>1·95</td>
</tr>
<tr>
<td>2·1</td>
<td>2·08</td>
<td>2·1</td>
<td>2·08</td>
<td>2·1</td>
<td>2·08</td>
<td>2·1</td>
<td>2·08</td>
<td>2·1</td>
<td>2·08</td>
</tr>
<tr>
<td>2·2</td>
<td>2·21</td>
<td>2·2</td>
<td>2·21</td>
<td>2·2</td>
<td>2·21</td>
<td>2·2</td>
<td>2·21</td>
<td>2·2</td>
<td>2·21</td>
</tr>
<tr>
<td>2·3</td>
<td>2·34</td>
<td>2·3</td>
<td>2·34</td>
<td>2·3</td>
<td>2·34</td>
<td>2·3</td>
<td>2·34</td>
<td>2·3</td>
<td>2·34</td>
</tr>
<tr>
<td>2·4</td>
<td>2·47</td>
<td>2·4</td>
<td>2·47</td>
<td>2·4</td>
<td>2·47</td>
<td>2·4</td>
<td>2·47</td>
<td>2·4</td>
<td>2·47</td>
</tr>
<tr>
<td>2·5</td>
<td>2·60</td>
<td>2·5</td>
<td>2·60</td>
<td>2·5</td>
<td>2·60</td>
<td>2·5</td>
<td>2·60</td>
<td>2·5</td>
<td>2·60</td>
</tr>
<tr>
<td>2·6</td>
<td>2·73</td>
<td>2·6</td>
<td>2·73</td>
<td>2·6</td>
<td>2·73</td>
<td>2·6</td>
<td>2·73</td>
<td>2·6</td>
<td>2·73</td>
</tr>
<tr>
<td>2·7</td>
<td>2·86</td>
<td>2·7</td>
<td>2·86</td>
<td>2·7</td>
<td>2·86</td>
<td>2·7</td>
<td>2·86</td>
<td>2·7</td>
<td>2·86</td>
</tr>
<tr>
<td>2·8</td>
<td>2·99</td>
<td>2·8</td>
<td>2·99</td>
<td>2·8</td>
<td>2·99</td>
<td>2·8</td>
<td>2·99</td>
<td>2·8</td>
<td>2·99</td>
</tr>
<tr>
<td>2·9</td>
<td>3·12</td>
<td>2·9</td>
<td>3·12</td>
<td>2·9</td>
<td>3·12</td>
<td>2·9</td>
<td>3·12</td>
<td>2·9</td>
<td>3·12</td>
</tr>
<tr>
<td>3·0</td>
<td>3·25</td>
<td>3·0</td>
<td>3·25</td>
<td>3·0</td>
<td>3·25</td>
<td>3·0</td>
<td>3·25</td>
<td>3·0</td>
<td>3·25</td>
</tr>
<tr>
<td>3·1</td>
<td>3·38</td>
<td>3·1</td>
<td>3·38</td>
<td>3·1</td>
<td>3·38</td>
<td>3·1</td>
<td>3·38</td>
<td>3·1</td>
<td>3·38</td>
</tr>
<tr>
<td>3·2</td>
<td>3·51</td>
<td>3·2</td>
<td>3·51</td>
<td>3·2</td>
<td>3·51</td>
<td>3·2</td>
<td>3·51</td>
<td>3·2</td>
<td>3·51</td>
</tr>
<tr>
<td>3·3</td>
<td>3·64</td>
<td>3·3</td>
<td>3·64</td>
<td>3·3</td>
<td>3·64</td>
<td>3·3</td>
<td>3·64</td>
<td>3·3</td>
<td>3·64</td>
</tr>
<tr>
<td>3·4</td>
<td>3·77</td>
<td>3·4</td>
<td>3·77</td>
<td>3·4</td>
<td>3·77</td>
<td>3·4</td>
<td>3·77</td>
<td>3·4</td>
<td>3·77</td>
</tr>
<tr>
<td>3·5</td>
<td>3·90</td>
<td>3·5</td>
<td>3·90</td>
<td>3·5</td>
<td>3·90</td>
<td>3·5</td>
<td>3·90</td>
<td>3·5</td>
<td>3·90</td>
</tr>
<tr>
<td>3·6</td>
<td>4·03</td>
<td>3·6</td>
<td>4·03</td>
<td>3·6</td>
<td>4·03</td>
<td>3·6</td>
<td>4·03</td>
<td>3·6</td>
<td>4·03</td>
</tr>
<tr>
<td>3·7</td>
<td>4·16</td>
<td>3·7</td>
<td>4·16</td>
<td>3·7</td>
<td>4·16</td>
<td>3·7</td>
<td>4·16</td>
<td>3·7</td>
<td>4·16</td>
</tr>
<tr>
<td>3·8</td>
<td>4·29</td>
<td>3·8</td>
<td>4·29</td>
<td>3·8</td>
<td>4·29</td>
<td>3·8</td>
<td>4·29</td>
<td>3·8</td>
<td>4·29</td>
</tr>
<tr>
<td>3·9</td>
<td>4·43</td>
<td>3·9</td>
<td>4·43</td>
<td>3·9</td>
<td>4·43</td>
<td>3·9</td>
<td>4·43</td>
<td>3·9</td>
<td>4·43</td>
</tr>
</tbody>
</table>

and cooled distilled water. Filter through a dry filter, and determine the hardness in the filtrate by titration with standard soap solution.

Determination of temporary hardness. The difference between the total hardness and the permanent hardness gives the temporary hardness of the water.

Procedure B. Titration method. Place 500 ml. of the water, or a smaller volume (250 or 100 ml.) if the water is very hard, into a large evaporating-dish or casserole, add a few drops of methyl orange or, preferably, methyl orange-indigo carmine indicator, and add standard 0·1N-hydrochloric acid from a burette until the end point is reached. It is advisable to add the same amount of indicator to 500 ml. of distilled water.
water and introduce the standard acid until the "acid" colour is produced. The tint can then be matched by that of the water under examination; the blank correction is also determined at the same time. Subtract the blank correction from the volume of standard acid used, and then calculate the corresponding weight of CaCO₃ and convert it into parts per 100,000.

\[
\text{Ca} (\text{HCO}_3)_2 + 2\text{HCl} = \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{CO}_2
\]

i.e.,

1 ml. 0·1N-HCl = 0·005005 g. CaCO₃

Note. The number of ml. of acid used is often regarded as the temporary hardness. This, however, includes some calcium carbonate which would remain in solution after boiling, and it is better to term it the alkalinity. An empirical deduction of 0·4 ml. for 0·1N-acid is then made to allow for the solubility of the calcium carbonate, and the difference represents temporary hardness.

**Determination of permanent hardness.** Measure out 250 ml. of the water into a conical flask, best of Pyrex glass, and boil for 30 minutes. Add an excess (say, 50 ml.) of standard 0·1N-sodium carbonate, and evaporate to dryness on the water-bath. Take up the residue in a little boiled-out distilled water, filter through a dry quantitative filter-paper, and wash the residue four times with hot water. Allow the filtrate to cool, and make it up to 250 ml. in a volumetric flask with boiled-out distilled water. Titrate 50 or 100 ml. with standard 0·1N-hydrochloric acid, using methyl orange or better, methyl orange-indigo carmine indicator.

Calculate the volume of residual 0·1N-sodium carbonate, and from this the volume of 0·1N-sodium carbonate consumed in precipitating the alkaline-earth salts of the strong acids.

\[
\begin{align*}
\text{CaSO}_4 + \text{Na}_2\text{CO}_3 &= \text{CaCO}_3 + \text{Na}_2\text{SO}_4 \\
\text{MgCl}_2 + \text{Na}_2\text{CO}_3 &= \text{MgCO}_3 + 2\text{NaCl}
\end{align*}
\]

1 ml. 0·1N-Na₂CO₃ = 0·005005 g. CaCO₃

Calculate the permanent hardness of the water (parts of CaCO₃ per 100,000).

**III. Determination of the hardness of water ("didiette" or "Trilon B" method).—Discussion.** The determination of the total hardness of water by titration with standard soap solution as described in the preceding section is, at best, subject to appreciable error owing to uncertainty in the end point. The introduction of disodium dihydrogen ethylenediamine tetra-acetate (disodium dihydrogen versenate)* by G. Schwarzenbach (1946) has rendered the determination both facile and accurate. The reagent forms soluble complex ions with calcium and magnesium ions.

**Ethylenediamine tetra-acetic acid** behaves virtually as a strong dibasic acid, and it is usually represented (G. Schwarzenbach, 1947) as a betaine structure:

\[
\begin{align*}
\text{HOOC} - \text{CH}_2^- &\quad \text{NH} - \text{CH}_2 - \text{CH}_2^- &\quad \text{NH} - \text{CH}_2 - \text{COO}^- \\
\text{OOC} - \text{CH}_2^- &\quad \text{CH}_2 - \text{COOH} &\quad = H_4V
\end{align*}
\]

* The author suggests the abbreviation "didiette," formed from the first two letters of each of the four parts of the full chemical name, be used. The commercial name for the dihydrate is "Trilon B."
The dihydrogen versenate ion reacts with calcium and with magnesium ions to form complex ions:

$$\text{Ca}^{++} + [\text{H}_2\text{V}]^- \rightarrow [\text{CaV}]^- + 2\text{H}^+$$

The sample of water is brought to a pH of 10 with an ammonium chloride–ammonium hydroxide buffer solution, and a few drops of an alcoholic solution of eriochromeswartz T are added as indicator. The latter forms a wine-red, slightly dissociated compound with magnesium ions. As the titration with a standard solution of sodium dihydrogen versenate proceeds, the calcium ions are first removed, then the magnesium ions and finally, at the end point, the magnesium in the wine-red magnesium–eriochromeswartz T complex is extracted, resulting in a sharp colour change from wine-red to blue.

It is usual to add a little magnesium chloride solution to the disodium dihydrogen versenate solution before it is standardised in order to ensure an adequate concentration of magnesium in the solution being titrated to form the coloured magnesium–indicator complex ion.

**Procedure.** Prepare the following solutions:

*Standard disodium dihydrogen ethylenediamine tetra-acetate (disodium dihydrogen versenate) solution.* Dissolve 4 g. of the solid reagent in 1 litre of distilled water and add 5 ml. of 0·1M-magnesium chloride solution.

*Indicator solution.* Dissolve 5 g. of the indicator powder, consisting of 1 part of eriochromeswartz T and 9 parts of hydroxylamine hydrochloride, in 100 ml. of methyl alcohol.

*Buffer solution.* Add 57 ml. of concentrated ammonia solution (sp. gr. 0·88) to 6·75 g. of A.R. ammonium chloride, stir until dissolved, and dilute to 100 ml.

*Standard calcium chloride solution.* Dissolve 1·000 g. of A.R. calcium carbonate in a little dilute hydrochloric acid, cool, and dilute to 1 litre in a volumetric flask.

Place 50 ml. (or any other suitable volume) of the sample of water in a Pyrex conical flask or in a porcelain evaporating-dish, add 1 ml. of the buffer solution and 0·2 ml. of the indicator. Introduce the disodium dihydrogen versenate solution from a burette with continuous stirring or shaking. Near the end point a slight blue coloration appears: the end point is taken when the reddish tinge is completely discharged and the solution has a pure blue colour.

Standardise the sodium dihydrogen versenate solution against 25–50 ml. of the standard calcium chloride solution (1 ml. = 0·001 g. CaCO₃) following the procedure given above.

Calculate the hardness of the sample of water (compare Section III, 147).

**III, 149. Determination of sodium.**—The sodium is precipitated as Na₂Zn(UO₂)₃(C₇H₃O₂)₉·6H₂O or as NaMg(UO₂)₃(C₇H₃O₂)₉·6·5H₂O (Section IV, 47B and C), and the uranium determined according to Section III, 91.

* Similar solutions are available from British Drug Houses, Ltd., Poole, Dorset, and from the Fisher Scientific Co., Pittsburgh.
* The British equivalent of eriochromeswartz T (Eriochrome Black T) is Soleochrome Black WDFA, and is manufactured by Imperial Chemical Industries Ltd. Dyestuffs Division.
III, 150. Determination of potassium.—The potassium is precipitated as \( \text{K}_2\text{Na}[\text{Co(NO}_2\text{]}_6] \) (Section IV, 480), and the nitrite in the precipitate determined with ceric sulphate (Section III, 78).

III, 151. Determination of cadmium.—The cadmium is precipitated as the \( \beta\)-naphthaquinoline complex \( [(\text{C}_1\text{aH}_9\text{N})_2\text{H}_4]\text{CdI}_4 \) (Section IV, 183). The precipitate is decomposed with ca. 20 ml. of 2N-ammonium or sodium hydroxide, and the solution treated successively with 60 ml. of 2N-hydrochloric or sulphuric acid, 5 ml. of 10 per cent potassium cyanide solution (1), and 2 ml. of starch solution. The mixture is then titrated with 0.025\(M\)-potassium iodate (Section III, 123) until the starch is completely decolorised.

\[
1 \text{ml. } 0.025M\text{-KIO}_3 = 0.001405 \text{ g. Cd}
\]

Note. 1. The cyanide method possesses the advantage that the acidity required is not so high as the other variation of the potassium iodate titration. Iodine cyanide does not affect starch.

III, 152. Determination of ferric iron with standard mercurous perchlorate solution.*—Discussion. Mercurous perchlorate reduces the ferric thiocyanate complex to the ferrous state; this forms the basis of a method for the direct titration of ferric iron (compare Section III, 86). A large excess of thiocyanate must be added to the ferric salt solution; the amount required depends upon the volume and the acid concentration. For volumes of 100–200 ml., about 4–6 g. of potassium or ammonium thiocyanate suffices, provided the solution does not contain more than ca. 5 ml. of concentrated sulphuric acid or nitric acid or 2–3 ml. of concentrated hydrochloric acid. Larger amounts of acids give high and erratic results; the solution must then be partially neutralised. As a rule it is best to work with only slightly acid solutions. The high concentration of thiocyanate prevents the precipitation of insoluble mercurous salts. The disappearance of the red colour at the end point is relatively sharp.

The reaction is not quite stoichiometric; in neutral or dilute acid solution the amount of perchlorate needed is ca. 1 per cent higher than is demanded by the stoichiometric ratio (the latter figure is readily obtained by standardisation with sodium chloride, Section III, 26B). The mercurous perchlorate solution should therefore be standardised against a ferric solution of known concentration, containing a known amount of acid. The procedure is said to be applicable to iron ores, steel, pyrites, bauxite, etc. Phosphoric and acetic acids and their salts give indistinct end points, and lead to high results.

Ferrous salts have no effect upon the reagent, and consequently a mixture of ferrous and ferric salts may be determined. The ferric-iron content of an aliquot part is first determined by the above method in the presence of a little sulphuric acid (ferrous salts tend to be unstable in hydrochloric acid solution); the ferrous-iron content is evaluated by boiling another aliquot part with bromine water to oxidise it to ferric iron, and the total ferric iron is titrated in the same way.

Procedure. Prepare an approximately 0.1N-mercurous perchlorate solution as detailed in Section III, 26; if the commercial red mercuric oxide does not react readily with the perchloric acid and mercury, it will be necessary to prepare the mercuric oxide by precipitation from

* W. Pugh, 1945.
mercuric chloride solution. Prepare also a 0.05M-ferric ammonium sulphate solution by dissolving 12.055 g. of A.R. iron alum (molecular weight = 964.42) in water and diluting to 250 ml. in a volumetric flask; check the concentration of the ferric iron by titration with 0.1N-potassium dichromate (Sections III, 67-68) or with 0.1N-cerium sulphate (Section III, 77).

Standardise the mercurous perchlorate solution as follows. Treat 25 ml. of the 0.05M-ferric solution with 6 g. of A.R. potassium thio-cyanate, dilute to 150 ml., add 1 ml. of concentrated hydrochloric acid, and run in the mercurous perchlorate solution from a burette until the red colour is discharged. Shake the mixture vigorously during the titration; the approach of the end point is indicated by the fading of the dark-red colour to a light orange. Henceforth the reagent should be added dropwise, and a minute or so allowed between the drop additions: it is advantageous to complete the titration at 60–70° C.

For further practice in the use of the reagent, the student should determine the iron content of an iron ore.* Dissolve a suitable quantity of the iron ore in concentrated hydrochloric acid, oxidise the ferrous iron to the ferric state by adding an excess of bromine water and boiling, boil off the excess of bromine, dilute to 150 ml., adjust the hydrochloric acid concentration by the addition of ammonia solution so as not to exceed the equivalent of 1 ml. of the concentrated acid, add 6 g. of solid potassium thiocyanate, and titrate with mercurous perchlorate solution as above and completing the titration at 60–70° C.

III, 153. Determination of zirconium as the normal selenite, Zr(SeO₃)₂₄.

—Discussion. Zirconium may be precipitated in very dilute acid solution with selenious acid as the basic selenite of somewhat variable composition; upon digestion of the precipitate at 80–100° C. for 5–20 hours, it passes into the highly crystalline normal zirconium selenite Zr(SeO₃)₂. The latter is filtered off, brought into solution, and the selenium content determined as detailed in Section III, 62, Method B.

Procedure. The zirconium salt solution should not be more than 0.6N in sulphuric acid or hydrochloric acid (0.3N for small quantities, < 10 mg.) or 0.35N in nitric acid; sulphate ions in high concentration prevent complete concentration, but in 0.6N-hydrochloric acid and a volume of 400 ml., 0.5 g. of sodium sulphate is permissible.

Treat the zirconium salt solution (200–300 ml.; 5–50 mg. of Zr) with 1–2 g. of pure selenious acid in the form of a 10 per cent solution, heat to boiling, and leave on a hot-plate for 5–20 hours, i.e., until the flocculent precipitate of basic selenite passes into the highly crystalline normal selenite (1). Filter the precipitate through a quantitative filter-paper, but first wash by decantation a few times with hot 0.5N-hydrochloric acid, and finally wash with cold water until the filtrate is free from selenious acid (2). Transfer the precipitate quantitatively to the original vessel with the aid of a little cold water, then add 6 ml. of 1:1 sulphuric acid and 5–10-ml. of 3 per cent sodium fluoride solution; warm gently until the precipitate dissolves completely. Transfer the solution to a 750-ml. conical flask, using a little warm dilute sulphuric acid containing a few drops of sodium fluoride solution.

* Either Ridsdale's "Iron Ore, No. 17" (one of the Analysed Samples for Students) or the Bureau of Analysed Samples "Iron Ore, A" (a British Chemical Standard) is suitable.

† A. Claassen, 1939.
Quantitative Inorganic Analysis

to rinse out the original vessel (3). After cooling, dilute to 200–250 ml., add 10–15 ml. of 2 per cent starch solution, two portions of 0·2 g. A.R. sodium bicarbonate to displace the air, followed by 20–40 ml. of 10 per cent potassium iodide solution (prepared from iodate-free potassium iodide). After standing for 2 minutes, titrate the liberated iodine with 0·1N-sodium thiosulphate.

\[ 1 \text{ ml. } N - Na_2S_2O_3 = 0.01140 \text{ g. Zr} \]

Notes. 1. The period of heating required depends upon such factors as the temperature of the solution and the presence or absence of sulphuric acid. The transformation is accelerated by sulphuric acid.

2. A test portion, acidified with sulphuric acid, should not liberate iodine from potassium iodide–starch after 1 minute.

3. To prevent attack of the flask by dilute hydrofluoric acid, add a few ml. of saturated borax acid solution. This is usually unnecessary.

III. 154. Determination of silica.*—Discussion. The compound, which must be free from phosphate or arsenate, is fused with sodium hydroxide, extracted with water, and the extract poured into excess of hydrochloric acid. In this way the whole of the silica is brought into solution as \( H_4SiO_4 \):

\[ Na_4SiO_3 + H_2O + 2HCl = H_4SiO_4 + 2NaCl \]

The solution is treated with a moderate excess of ammonium molybdate solution and with sufficient hydrochloric acid to give a final pH of about 1·5, whereupon silicomolybdic acid forms rapidly:

\[ H_4SiO_4 + 12(NH_4)_2MoO_4 + 24HCl = H_4[SiO_4,12MoO_3] + 24NH_4Cl + 12H_2O \]

The solution is strongly acidified with hydrochloric acid and quinoline hydrochloride solution is added; an insoluble quinoline silicomolybdic is precipitated:

\[ 4C_9H_7HCl + H_4[SiO_4,12MoO_3] = (C_9H_7)_4H_4[SiO_4,12MoO_3] + 4HCl \]

The precipitate is filtered, washed, and dissolved in excess of \( N \)-sodium hydroxide solution; the residual sodium hydroxide is determined by titration with 0·5N-hydrochloric acid:

\[ (C_9H_7N)_4H_4[SiO_4,12MoO_3] + 24NaOH = 4C_9H_7N + SiO_2 + 12Na_2MoO_4 + 2H_2O \]

It is evident from the equation that the equivalent weight of silica (\( SiO_2 \)) is one twenty-fourth of its molecular weight, i.e., 60·06/24 = 2·5025.

Procedure. Prepare the following reagents:

Quinoline solution, 2 per cent. Add 20 ml. of pure quinoline to about 800 ml. of hot water acidified with 25 ml. of concentrated hydrochloric acid, stirring constantly. Allow to cool, and dilute to 1 litre with distilled water.

Ammonium molybdate solution, 10 per cent. Dissolve 50 g. of A.R. ammonium molybdate in 500 ml. of water, allow to stand for 24 hours, and filter. This solution may dissolve silica from the glass bottle, and should be used within a week.

* H. N. Wilson, 1949.
Volumetric Analysis

Thymol blue indicator solution. Dissolve 0.4 g. of thymol blue in 200 ml. of rectified spirit, add 8.6 ml. of 0.1N-sodium hydroxide, and dilute to 1 litre with water.

Cresol red-thymol blue indicator solution. Grind 0.1 g. of cresol red with 5.3 ml. of 0.1N-sodium hydroxide until dissolved and dilute to 100 ml. with water. Dissolve 0.1 g. of thymol blue in 20 ml. of rectified spirit, add 2.1 ml. of 0.1N-sodium hydroxide, and dilute to 100 ml. with water. Mix the two solutions.

Weigh out 7 g. of A.R. sodium hydroxide into a nickel crucible (5 cm. diameter) and fuse over a Bunsen burner until the water is driven off and a quiet melt is obtained: allow to cool. Transfer 0.5000 g. of the finely ground sample (1), after ignition if necessary (2), into the nickel crucible, and gently fuse over a medium Bunsen flame for 3 minutes, finally attaining a dull red heat (3). Allow the crucible to cool to about 40–50° C. and place it in an upright position in a tall-form 500-ml. beaker, and cover with a clock glass. Raise the clock glass slightly, fill the crucible with boiling water with the aid of a wash bottle and immediately replace the clock glass. The crucible should be at such a temperature that the heat of solution maintains the water at the boiling point until all is dissolved, but not so hot that liquid is thrown out of the beaker. When the vigorous reaction is over, wash down the clock glass and the sides of the beaker. Remove the crucible with a pair of clean tongs, and carefully wash it inside and out with hot water. No undissolved melt should remain, but, as a precaution, rinse the crucible with a few ml. of warm dilute hydrochloric acid: do not add the acid washings to the alkaline extract but collect them in a 500-ml. Pyrex "iodine flask," which should be marked at 170 ml.

Introduce 20 ml. of concentrated hydrochloric acid into the "iodine flask," and pour the alkaline extract into the acid, swirling during the addition. Complete the transfer with the aid of a jet of hot water. Heat the flask on a hot plate until the solution is clear, but do not boil. Cool rapidly to room temperature and dilute to 170 ml. with distilled water. Add 3 g. of sodium hydroxide pellets and rotate the flask until dissolved. Add 8 drops of thymol blue indicator, then concentrated hydrochloric acid dropwise, swirling constantly, until the indicator colour changes from blue, through yellow, just to red. The solution should become clear again in a few minutes. Add 8 ml. of dilute hydrochloric acid (1:9), 5 ml. of dilute acetic acid (1:2), and then 30 ml. of the ammonium molybdate reagent, mixing well by swirling the contents of the flask during the addition of the reagents and continuing the vigorous mixing for one minute after the molybdate solution has been added. Immerse the flask in a boiling water-bath, and raise the temperature of the contents to 80–90° C. during 10–12 minutes. Remove from the bath, add 40 ml. of dilute hydrochloric acid (1:1), and immediately precipitate the silica by running in 65 ml. of the quinoline reagent from a burette with a wide jet with vigorous and constant swirling of the contents of the flask during the addition. Return the flask to the hot water-bath, raise the temperature again to 80–90° C. for a further 5 minutes, and shake occasionally. Cool rapidly to 15° C. or below and allow the precipitate to settle.

Fit a 3-in. funnel with a porcelain filter cone, prepare a good paper-pulp pad (well tamped down), and filter with suction. Decant as much as possible of the mother liquor, wash twice by decantation with 25–30
ml. of water, and transfer the precipitate to the pad. Wash the precipitate thoroughly with six 30-ml. portions of cold (<15° C.) water, sucking dry after each washing.

Remove the precipitate and filter-pad from the funnel (e.g., by blowing them out on to a small filter-paper), and transfer to the original flask. Run 30·0 ml. of N-sodium hydroxide solution down the side of the funnel into the flask (simultaneously removing any traces of precipitate that adhere to the glass), wash the funnel with a little distilled water, close the flask with a stopper, and shake vigorously until all the yellow precipitate has dissolved. Add a few drops of cresol red–thymol blue indicator, and back-titrate with 0·5N-hydrochloric acid until the indicator, at first blue, just changes through rose colour to yellow. Calculate the volume of N-sodium hydroxide which has reacted with the quinoline silicomolybdate complex.

Carry out a "blank" determination on all the reagents; most of the "blank," which usually amounts to 0·6 ml., is due to sodium hydroxide. Deduct the "blank" N-sodium hydroxide volume from the mean titration, and calculate the silica content of the sample (4).

\[
1 \text{ ml. } N-\text{NaOH} = 0.002503 \text{ g. } \text{SiO}_2
\]

Notes. 1. The experimental details apply to samples containing up to 12 per cent of silica: if more than this percentage is present, the extract from the fusion must be made up to a convenient volume, say 250 ml., and an aliquot portion taken for analysis. Alternatively, a smaller sample may be used. The portion finally taken for analysis must not contain more than 60 mg. of silica.

2. If organic matter, carbon, coke dust, etc., be present, ignite 0·5000 g. of the sample (ground in an agate mortar) at 950–1000° C. in a muffle furnace until the carbonaceous matter is burnt off: 15 minutes usually suffice. Allow the sample to cool.

3. Some samples of refractory materials may require a somewhat longer heating. Samples rich in silica (>20 per cent) must be treated very carefully at this point: the reaction is violent, and portions of the sample may be lost through spraying.

4. The process is applicable to the determination of silica in common siliceous materials, e.g., anhydrite, cement, cement clinker, limestone, silicon iron, fireclay, and refractory brick.

III. 155. Determination of calcium (urea hydrolysis method).—

Discussion. The procedure described in Section III, 54 yields a relatively fine precipitate of calcium oxalate and requires a digestion period of about an hour; the precipitate is formed during the addition of the ammonium oxalate and the subsequent addition of the ammonia solution (which raises the pH). In the urea hydrolysis method, acid is added to the solution to produce a pH of about 1·0; this is followed by ammonium oxalate and urea. Upon boiling the solution, the urea gradually undergoes hydrolysis:

\[
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} = 2\text{NH}_3 + \text{CO}_2
\]

and the \( \text{pH} \) rises to the point of calcium oxalate precipitation. This may take 10–15 minutes. The crystals precipitated from the hot solution are relatively large, and may be filtered off shortly after formation; this eliminates the digestion period required in the alternative method. The solution must remain clear until boiling is commenced to hydrolyse the urea.
**Procedure.** Weigh out accurately 0.15–0.20 g. of calcium carbonate, preferably of A.R. grade, into a 400-ml. beaker. Add 20 ml. of water and cover the beaker with a clock-glass. Introduce 10 ml. of dilute hydrochloric acid (1:1) and warm, if necessary, until the solid has dissolved. Dilute to 200 ml., and add a few drops of methyl-red indicator; sufficient acid must be present in the solution to prevent the precipitation of calcium oxalate when ammonium oxalate solution is added. Now introduce 15 ml. of saturated ammonium oxalate solution and 15 g. of urea. Boil the solution gently until the methyl red changes colour to yellow (at \( pH \approx 5 \)). Filter through a coarse filter-paper, or, with suction, on a small filter-paper supported by a Gooch crucible. Wash the precipitate with cold 0.1 per cent ammonium oxalate solution. Transfer the filter-paper and precipitate (or the Gooch crucible and precipitate) to the original beaker, dissolve the precipitate in hot dilute sulphuric acid, and titrate immediately with standard 0.1N-potassium permanganate solution. Repeat the determination with two other portions of the calcium carbonate.

Calculate the percentage of Ca in the sample of calcium carbonate.

**Note.** The precipitate may also be filtered off in a porous-porcelain crucible and weighed as \( CaCO_3 \) after drying at \( 100^0 \) C. for 30–45 minutes and heating at \( 500 \pm 25^0 \) C. to constant weight in an electrically heated muffle furnace. If the latter is not available, heating may be carried out in a large nickel crucible, the cover of which is provided with a \( 500^0 \) C. thermometer; an asbestos pad is placed in the bottom to support the porous-porcelain crucible; the thermometer is held in a clamp so that its bulb almost touches the asbestos pad. A Bunsen burner, with screw-clip adjustment, is used as the source of heat.

**III. 156. Determination of fluorine.**—**Discussion.** Fluoride, or hydrofluosilicate, may be titrated with standard thorium nitrate solution using sodium alizarin sulphonate as indicator: at the end point a pink colour of a thorium lake appears. The formation of the coloured lake with the dyestuff is prevented by fluoride or hydrofluosilicate ions; the latter are removed by the thorium ions and thereafter the coloured lake is produced. To secure a sharp end point, it is important to maintain a \( pH \) of 2.9–3.4: a monochloroacetic acid-sodium monochloroacetate buffer may be used. It is claimed that as much as 50 mg. of fluorine may be titrated in aqueous solution using 0.1N-thorium nitrate (Rowley and Churchill, 1937).

Numerous elements interfere in this titration, although it may be applied directly to the determination of a number of simple fluorides, such as those of lithium, sodium, and potassium. The most satisfactory method of eliminating interfering elements is to separate the fluorine as hydrofluosilicic acid by distillation with perchloric acid or with sulphuric acid: quantitative recovery of the fluorine usually occurs at any temperature between \( 130^0 \) and \( 160^0 \) C., and a temperature of about \( 135^0 \) C. is generally employed. With perchloric acid (which possesses many advantages, since most metal perchlorates are soluble), the temperature must not be allowed to rise above \( 135^0 \) C. if organic matter is known to be present, as otherwise an oxidising action may occur which is unduly violent; in such cases, sulphuric acid is preferable. The use of rubber stoppers in the flask may introduce an element of danger when perchloric acid is employed: for this reason ground-glass joints are recommended.
Two procedures will be described, one illustrative of the simple titration in the absence of interfering elements, and the other utilising the distillation technique.

Procedure. Prepare the following solutions: 0.05N-Thorium nitrate solution: dissolve 6.90 g. of A.R. thorium nitrate Th(NO₃)₄·4H₂O in water, and dilute to 1 litre in a volumetric flask. Sodium alizarin sulphonate indicator: dissolve 0.10 g. of the solid (indicator quality) in 100 ml. of water.

Standard sodium fluoride solution: dissolve 2.211 g. of A.R. sodium fluoride, previously dried at 120° C. to constant weight, in 1 litre of water in a volumetric flask. One ml. of this solution corresponds to 1 mg. of F.

Chloroacetic acid-sodium monochloracetate buffer: dissolve 9.45 g. of A.R. monochloracetic acid and 2.00 g. of A.R. sodium hydroxide in 100 ml. of water (buffer solution A). Alternatively, dissolve 9.45 g. of A.R. monochloracetate acid in 100 ml. of water (1M solution), neutralise to phenolphthalein with sodium hydroxide solution, add to the neutralised solution 100 ml. of 1M-chloroacetic acid, and dilute to 500 ml. (buffer solution B).

Prepare a solution of potassium fluoride by dissolving about 0.6 g., accurately weighed, of the solid (rendered anhydrous by heating the dihydrate to 300–400° C. and cooling in a desiccator) in 250 ml. of water in a volumetric flask. Remove 25 ml. of this solution, dilute to 100 ml., add 12 drops of the sodium alizarin sulphonate indicator and sufficient dilute hydrochloric acid (1 : 200) to just discharge the pink colour. Then add 1 ml. of buffer solution A and titrate with the thorium nitrate solution to a permanent pink coloration. For accurate work, a blank determination should be made.

Standardise the thorium nitrate solution by titrating 25 ml. of the standard sodium fluoride solution in a similar manner.

Calculate the percentage of fluorine in the sample of anhydrous potassium fluoride.

For practice in the distillation technique, the student may determine the percentage of fluorine in a phosphate rock. Fit the main neck of a 100-ml. Claisen flask with a two-holed rubber stopper through which pass a 200° C. thermometer and a glass tube, both of which reach almost to the bottom of the flask. Close the side neck of the flask with a rubber stopper and attach a condenser to the side arm. Place a few glass beads in the flask. Connect the glass tube to a Pyrex flask charged with distilled water and fitted with the usual safety tube: this will serve as a steam supply.

Weigh out accurately about 0.5 g. of the phosphate rock† into the flask, and introduce 10 ml. of A.R. perchloric acid (60 per cent) and 5 ml. of water. Heat the flask in an air-bath until the temperature of the contents rises, reaches 100–110° C., then pass in steam, and continue the distillation at about 135° C. until the volume of the distillate is 150 ml. Neutralise the distillate with N-sodium hydroxide solution (phenolphthalein) and make it up to a volume of 250 ml. Titrate 50-ml. portions as follows. Add 12 drops of the sodium alizarin sulphonate indicator to each.

* Obtainable from, for example, Mallinekrodt Chemical Works, 70-74 Gold Street, New York 8; Merck and Co., Inc., Rahway, N.J.; or from J. T. Baker Chemical Co., Phillipsburg, N.J., U.S.A.

† The Bureau of Standards "phosphate rock" No. 56B or No. 120, which contains 3–4 per cent of fluorine, is suitable for this determination.
ate indicator and 0.1N-hydrochloric acid until the pink colour is just discharged. Now add 2.5 ml. of the buffer solution B, and titrate with the standard 0.05N-thorium nitrate solution. For work of the highest accuracy subtract the indicator blank from the volume of thorium nitrate solution used.

Calculate the percentage of fluorine in the sample of phosphate rock.

Note. The end point with sodium alizarin sulphonate is sometimes difficult to detect; in such cases the addition of a protective colloid may be advantageous. The indicators purpurin sulphonate and eriochrome-cyanin-R have been recommended as alternatives by Willard and Horton (1950). The author finds that with appreciable concentrations of fluoride ion considerable experience is required to obtain satisfactory results and that a comparison solution is highly desirable.
III, 157. SELECTED BIBLIOGRAPHY ON VOLUMETRIC ANALYSIS

CHAPTER IV

GRAVIMETRIC ANALYSIS

IV, 1. General discussion.—Before commencing experimental work in gravimetric analysis, the student should be familiar with the general theory underlying the chief experimental processes outlined in Sections I, 54–77. He should also read the account of the technique of gravimetric analysis given in Sections II, 26–39; this will assume a greater significance when the various processes have actually been employed in practice. It is proposed, in the first place, to give an account of a number of typical gravimetric determinations. These estimations may be performed with substances which are readily obtainable in a state of purity (e.g., of analytical reagent quality), and the experimental error can therefore be checked by calculation. Many may, however, prefer to carry out the analyses with solutions or solids of "unknown" composition. A list of solutions and of solids which are suitable for this purpose is given in the Appendix, Section A, 7. These determinations should be carried out before those described under the heading of "SYSTEMATIC GRAVIMETRIC ANALYSIS" are attempted. In general, the experimental procedures will not be given in such detail in the latter.

IV, 2. Note-book, entries, and calculations.—A note-book of not less than quarto size and provided with stout cardboard covers will be found suitable for the entry of results. The right-hand page should contain the nature of the determination, the date when it was commenced (and, if desired, completed), a description in the past tense of the experimental details of the estimation, together with any relevant equations. The actual experimental results (weights, etc.), should be entered on the left-hand page; essential details of the calculations should also be recorded here. Finally, a line or two should be devoted to the main results of the analysis.

Experimental results should on no account be entered on scraps of paper, for these are readily lost.

IV, 3. Calculations of gravimetric analysis. Chemical factors.—The calculation of the weight of a constituent in a given precipitate follows directly from the proportion:

\[ \frac{M_n A_p}{nM} : w :: x \]

where \( M_n A_p \) is the molecular weight of the precipitate, \( M \) the atomic (or molecular) weight of the element (or radical) sought, \( n \) the number of atomic (or molecular) weights of \( M \) in the molecular weight \( M_n A_p \), \( w \) is the weight of precipitate, and \( x \) is the weight of the constituent desired. Furthermore, if \( W \) is the weight of the sample used, the percentage of the constituent sought \( y \) is given by:

\[ x : W :: y : 100 \]

or

\[ y = \frac{x \times 100}{W} \]
Example. 1·000 Gram of an iron compound, after suitable treatment, yielded 0·1565 g. of ferric oxide. Calculate the percentage of iron in the compound.

\[
\text{Fe}_2\text{O}_3 : 2\text{Fe} :: 0·1565 : x \\
159·68 : 2 \times 55·84 :: 0·1565 : x
\]
(Mol. wt. of Fe\(_2\text{O}_3\)) \((2 \times \text{At. wt. of Fe})\)

\[
x = \frac{111·68}{159·68} \times 0·1565 = 0·6994 \times 0·1565
\]

\(= 0·1095 \text{ g. of Fe}\)

Now \(0·1095 : 1·0000 :: y : 100\)

\[y = 10·95 \text{ per cent of Fe}\]

Instead of evaluating proportions like the above for each determination, we can arrive at the same result by one multiplication if we multiply the weight of the precipitate by that number which represents the weight of the constituent corresponding to 1 g. of precipitate. Such a number is called a chemical factor. For example, the factor for Fe in Fe\(_2\text{O}_3\) is 0·6994, and if, in the above example, we multiply 0·1565 by this number, we obtain 0·1095, which is the same result as is obtained by evaluating the proportion.

A table of important chemical conversion factors, together with their logarithms, is given in the Appendix, Section A, 2.

**SIMPLE GRAVIMETRIC DETERMINATIONS**

**IV. 4. Determination of water of hydration in crystallised barium chloride.**—Discussion. Barium chloride dihydrate loses all its water of crystallisation above 100° C. Much higher temperatures can be used in this dehydration, for anhydrous barium chloride is non-volatile and stable even at fairly high temperatures.

\[
\text{BaCl}_2\cdot2\text{H}_2\text{O} = \text{BaCl}_2 + 2\text{H}_2\text{O}
\]

With some hydrated salts, special temperature limits must be observed.

**Procedure.** Heat a crucible and lid to dull redness for several minutes, allow to cool in a desiccator, and weigh after 30 minutes. Introduce into the crucible 1–1·5 g. of A.R. barium chloride, and weigh again. Place the covered crucible, resting upon a pipe-clay or silica triangle, about 15 cm. above a small flame (not more than 5–6 cm. high). At intervals of a few minutes increase the flame gradually until the bottom of the crucible is heated to dull redness. Maintain the crucible at this temperature for about 10 minutes, allow it to cool in a desiccator for 30 minutes, and weigh. Repeat the process until constant weight (two consecutive weighings agreeing within 0·0002 g.) is obtained.

From the loss in weight, calculate the percentage of water in barium chloride dihydrate.

A number of determinations may be carried out by simple ignition. These include iron in ferric ammonium alum \((\text{NH}_4)_2\text{SO}_4\cdot\text{Fe}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3\), aluminium in ammonium alum \((\text{NH}_4)_2\text{SO}_4\cdot\text{Al}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3\), bismuth in bismuth oxynitrate and carbonate (residue is Bi\(_2\text{O}_3\)), and zinc in basic zinc
Gravimetric Analysis

carbonate (residue is ZnO). The conversion factors (see Appendix, Section A, 2) must, of course, be known.

Note. Similar estimations may be carried out with magnesium sulphate heptahydrate (MgSO_{4} \cdot 7H_{2}O = MgSO_{4} + 7H_{2}O), borax or disodium pyroborate decahydrate (Na_{2}B_{4}O_{7} \cdot 10H_{2}O = Na_{2}B_{4}O_{7} + 10H_{2}O), and with disodium hydrogen phosphate dodecahydrate (2Na_{2}HPO_{4} \cdot 12H_{2}O = Na_{2}P_{2}O_{7} + 25H_{2}O).

IV, 5. Determination of chloride as silver chloride.—Discussion. The aqueous solution of the chloride is acidified with dilute nitric acid in order to prevent the precipitation of other silver salts, such as the phosphate and carbonate, which might form in neutral solution, and also to produce a more readily filterable precipitate. A slight excess of silver nitrate solution is added, whereupon silver chloride is precipitated:

\[
Cl^{-} + Ag^{+} \rightarrow AgCl
\]

The precipitate, which is initially colloidal, is coagulated into curds by heating the solution and stirring the suspension vigorously; the supernatant liquid becomes almost clear. The precipitate is collected in a filter-crucible, washed with very dilute nitric acid, in order to prevent it from becoming colloidal (Section I, 36), dried at 130–150°C, and finally weighed as AgCl. If a quantitative filter-paper is used for filtration (Section II, 28), a procedure which is not recommended, the filter-paper is finally washed with a little water to remove acid, which would attack the paper when dried. The paper and precipitate are dried at 100°C, and the paper is burnt separately (Section II, 36c); the ash is treated with a little nitric acid and a drop or two of concentrated hydrochloric acid, and evaporated on the water-bath to convert the reduced silver back to silver chloride. The main precipitate is then added to the crucible, and the whole dried at 130–150°C.

Silver chloride has a solubility in water of 1·4 mg. per litre at 20°C, and 21·7 mg. per litre at 100°C. The solubility is less in the presence of very dilute nitric acid (up to 1 per cent.), and is very much less in the presence of moderate concentrations of silver nitrate (see Section I, 8; the optimum concentration of silver nitrate is 0·05 g. per litre, but the solubility is negligibly small up to about 1·7 g. per litre). Under the conditions of the precipitation, very little occlusion occurs. If silver chloride is washed with pure water, it may become colloidal and run through the filter. For this reason the wash solution should contain an electrolyte (compare Section I, 56). Nitric acid is generally employed because it is without action on the precipitate and is readily volatile; its concentration need not be greater than 0·01N. Completeness of washing of the precipitate is tested for by determining whether the excess of the precipitating agent, silver nitrate, has been removed. This may be done by adding 1 or 2 drops of 0·1N-hydrochloric acid to 3–5 ml. of the washings collected after the washing process has been continued for some time; if the solution remains clear or exhibits only a very slight opalescence, all the silver nitrate has been removed.

Silver chloride is light sensitive; decomposition occurs into silver and chloride, the silver remains colloidal dispersed in the silver chloride and thereby imparts a purple colour to it. The decomposition by light is only superficial, and is negligible unless the precipitate is
exposed to direct sunlight and is stirred frequently. Hence the determination must be carried out in subdued light as possible, and when the solution containing the precipitate is set aside, it should be placed in the dark (e.g., in a locker), or the vessel containing it should be covered with thick brown paper.

**Procedure.** Weigh out accurately about 0.2 g. (or an amount containing approximately 0.1 g. of chlorine) into a 250-350-ml. beaker provided with a stirring-rod and covered with a clock-glass. Add about 150 ml. of water, stir until the solid has dissolved, and add 0.5 ml. of concentrated nitric acid. To the cold solution add 0.1N-silver nitrate slowly and with constant stirring. Only a slight excess should be added; this is readily detected by allowing the precipitate to settle and adding a few drops of silver nitrate solution, when no further precipitate should be obtained. **Carry out the determination in subdued light.** Heat the suspension nearly to boiling, while stirring constantly, and maintain it at this temperature until the precipitate coagulates and the supernatant liquid is clear (2-3 minutes). Make certain that precipitation is complete by adding a few drops of silver nitrate solution to the supernatant liquid. If no further precipitate appears, set the beaker aside in the dark, and allow the solution to stand for at least 1-2 hours before filtration. In the meantime prepare a filter-crucible (Gooch, porous-porcelain or sintered-glass—the last-named is most convenient); the crucible must be dried at the same temperature as is employed in heating the precipitate (133-150°C.) and allowed to cool in a desiccator (see Sections II, 31, 33 for details). Collect the precipitate in the weighed filter-crucible (Section II, 35). Wash the precipitate two or three times by decantation with cold 0.01-0.02N-nitric acid before transferring the precipitate to the crucible. Remove the last small particles of silver chloride adhering to the beaker with a "policeman" (Section II, 10L). Wash the precipitate in the crucible with 0.01-0.02N-nitric acid added in small portions (see Sections I, 60 and II, 34) until 3-5 ml. of the washings, collected in a test-tube, give no turbidity with 1 or 2 drops of 0.1N-hydrochloric acid.† Place the crucible and contents in an air-oven at 130-150°C. for 1 hour, allow to cool in a desiccator, and weigh. Repeat the heating and cooling until constant weight is attained.

Calculate the percentage of chlorine in the sample.† The factor for converting silver chloride to chlorine is 0.24737.

**Note on the gravimetric standardisation of hydrochloric acid.** The gravimetric standardisation of hydrochloric acid by precipitation as silver chloride is a convenient and accurate method, which has the additional advantage of being independent of the purity of any primary standard (compare Section

---

* A.R. Potassium or sodium chloride, dried at 110-120°C., is suitable.
† A rapid method for weighing the silver chloride, collected in a porous-porcelain or sintered-glass crucible, is as follows. (This method should not be used by elementary students or beginners in the study of quantitative analysis.) After washing the precipitate with very dilute nitric acid, wash the walls of the crucible five or six times with small volumes of rectified spirit (a small pipette or a drawn-out glass tube is useful for this purpose), followed by several times with small volumes of anhydrous ether. Suck the precipitate dry at the pump for 10 minutes, wipe the outside of the crucible with a clean linen cloth, leave in a vacuum desiccator for 10 minutes, and weigh as AgCl. The procedure may be employed for silver bromide, iodide, and thiocyanate. The results are usually slightly high.

† In this and all other gravimetric determinations, duplicate estimations are advisable. Both determinations may be carried out simultaneously, or if this is not convenient, the second should be commenced as soon as possible after the first is in progress.
III, 4). Measure out from a burette 30–40 ml. of the, say, 0·1N-hydrochloric acid which is to be standardised. Dilute to 150 ml., precipitate (but omit the addition of nitric acid), filter, and weigh the silver chloride. From the weight of the precipitate, calculate the chloride concentration of the solution, and thence the normality of the hydrochloric acid.

IV, 6. Determination of sulphate as barium sulphate.—Discussion. The method consists in slowly adding a dilute solution of barium chloride to a hot solution of the sulphate slightly acidified with hydrochloric acid:

\[ \text{Ba}^{++} + \text{SO}_4^{--} \rightarrow \text{BaSO}_4 \]

The precipitate is filtered off, washed with water, carefully ignited at a red heat, and weighed as barium sulphate. The percentage of sulphate is calculated from the weight of barium sulphate.

The reaction appears to be a simple one, but is in reality subject to numerous possible errors; satisfactory results can be obtained only if the experimental conditions are carefully controlled. Before some of these are discussed, the student is recommended to read Sections 1.56–59.

Barium sulphate has a solubility in water of about 3 mg. per litre at the ordinary temperature. The solubility is increased in the presence of mineral acids, because of the formation of the bisulphate ion (\(\text{SO}_4^{--} + \text{H}^+ \rightleftharpoons \text{HSO}_4^-\); thus the solubilities at room temperature in the presence of 0·1, 0·5, 1·0, and 2·0N-hydrochloric acid are 10, 47, 87, and 101 mg. per litre respectively, but the solubility is less in the presence of a moderate excess of barium ions. Nevertheless, it is customary to carry out the precipitation in weakly acid solution in order to prevent the possible formation of the barium salts of such anions as chromate, carbonate, and phosphate, which are insoluble in neutral solutions; moreover, the precipitate thus obtained consists of large crystals, and is therefore more easily filtered (compare Section 1.57). It is also of great importance to carry out the precipitation at boiling temperature, for the relative supersaturation is less at higher temperatures (compare Section 1.57). The concentration of hydrochloric acid is, of course, limited by the solubility of the barium sulphate, but it has been found that a concentration of 0·5N is suitable; the solubility of the precipitate in the presence of barium chloride at this acidity is negligible. The precipitate may be washed with cold water, and losses, owing to solubility influences, may be neglected except for the most accurate work.

Barium sulphate exhibits a remarkable tendency to carry down other salts (see co-precipitation, Section 1.58). Whether the results will be low or high will depend upon the nature of the co-precipitated salt. Thus barium chloride and barium nitrate are readily co-precipitated. These salts will be an addition to the true weight of the barium sulphate, hence the results will be high, since the chloride is unchanged upon ignition and the nitrate will yield barium oxide. The error due to the chloride will be considerably reduced by the very slow addition of hot dilute barium chloride solution to the hot solution, which is constantly stirred; that due to the nitrate cannot be avoided, and hence nitrate ion must always be removed by evaporation with a large excess of hydrochloric acid before precipitation. Chlorate has a similar effect to nitrate, and is similarly removed.
In the presence of certain cations (sodium, potassium, lithium, calcium, aluminium, chromium, and ferric iron), co-precipitation of the sulphates of these metals occurs, and the results will accordingly be low. This error cannot be entirely avoided except by the removal of the interfering ions. Aluminium, chromium, and iron may be removed by precipitation, and the influence of the other ions, if present, is reduced by considerably diluting the solution and by digesting the precipitate (Section I, 58). It must be pointed out that the general method of re-precipitation cannot be employed in order to obtain a purer precipitate, because no simple solvent (other than concentrated sulphuric acid) is available in which the precipitate may be dissolved.

Pure barium sulphate is not decomposed when heated in dry air until a temperature of about 1400° C. is reached:

\[ \text{BaSO}_4 \rightarrow \text{BaO} + \text{SO}_3 \]

The precipitate is, however, easily reduced to sulphide at temperatures above 600° C. by the carbon of the filter-paper:

\[ \text{BaSO}_4 + 4\text{C} = \text{BaS} + 4\text{CO} \]

The reduction is avoided by first charring the paper without inflaming, and then burning off the carbon slowly at a low temperature with free access of air. If a reduced precipitate is obtained, it may be re-oxidised by treatment with sulphuric acid, followed by volatilisation of the acid and re-heating. The final ignition of the barium sulphate need not be made at a higher temperature than 600–800° C. (dull red eat). A Vitreosil or porous porcelain filter-crucible may be used, and the difficulty of reduction by carbon is entirely avoided.

**Procedure.** Weigh out accurately about 0·3 g. of the solid * (or a sufficient amount to contain 0·05–0·06 g. of sulphur) into a 400-ml. beaker, provided with a stirring-rod and clock-glass cover. Dissolve the solid in about 25 ml. of water, add 0·3–0·6 ml. of concentrated hydrochloric acid, and dilute to 200–225 ml. Heat the solution to boiling, add dropwise from a burette or pipette 10–12 ml. of 5 per cent barium chloride solution (5 g. BaCl₂.2H₂O in 100 ml. of water—ca. 0·2M). Stir the solution constantly during the addition. Allow the precipitate to settle for a minute or two. Then test the supernatant liquid for complete precipitation by adding a few drops of barium chloride solution. If a precipitate is formed, add slowly a further 3 ml. of the reagent, allow the precipitate to settle as before, and test again; repeat this operation until an excess of barium chloride is present. When an excess of the precipitating agent has been added, keep the covered solution hot, but not boiling, for an hour (steam-bath, low-temperature hot-plate, or small flame) in order to allow time for complete precipitation.† The volume of the solution should not be allowed to fall below 150 ml.; if the clock-glass covering the beaker is removed, the under side must be rinsed off into the beaker by means of a stream of water from a wash-bottle. The precipitate should settle readily, and a clear supernatant liquid should be obtained. Test the latter with a few drops of barium chloride solution for complete precipitation. If no precipitate is obtained, another 3 ml. of reagent should be added and the test repeated.

* A.R. Potassium sulphate may be employed.
† An equivalent result is obtained by allowing the solution to stand at the ordinary temperature for about 18 hours.
obtained, the barium sulphate is ready for filtration. The determination may be completed by either of the following processes.

(i) Filter-paper method. Decant the clear solution through an ashless filter-paper (Whatman, No. 40 or 540) (Section II, 28), and collect the filtrate in a clean beaker. Test the filtrate with a few drops of barium chloride: if a precipitate forms, the entire sample must be discarded and a new determination commenced. If no precipitate forms, discard the liquid, rinse out the beaker, and place it under the funnel; this is in order to avoid the necessity of re-filtering the whole solution if any precipitate should pass through the filter. Transfer the precipitate to the filter with the aid of a jet of hot water from the wash bottle (Section II, 35). Use a rubber-tipped rod ("policeman") to remove any precipitate adhering to the walls of the beaker or to the stirring-rod, and transfer the precipitate to the filter-paper. Wash the precipitate with small portions of hot water. Direct the jet as near the top of the filter-paper as possible, and let each portion of the wash solution run through before adding the next (Section II, 34). Continue the washing until about 5 ml. of the wash solution gives no opalescence with a drop or two of silver nitrate solution. Eight or ten washings are usually necessary.

Fold the moist paper around the precipitate and place it in a weighed porcelain or silica (Vitreosil) crucible, previously ignited to redness and cooled in a desiccator. Dry the paper by placing the loosely covered crucible upon a triangle several centimetres above a small flame (Section II, 36). Then gradually increase the heat until the paper chars and volatile matter is expelled. Do not allow the paper to burst into flame, as mechanical loss may thus ensue. When the charring is complete, raise the temperature of the crucible to dull redness and burn off the carbon with free access of air* (crucible slightly inclined with cover displaced, Fig. II, 36, 1). When the precipitate is white,† ignite the crucible at a red heat for 10–15 minutes. Then allow the crucible to cool somewhat in the air, transfer it to a desiccator, and, when cold, weigh the crucible and contents. Repeat the ignition with 10-minute periods of heating, subsequent cooling in a desiccator, etc., until constant weight (± 0·0002 g.) is attained.

Alternatively, place the moist paper and precipitate in a Vitreosil crucible with interior-fitting serrated lid (Main-Smith crucible) of suitable size, and proceed as detailed in Section II, 36B and in the preceding paragraph.

Calculate the percentage of SO₄ in the sample. The factor for converting BaSO₄ to S is 0·13735.

(ii) Filter-crucible method. Clean, ignite, and weigh either a porous-porcelain filter-crucible (e.g., Selas or Royal Worcester, see Section II, 33) or a Vitreosil filtering-crucible (porosity, No. 4). Carry out the ignition either upon a crucible-ignition dish or by placing the crucible inside a nickel crucible (Fig. II, 37, 4) at a red heat (or, if available, in an electric muffle furnace at 600–800° C.), allow to cool in a desiccator and weigh. Filter the supernatant liquid, after digestion of the precipitate, through the weighed crucible, using gentle suction. Reject the filtrate.

* Any dark matter on the crucible cover may be removed by placing it, clean side down, on a triangle, and heating it for some time.
† If the precipitate is slightly discoloured, add a drop or two of dilute sulphuric acid, evaporate gently, etc. This operation is best carried out in a Main-Smith crucible.
after testing for complete precipitation with a little barium chloride solution. Transfer the precipitate to the crucible and wash with warm water until 3-5 ml. of the filtrate give no precipitate with a few drops of silver nitrate solution. Dry the crucible and precipitate in the steam-oven or at 100-110° C., and then ignite in a manner similar to that used for the empty crucible for periods of 15 minutes until constant weight is attained (1).

Note. 1. A rapid method for weighing the precipitate is as follows. (This procedure should not be employed by elementary students or beginners in the study of quantitative analysis.) Filter off the precipitated barium sulphate through a weighed crucible (Gooch, sintered-glass, or porous-porcelain) and wash it with hot water until the chloride reaction of the washings is negative. Then wash five or six times with small volumes of rectified spirit, followed by five times with small volumes of anhydrous ether. Suck the precipitate dry on the pump for 10 minutes, wipe the outside of the crucible dry with a clean linen cloth, leave in a vacuum desiccator for 10 minutes (or until constant in weight), and weigh as \( \text{BaSO}_4 \). The result is of a moderate order of accuracy.

Calculate the percentage of \( \text{SO}_4 \) in the sample.

Precipitation of sulphate as barium sulphate using agar-agar as coagulant.—Discussion. Positively charged barium sulphate, which is obtained when sulphate is precipitated by excess of barium ions, can be coagulated by the addition of a trace of agar-agar. About 1 mg. of agar-agar will cause the flocculation of about 0.1 g. of barium sulphate, but in practice somewhat larger quantities are generally used. The resulting precipitate does not creep up the sides of the vessel.

Negatively charged barium sulphate, obtained in the determination of barium, is not appreciably improved by agar-agar; this precipitate, as a rule, presents little difficulty in filtration.

Procedure. Prepare the agar-agar solution by stirring 0.50 g. of the purest available agar-agar with 50 ml. of cold water, and pouring this into 450 ml. of water at near the boiling point. Stir the solution constantly as it is heated to the boiling point. Allow to cool. The solution is stable for several weeks.

For practice in this determination proceed as described in the paragraph prior to “(i) Filter-paper method” to the point where excess of barium chloride solution has been added. Treat the hot liquid containing the freshly precipitated barium sulphate with 10 ml. of the agar-agar solution; add the latter drop by drop with constant stirring during several minutes. Under these conditions the barium sulphate coagulates in a few minutes. After settling, the precipitate somewhat resembles silver chloride. Collect the precipitate as before on a Whatman No. 541 filter-paper, dry and ignite in a Main-Smith crucible: add a drop or two of dilute sulphuric acid to convert any barium sulphide present to barium sulphate, and ignite again to constant weight. The precipitate may also be filtered on a weighed sintered-glass crucible porosity No. 3, and dried at 120-130° C. The weight of the precipitate is usually 1-2 per cent high, due largely to the presence of a little adsorbed moisture. This order of accuracy may suffice for certain technical analyses when the proportion of sulphur is small.

IV. 7. Determination of sulphur in iron pyrites.—Discussion. The methods to be described apply to most insoluble sulphides. In these
Gravimetric Analysis

The sulphur is oxidised to sulphuric acid, and determined as barium sulphate. Two procedures are available for effecting the oxidation.

A. Dry Process. The oxidation is carried out by fusion with sodium peroxide, or, less efficiently, with sodium carbonate and potassium nitrate:

\[ 2\text{FeS}_2 + 15\text{Na}_2\text{O}_2 = \text{Fe}_2\text{O}_3 + 4\text{Na}_2\text{SO}_4 + 11\text{Na}_2\text{O} \]

The sulphide is fused in an iron or nickel crucible with the sodium peroxide (platinum is strongly attacked—Sections II, 16, and II, 37), the fused mass treated with water, filtered, and acidified. The excess of peroxide is removed by boiling, and the sulphate ion precipitated with barium chloride. The decomposition of the sulphide is rapid, but the method has several disadvantages. Amongst these may be mentioned: the slight attack on the metal crucible, thus preventing the subsequent determination of the metal content of the sample; the introduction of appreciable quantities of sodium salts, thus increasing the error due to co-precipitation (Sections I, 58 and IV, 6); and the danger of contamination by the sulphur from the flame gases, since sulphur dioxide is rapidly absorbed by the alkaline melt. The last error may be minimised by fitting the crucible into a hole in a sheet of asbestos or "uralite," and keeping the crucible covered during the ignition (see Section II, 38).

B. Wet Process. The sulphide is oxidised (i) by bromine in carbon tetrachloride solution, followed by nitric acid, (ii) by sodium chlorate and hydrochloric acid, or (iii) by a mixture of nitric and hydrochloric acids and a little bromine. The use of the first-named oxidising agent will be described; the reaction may be represented by:

\[ 2\text{FeS}_2 + 6\text{HNO}_3 + 15\text{Br}_2 + 16\text{H}_2\text{O} \]
\[ = 2\text{Fe(NO}_3)\text{}_3 + 4\text{H}_2\text{SO}_4 + 30\text{HBr} \]

The method has the advantage of not introducing any metallic ions, but it is essential to remove the excess of nitric acid (see Discussion in Section IV, 6). The action is slower than by the fusion method.

Procedure. A. Dry Process. Dry some finely powdered pyrites \* at 100° C. for 1 hour. Fit an iron or nickel crucible into a hole in an asbestos or "uralite" board sufficiently large to allow two-thirds of the crucible to project below the board. Place about 1 g. of A.R. anhydrous sodium carbonate into the crucible, and weigh accurately into it 0.4-0.5 g. of the pyrites. Add 5-6 g. of sodium peroxide, and mix well with a stout copper or nickel wire or with a thin glass rod. Wipe the wire or rod, if necessary, with a small piece of quantitative filter-paper, and add the latter to the crucible; cover the mixture with a thin layer of peroxide. Place the crucible in the hole in the asbestos or "uralite" sheet, and heat it with a very small flame. Increase the temperature gradually until after 10-15 minutes the crucible is at a dull red heat (the lower the temperature, the less is the crucible attacked) and just sufficient to keep the mass completely fused. Remove the cover occasionally and examine the contents; be sure that the whole mass is fluid. Maintain the mass fluid for 15 minutes to complete the oxidation. Allow to cool, extract the crucible with water in a covered 600-ml. beaker, rinse off the crucible-cover into the beaker, remove the crucible

\* Risedale's "Iron Pyrites, No. 44aG" (one of the Analysed Samples for Students) is suitable.
with a glass rod and wash it well; dilute to 300 ml. Boil the solution for 15 minutes in order to destroy the excess of peroxide (\( \text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2\text{O}_2 \)), neutralise part of the alkali by adding 5–6 ml. of concentrated hydrochloric acid with stirring, add a Whatman "accelerator" or a quarter of an "ashless tablet," and filter through a Whatman No. 541 filter-paper. Wash the residue at least ten times with hot 1 per cent sodium carbonate solution. Acidify the combined filtrate and washings contained in a 800–1000-ml. beaker with concentrated hydrochloric acid, using methyl red or methyl orange as indicator, and add 2 ml. of acid in excess. Dilute, if necessary, to 600 ml., and heat to boiling. Precipitate the sulphuric acid by the slow addition with stirring of a boiling 5 per cent solution of barium chloride; the latter is added in slight excess of the calculated amount required, assuming the pyrites to be pure FeS\(_2\). Complete the determination as in Section IV, 6.

Calculate the percentage of sulphur in the sample.

B. Wet Process. Dry some finely powdered iron pyrites (1) at 100° C. for 1 hour. Weigh out accurately 0.4–0.5 g. of the pyrites into a dry 400-ml. beaker, add 8 ml. of a mixture of 2 volumes of pure liquid bromine and 3 volumes of pure carbon tetrachloride (fume cupboard!), and cover with a clock-glass. Allow to stand in the fume cupboard for 15–20 minutes and swirl the contents of the beaker occasionally during this period. Then add 15 ml. of concentrated nitric acid down the side of the beaker, and allow to stand for another 15–20 minutes, swirling occasionally as before. Heat the covered beaker below 100° C. by placing it on a thick asbestos board over a steam-bath until all action has ceased and most of the bromine has been expelled (about 1 hour). Raise the clock-glass cover by glass hooks resting on the rim of the beaker, or displace it to one side, and evaporate the liquid to dryness on the steam-bath. Add 10 ml. of concentrated hydrochloric acid, mix well, and again evaporate to dryness to eliminate most of the nitric acid. Place the beaker in an oven or in an air-bath at 95–100° C. for 30–60 minutes in order to dehydrate any silica which may be present (2). If the dry residue is heated at a temperature above 100° C., loss of sulphuric acid may occur and the determination will be rendered useless. Moist the cold, dry residue with 1–2 ml. of concentrated hydrochloric acid and, after an interval of 3–5 minutes, dilute with 50 ml. of hot water, and rinse the sides of the beaker and the cover-glass with water. Digest the contents of the beaker at 100° C. for 10 minutes in order to dissolve all soluble salts. Allow the solution to cool for 5 minutes, and add 0.2–0.3 g. of aluminium powder to reduce the ferric iron. Gently swirl (or stir) until the solution becomes colourless. Allow to cool, add a Whatman "accelerator," stir, and rinse down the cover-glass and the sides of the beaker. Filter through a Whatman No. 540 paper, and collect the filtrate in an 800-ml. beaker; wash the filter thoroughly with hot water. Dilute the combined filtrate and washings to 600 ml. and add 2 ml. of concentrated hydrochloric acid. Precipitate the sulphate in the cold (3) by running in from a burette, without stirring, a 5 per cent solution of barium chloride at a rate not exceeding 5 ml. per minute until an excess of 5–10 ml. is present (4). When all the precipitant has been added, stir gently and allow the precipitate to settle for 2 hours, but preferably overnight. Filter

* This is unnecessary if a Fisher "speedy-vap" cover is used.
Gravimetric Analysis

through a No. 540 filter-paper or, preferably, through a porous-porcelain filter-crucible, wash with warm water until free from chloride, and ignite to constant weight as described under A.

Calculate the percentage of sulphur in the sample.

Notes. 1. The procedure is applicable to most mineral sulphides; many of these contain silica, and provision is made for the removal of this impurity in the experimental details.

2. If the iron pyrites or the sample of sulphide contains no appreciable proportion of silica, the heating at 95–100° C. may be omitted.

3. If a drop or two of stannous chloride solution is added to prevent reoxidation of the ferrous salt by air, precipitation of the barium sulphate may be made in boiling solution according to the usual procedure (Section VI, 6).

4. Calculate the volume of 5 per cent barium chloride solution which must be added from the approximate sulphur content of the iron pyrites FeS₂ or of the mineral sulphide.

IV, 8. Determination of iron as ferric oxide.—Discussion. The solution containing the ferric salt * is treated with a slight excess of ammonium hydroxide solution to precipitate ferric hydroxide: †

\[
\text{FeCl}_3 + 3\text{NH}_4\text{OH} = \text{Fe(OH)}_3 + 3\text{NH}_4\text{Cl}
\]

Other elements that are precipitated by ammonia solution must, of course, be absent. These include aluminium, trivalent chromium, titanium, and zirconium. In the presence of an oxidising agent (even atmospheric oxygen) manganese may be precipitated as the hydrated dioxide. Anions, such as arsenate, phosphate, vanadate, and silicate, which yield insoluble compounds of iron in weakly basic media, must be absent. The presence of a sufficient quantity of salts of organic hydroxy-acids (e.g., citric, tartaric, and salicylic acids), hydroxy compounds (e.g., glycerine and sugars), alkali pyrophosphate and fluorides must be guarded against, because of the formation of complex salts and the consequent non-precipitation of ferric hydroxide.

The solubility product of ferric hydroxide is of the order of \(10^{-38}\), so that quantitative precipitation occurs even in weakly acid solution, and errors due to washing will be negligibly small. The precipitate first forms as a dispersed phase, but on heating in the presence of electrolytes it coagulates to a gelatinous mass, which settles out of suspension; prolonged heating tends to break up the aggregates and causes the precipitate to become slimy. The hydrated ferric oxide is a typical example of a flocculated colloid. The coagulation of a colloidal precipitate, and especially the agglomeration of the primary particles, is aided considerably by raising the temperature of the solution. Hence precipitation is carried out at or near the boiling point, and the liquid is maintained at this temperature for a short time after precipitation.

As might be expected from its colloidal character, hydrated ferric oxide has a great tendency to adsorb other ions present. If precipita-

* Ferrous iron is only partially precipitated by ammonia solution in the presence of ammonium salts.

† The precipitate is usually given the formula \(\text{Fe}_3\text{OH}_4\), ferric hydroxide. Actually the water content is somewhat indefinite; the formula of the precipitate is more accurately represented by \(\text{Fe}_3\text{O}_4\times\text{H}_2\text{O}\), and is termed a hydrate or hydroxide oxide. Throughout this book the terms hydrated oxide and hydroxide will be used synonymously.

\[
2\text{Fe}^{+++} + 6\text{NH}_4\text{OH} + y\text{H}_2\text{O} = \text{Fe}_3\text{O}_4\times\text{H}_2\text{O} + 6\text{NH}_4^+\]
Quantitative Inorganic Analysis

Quantitative analysis is made from basic solution, the primary adsorbed ion is the hydroxyl ion (Section I, 56), and this readily holds by secondary adsorption positive ions which may be present. If there is a large excess of ammonium ions in the precipitating and wash solutions, the adsorption of other cations can be kept at a minimum; since ammonium salts are volatilised upon ignition of the precipitate, little harm is caused by the adsorption. Divalent ions are more strongly adsorbed than monovalent ions (Section I, 58). If the extent of co-precipitation is large, re-precipitation may be employed, since the precipitate is soluble in dilute acids.

The gelatinous precipitate of ferric hydroxide is always filtered through filter-paper. Application of suction, in order to hasten filtration, should not be used, since the effect of the suction is merely to force the small particles of the precipitate into the pores of the filtering medium. It may often happen that with suction the liquid will pass through more rapidly; this does not mean that the washing process is accelerated, since the liquid runs through small channels and does not permeate the main body of the precipitate. For this reason ferric hydroxide is best washed by decantation; the precipitate may then be thoroughly stirred with the wash liquid. To prevent peptisation and the production of slimy material, an electrolyte is used in the wash liquid. The most satisfactory is ammonium nitrate; this volatilises upon ignition and assists somewhat in the subsequent ignition of the precipitate. Ammonium chloride is unsuitable, because ferric chloride, which is volatile, is formed during the ignition:

\[
\text{Fe}_2\text{O}_3 + 6\text{NH}_4\text{Cl} = 2\text{FeCl}_3 + 6\text{NH}_3 + 3\text{H}_2\text{O}
\]

It is advisable, therefore, to wash out nearly all the ammonium chloride present in the hydrated ferric oxide: very small amounts, however, will not lead to any significant error. To assist filtration, a hot wash solution should be employed. The filtration and washing of any gelatinous precipitate is hastened by the use of ashless filter-paper pulp (macerated filter-paper, Section II, 29). Under no circumstances should the precipitate be allowed to stand in the filter-paper before washing is complete, because it shrinks rapidly as it partially dries, and channels, which permit the wash liquid to run through, are formed in the precipitate.

Hydrated ferric oxide upon ignition at 1000° C. yields ferric oxide; at higher temperatures triferric tetroxide is slowly formed. The ignition should be carried out under good oxidising conditions, especially during the burning of the filter-paper, for otherwise partial reduction to the magnetic oxide \(\text{Fe}_3\text{O}_4\), or even to the metal, may occur. These reduction products are only slowly converted into ferric oxide upon continued heating with free access of air. Such reduction is avoided by burning off the carbon at a low heat, by maintaining at all times free access of air, and by excluding the reducing gases from the flame.

Procedure. For practice in this determination, the student may employ either A.R. ferrous ammonium sulphate \(\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O}\) or A.R. ferric ammonium sulphate \((\text{NH}_4)_2\text{SO}_4\cdot\text{Fe}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O}\).* The former is to be preferred, as this estimation involves oxidation of the ferrous salt to the ferric state. Weigh out accurately about 0·8 g. of ferrous ammonium sulphate into a 400-ml. beaker provided with a

* Alternatively, the sample supplied by the instructor may be used.
clock-glass and stirring-rod. Dissolve it in 50 ml. of water and 10 ml. of dilute hydrochloric acid (1:1). Add 1–2 ml. of concentrated nitric acid † to the solution, and boil gently until the colour is clear yellow (3–5 minutes is usually necessary) (1). Dilute the solution to 200 ml.; ‡ heat to boiling, and slowly add pure 1:1 ammonia solution (2) in a slow stream from a small beaker until a slight excess is present, as is shown by the odour of the steam above the liquid (3). Boil the liquid gently for 1 minute, and allow the precipitate to settle. The supernatant liquid should be colourless. As soon as most of the precipitate has settled, decant the supernatant liquid through an ashless filter-paper, but leave as much of the precipitate as possible in the beaker. It is essential that the filter-paper fits the funnel properly (Section II, 28), so that the stem of the funnel is always filled with liquid, otherwise filtration will be very slow. Add about 100 ml. of boiling 1 per cent ammonium nitrate solution to the precipitate, stir the mixture thoroughly, and allow to settle. Decant as much liquid as possible through the filter. Wash the precipitate three to four times by decantation with 75–100-ml. portions of hot 1 per cent ammonium nitrate solution. Transfer the precipitate (and macerated filter-paper, if employed) to the filter (Section II, 35); any small particles adhering to the sides of the vessel or to the glass rod are dislodged with the aid of a "policeman," and subsequently transferred to the main precipitate with the assistance of hot water from a wash-bottle. Wash the ferric hydroxide several times with hot ammonium nitrate solution (4) until no test (or, at most, a very slight test) for chloride is obtained from the washings. Allow each portion of the wash liquid to run through before adding the next portion; do not fill the filter more than three-fourths full of the precipitate. While the filtration is in progress, ignite a clean crucible (porcelain, silica, or platinum) at a red heat, cool in a desiccator for 30 minutes, and weigh. When the filter-paper has drained thoroughly, fold over the edges, and transfer to the weighed crucible (5). Proceed as described in Section IV, 6. Heat gradually until dry, char the paper without inflaming, and burn off the carbon at as a low a temperature as possible under good oxidising conditions, i.e., with free access of air in order to avoid reduction of the ferric oxide. Finally, ignite the precipitate at a red heat for 15 minutes and take care to exclude the flame gases from the interior of the crucible, cool in a desiccator for 30 minutes, and weigh. Repeat the ignition (10–15 minutes) until constant weight is obtained (to within 0.0002 g.).

From the weight of ferric oxide obtained, calculate the percentage of iron in the salt used. The factor for converting Fe₂O₃ to Fe is 0.69940.

† The reaction is:

\[ 3\text{Fe}^{++} + \text{NO}_3^- + 4\text{H}^+ = 3\text{Fe}^{+++} + \text{NO} + 2\text{H}_2\text{O} \]

The disadvantage of this procedure is that the presence of nitrates is undesirable if sulphate is subsequently to be determined in the filtrate as BaSO₄, necessitating one or more evaporations to dryness with hydrochloric acid to remove the nitric acid. This difficulty may be avoided by employing either bromine water (2Fe³⁺ + Br₂ = 2Fe⁴⁺ + 2Br⁻) or hydrogen peroxide for the oxidation. Add 10–15 ml. of saturated bromine water to the hot solution (i.e., in moderate excess as indicated by the colour of the solution and the persistent odour of bromine—caution!) and boil to complete the oxidation and to remove most of the excess of bromine. The hydrogen peroxide is conveniently employed as the "100-volume" solution. Add 1 ml. of the latter and destroy the excess of reagent by boiling.

‡ If A.R. iron alum is used, dissolve 1·3 g. (or a sufficient amount of a ferric salt containing about 0·15 g. of iron) in 200 ml. of water, add 10 ml. of 1:1 hydrochloric acid, and proceed as described.
Notes. 1. At this stage it is advisable to test the solution for the complete oxidation of the iron. Transfer a drop of the solution to a test-tube by means of a stirring-rod, and dilute with about 1 ml. of water. Add a few drops of a freshly prepared potassium ferricyanide solution. If a blue colour appears, ferrous iron is still present in the solution, and more nitric acid must be added.

2. Filtered ammonia solution should be used in order to prevent the introduction of silica, which is often present in suspension in alkaline solutions.

3. At this point it is advantageous to add a little macerated filter-paper, best in the form of a Whatman "accelerator" or one-fourth of an "ashless tablet." For further details, see Section II, 29.

4. If desired, hot water from a wash bottle may be substituted at this stage; peptisation is negligible.

5. The most convenient crucible is a silica crucible with an interior-fitting serrated lid (Main-Smith type). See Section II, 36B.

A more easily filterable precipitate may be obtained by the basic benzoate method (compare Section IV, 28C). Treat the acid solution, containing at least 1 g. of ammonium chloride, with dilute ammonia solution until the precipitate first formed dissolves very slowly upon stirring. Add 1 ml. of glacial acetic acid and 20 ml. of 10 per cent ammonium benzoate solution. Boil gently for 5 minutes, filter, and wash with hot 1 per cent ammonium benzoate solution containing 2 per cent of acetic acid. Complete the determination as above.

For other methods for the determination of iron, see Section IV, 31.

IV, 9. Determination of aluminium as aluminium oxide.—Discussion.

The aluminium is precipitated as the hydrated oxide by means of ammonia solution in the presence of ammonium chloride. The gelatinous precipitate is washed, converted into the oxide by ignition, and weighed as Al₂O₃.

This determination is subject to several sources of error, most of which will now be discussed. Aluminium hydroxide is amphoteric in character:

\[
\begin{align*}
\text{Al(OH)}_3 + 3\text{H}^+ & \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O} \\
\text{Al(OH)}_3 + \text{OH}^- & \rightarrow \text{AlO}_2^- + 2\text{H}_2\text{O}
\end{align*}
\]

Precipitation commences at approximately pH 4, and is complete when the pH lies between 6.5 and 7.5. The latter pH range can be maintained by the use of methyl red as indicator. The amount of ammonia solution employed for precipitation must clearly be controlled. This is achieved by the addition of ammonium chloride, which exerts a buffering effect (Section I, 20) and also assists the coagulation of the initially colloidal precipitate. The presence of ammonium salts reduces to a minimum the co-precipitation of the divalent metals, such as calcium and magnesium (see Section IV, 8) and other cations. A readily filterable precipitate is obtained by precipitation in hot solution. The precipitate cannot be washed with hot water, for aluminium hydroxide is readily peptised (Section I, 56), and will run through the filter. A 2 per cent solution of either ammonium chloride or ammonium nitrate is satisfactory; the presence of ammonium chloride in the precipitate causes no appreciable volatilisation of aluminium during the subsequent ignition (contrast ferrio oxide).

The aluminium oxide obtained by igniting aluminium hydroxide is hygroscopic unless the temperature has been raised to at least 1200° C.,
Gravimetric Analysis

when apparently a non-hygroscopic form of the oxide is formed. For this reason the precipitate is best ignited in a silica crucible (porcelain is slightly hygroscopic when heated to a high temperature) over a Meker or Fisher burner or with a blast lamp.

Procedure. Weigh out accurately about 1.8 g. of A.R. ammonium aluminium sulphate \((\text{NH}_3)_2\text{SO}_4\cdot\text{Al}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O}\) (or a weight of a sample containing about 0.1 g. of aluminium) into a 400- or 600-ml. beaker, provided with a clock-glass cover and a stirring-rod. Dissolve it in 200 ml. of water, add 5 g. of pure ammonium chloride, a few drops of methyl red indicator (0.2 per cent alcoholic solution) (1), and heat just to boiling. Add pure dilute ammonia solution (1 : 1) dropwise from a burette until the colour of the solution changes to a distinct yellow. Boil the solution for 1 or 2 minutes, and filter at once through a suitable quantitative filter-paper (Section II, 28) (2). Wash the precipitate thoroughly with hot 2 per cent ammonium nitrate or chloride solution made neutral with ammonia solution to methyl red (or to phenol red). Place the paper with the precipitate in a previously ignited silica or platinum crucible (3), dry, char, and ignite for 10–15 minutes with a Meker or Fisher high-temperature burner. Allow the crucible to cool in a desiccator, and weigh. Ignite to constant weight.

Calculate the percentage of aluminium in the sample. The factor for converting \(\text{Al}_2\text{O}_3\) to \(\text{Al}\) is 0.52913.

Notes. 1. Phenol red \([pH\ \text{range: 6.4 (yellow) to 8.0 (red)}]\) has been recommended. 0.5 ml. of a 0.1 per cent solution of the indicator is added; the colour change upon the addition of ammonia solution is from yellow to orange.

2. Macerated filter-paper (Section II, 29) may be added in order to assist the subsequent filtration.

3. A silica crucible of the Main-Smith type (Section II, 36B) considerably simplifies this operation.

For other methods for the determination of aluminium, see Section IV, 28.

IV, 10. Determination of calcium as oxalate.—Discussion. The calcium is precipitated as calcium oxalate \(\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}\) by treating a hot hydrochloric acid solution with ammonium oxalate, and slowly neutralising with ammonium hydroxide solution:

\[
\text{Ca}^{++} + 2\text{C}_2\text{O}_4^{--} + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}
\]

The precipitate is washed with dilute ammonium oxalate solution and then weighed in one of the following forms:

(i) as \(\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}\) by drying at 100–115°C for 1–2 hours. This method is not recommended for accurate work, because, \textit{inter alia}, of the hygroscopic nature of the oxalate and the difficulty of removing the co-precipitated ammonium oxalate at this low temperature.

(ii) As \(\text{CaCO}_3\) by drying at 475–525°C in an electric muffle furnace. This is the most satisfactory method, since calcium carbonate is non-hygroscopic.

\[
\text{CaC}_2\text{O}_4 = \text{CaCO}_3 + \text{CO}_2
\]

(iii) As \(\text{CaO}\) by igniting at 1200°C. This method is widely used, but the resultant lime has a comparatively small molecular weight and is
hygroscopic; precautions must therefore be taken to prevent absorption of moisture (and of carbon dioxide).

\[ \text{CaCO}_3 = \text{CaO} + \text{CO}_2 \]

Calcium oxalate monohydrate has a solubility of 0.0067 g. and 0.0140 g. per litre at 25° and 95° C. respectively. The solubility is less in neutral solutions containing moderate concentrations of ammonium oxalate owing to the common-ion effect (Section I, 9); hence a dilute solution of ammonium oxalate is employed as the wash liquid in the gravimetric determination. Calcium oxalate being the salt of a weak acid, its solubility increases with increasing hydrogen-ion concentration of the solution because of the removal of the oxalate ions (compare Section I, 13) to form the weak bi-oxalate ions and oxalic acid:

\[
\begin{align*}
\text{CaC}_2\text{O}_4 \text{ (solid)} & \rightleftharpoons \text{Ca}^{++} + \text{C}_2\text{O}_4^{-} \\
\text{C}_2\text{O}_4^{-} + \text{H}^{+} & \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4 \\
\text{HC}_2\text{O}_4^{-} + \text{H}^{+} & \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4
\end{align*}
\]

Calculation shows that precipitation is quantitative at a pH of 4 or higher.

Precipitation from cold neutral or ammoniacal solutions yields a very finely divided precipitate, which is difficult to filter. Satisfactory results are obtained by adding ammonium oxalate to a hot acid solution of the calcium salt (more or less calcium oxalate may precipitate, depending upon the pH of the solution), and finally neutralising with ammonium hydroxide solution. The precipitate formed, after digesting for about an hour, consists of relatively coarse crystals which are readily filtered. The best results are given by the urea—hydrolysis method, details of which will be found in Section III, 155.

In this determination all those metals (e.g., copper, lead, zinc) which form slightly soluble oxalates must be absent. The problem which frequently arises in practice is the precipitation of calcium in the presence of magnesium and the alkali metals. The amount of the alkali metals which is precipitated is usually small; in the presence of large amounts of sodium, re-precipitation may be desirable. Magnesium may be co-precipitated (Section I, 58) to a considerable extent, but the amount of this may be considerably reduced by not boiling the solution, and not allowing the precipitate to stand in contact with the solution too long before filtration (post-precipitation, Section I, 58, is thus minimised). By using a very large excess of ammonium oxalate, magnesium is held in solution in the form of a complex salt with the oxalate ion; furthermore, magnesium oxalate readily forms quite stable supersaturated solutions. If the concentration ratio of magnesium to calcium is extremely large, a second precipitation is usually necessary.

As already pointed out, the two forms in which calcium oxalate is best weighed are the carbonate and oxide. The theory of the decomposition of calcium oxalate is of some interest in this connexion. Decomposition of the oxalate into the carbonate is rapid at about 475° C. At higher temperatures, the dissociation of calcium carbonate (\( \text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 \)) comes into play. At any given temperature, a mixture of \( \text{CaCO}_3 \), \( \text{CaO} \), and \( \text{CO}_2 \) in equilibrium with one another exerts a certain definite pressure of carbon dioxide. If the partial
pressure of the carbon dioxide in the surrounding atmosphere is greater than the equilibrium pressure for that temperature, the above reaction will proceed from right to left, and eventually the oxide will be completely converted into the carbonate. Otherwise expressed, calcium carbonate cannot be decomposed into the oxide so long as the pressure of carbon dioxide in the surrounding atmosphere is greater than the equilibrium pressure of the system CaCO₃-CaO-CO₂ at the temperature of heating. Atmospheric air contains about 0.03 per cent of carbon dioxide by volume; when the pressure is 760 mm., this corresponds to 760 x 0.0003 = 0.228 mm. of mercury. Calcium carbonate will therefore be perfectly stable in the atmosphere so long as the decomposition pressure does not exceed 0.23 mm. of mercury. The dissociation pressures of calcium carbonate, expressed in mm. of mercury, at various temperatures are collected in the following table:

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>Dissociation Pressure</th>
<th>Temp., °C</th>
<th>Dissociation Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>7.8 x 10⁻⁹</td>
<td>700</td>
<td>31.2</td>
</tr>
<tr>
<td>400</td>
<td>0.3 x 10⁻³</td>
<td>800</td>
<td>208</td>
</tr>
<tr>
<td>500</td>
<td>0.15</td>
<td>882</td>
<td>780</td>
</tr>
<tr>
<td>600</td>
<td>2.98</td>
<td>900</td>
<td>984</td>
</tr>
</tbody>
</table>

Thus calcium carbonate will not commence to dissociate appreciably in the atmosphere until a temperature of slightly above 600° C. Actual experiment has shown that complete decomposition of calcium oxalate into the carbonate occurs at a temperature between 475° and 525° C.; above 550° C. the calcium carbonate commences to lose carbon dioxide. For the weighing of calcium oxalate as calcium carbonate, fine temperature control is necessary; this can be achieved only by the use of an electrically heated muffle furnace, provided with a pyrometer or suitable thermometer. If such equipment is available, the method should be used in preference to all others; the oxalate must be filtered through a Gooch (preferably of silica) or porcelain filtering-crucible and not through filter-paper.

Above 882° C. calcium carbonate is completely decomposed into the oxide, but unless the carbon dioxide is removed by diffusion, convection, etc., by conducting the ignition in a loosely covered crucible, there will be a re-combination of calcium oxide and carbon dioxide on cooling, with the formation of some calcium carbonate. In practice, it is found that the rate of decomposition at about 900° C. is very slow, and it is best to use a temperature of 1100–1200° C. This temperature is not easily attained in a porcelain or silica crucible unless an electrically heated muffle furnace is employed. However, quantities up to 1 g. can be completely decomposed in a platinum crucible by the use of a Meker or Fisher high-temperature burner. The residue of calcium oxide is hygroscopic (unless heated for a considerable time above 1200° C.). The crucible should be kept covered in a desiccator, containing pure concentrated sulphuric acid, freshly ignited quicklime, or stick sodium hydroxide, for only 25–30 minutes, and weighed.

Procedure. Weigh out accurately sufficient of the sample to contain 0.2 g. of calcium * into a covered 400- or 600-ml. beaker provided with

* 0.5 Gram of A.R. calcium carbonate, or of calcite, which has been finely powdered in an agate mortar and dried at 110–130° C. for 1 hour, is suitable.
Quantitative Inorganic Analysis

a stirring-rod. Add 10 ml. of water, followed by about 15 ml. of dilute hydrochloric acid (1:1). Heat the mixture until the solid has dissolved, and boil gently for several minutes in order to expel carbon dioxide. Rinse down the sides of the beaker and the clock-glass, and dilute to 200 ml.; add 2 drops of methyl red indicator. Heat the solution to boiling, and add very slowly a warm solution of 2 g. of ammonium oxalate in 50 ml. of water. Add to the resultant solution filtered dilute ammonia solution (1:1) dropwise and with stirring until the mixture is neutral or faintly alkaline (colour change from red to yellow). Allow the solution to stand without further heating for at least an hour. After the precipitate has settled, test the solution with a few drops of ammonium oxalate solution for complete precipitation. The subsequent procedure will depend as to whether the calcium oxalate is to be weighed as the carbonate or as the oxide.

**Weighing as calcium carbonate.** Decant the clear supernatant liquid through a weighed silica Gooch crucible or a porous-porcelain filtering-crucible. Transfer the precipitate to the crucible with a jet of water from the wash-bottle; any precipitate adhering to the beaker or to the stirring-rod is transferred with the aid of a rubber-tipped rod (“policeman”). Wash the precipitate with a cold, very dilute ammonium oxalate solution (0·1–0·2 per cent) at least 5 times, or until the washings give no test for chloride ion (add dilute nitric acid and a few drops of silver nitrate solution to 5 ml. of the washings). Dry the precipitate in the steam-oven or at 100–120° C. for 1 hour, and then transfer to an electrically heated muffle furnace, maintained at 500 ± 25° C. for 2 hours. Cool the crucible and contents in a desiccator, and weigh. Further heating at 500° C. should not affect the weight. As a final precaution, moisten the precipitate with a few drops of saturated ammonium carbonate solution, dry at 110° C., and weigh again. A gain in weight indicates that some oxide was present; this should not occur.

Calculate the percentage of calcium in the sample. The factor for converting CaCO₃ to Ca is 0·40044.

**Weighing as calcium oxide.** Decant the clear, supernatant liquid through a Whatman No. 40 or 540 filter-paper, transfer the precipitate to the filter (Section II, 35), and wash with a cold 0·1–0·2 per cent ammonium oxalate solution until free from chloride. Transfer the moist precipitate to a previously ignited and weighed platinum crucible, and ignite gently at first over a Bunsen flame and finally for 10–15 minutes with a Méker or Fisher high-temperature burner until two successive weighings do not differ by more than 0·0003 g. The crucible and contents are weighed after cooling in a desiccator containing pure concentrated sulphuric acid or stick sodium hydroxide (but not calcium chloride) for 25 minutes only.

Calculate the percentage of calcium in the sample. The factor for converting CaO to Ca is 0·71469.

For other methods for the determination of calcium, see Section IV, 43.

**IV, 11. Determination of magnesium as the ammonium phosphate hexahydrate and as the pyrophosphate.**—Discussion. A cold acid solution of the magnesium salt is treated with an excess of diammonium hydrogen phosphate, and then excess of ammonia solution is added
to precipitate magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$, at room temperature:

$$\text{MgCl}_2 + (\text{NH}_4)_2\text{HPO}_4 + \text{NH}_4\text{OH} = \text{MgNH}_4\text{PO}_4 + 2\text{NH}_4\text{Cl} + \text{H}_2\text{O}$$

This precipitate possesses a relatively high solubility (about 65 mg. per litre at 10° C. in pure water, but less in the presence of ammonium hydroxide) and therefore forms more slowly than, for example, barium sulphate; the solution should therefore stand for at least several hours before filtration. The precipitate is washed with 1·5M-ammonium hydroxide solution † (say, 1 : 9) and then weighed either as the hexahydrate $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$ or as the pyrophosphate $\text{Mg}_2\text{P}_2\text{O}_7$.

For the former, the precipitate is washed with alcohol, followed by anhydrous ether, and weighed after standing at room temperature (preferably in a desiccator) for about 20 minutes. This method is of moderate accuracy, and is recommended here because of difficulties which attend the ignition of the precipitate and the time saving achieved.

For the latter, the precipitate is ignited at a high temperature (1100° C.) to magnesium pyrophosphate and weighed as such:

$$2\text{MgNH}_4\text{PO}_4 = \text{Mg}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O}$$

To obtain a precipitate of the correct composition ($\text{MgNH}_4\text{PO}_4$) at the first precipitation is a difficult matter owing to the co-precipitation of ammonium phosphate and magnesium phosphates; however, if the experimental conditions are carefully chosen and a pure magnesium salt is used, a precipitate of normal composition is formed. If the precipitation takes place in the presence of much ammonium salts, the precipitate contains $\text{Mg}_3(\text{PO}_4)_2$ or $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$; the former is unchanged by ignition, and the latter gives magnesium metaphosphate. If the precipitation is made in the presence of much potassium or sodium salts, the precipitate is contaminated with magnesium potassium (or sodium) phosphate. Hence if much ammonium, potassium, or sodium salts are present, re-precipitation is essential. In any case, re-precipitation is desirable to procure the best results. The double-precipitation process will accordingly be described. It is an experimental fact that the precipitate is practically insoluble in 10 per cent ammonia solution: this is accordingly used as the wash liquid.

Great care must be taken in the conversion of magnesium ammonium phosphate into the pyrophosphate. The carbon must be burnt off at as low a temperature as possible, because of the danger of the reduction of the phosphate precipitate if the heating is strong while carbon remains; if a platinum crucible is used, the resultant phosphorus may lead to serious injury of the crucible. Furthermore, if the heating is rapid, a dark-coloured product is obtained. For these reasons, the charring of the paper and the burning off of the carbon are conducted at as low a temperature as possible; the temperature must be raised very gradually. Some authors recommend, particularly for

* The precipitation should be carried out at 15–30° C. in order to ensure the absence of the monohydrate, $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$. The latter salt forms and is stable in solutions above 62° C.; when once formed, it takes about 24 hours standing at room temperature before it is converted into the hexahydrate.

† The approximate solubilities, expressed as mg. of $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$ per litre, at room temperature in ammonium hydroxide solutions of various concentrations are: 0·12M, 12; 0·3M, 6; 0·6M, 3; 1·2M, 1; 1·7M, 0·8.
Quantitative Inorganic Analysis

elementary students, that the filter paper be ignited apart from the precipitate (Section II, 366) in order to minimise this danger. It is preferable, however, to collect the precipitate in a porous-porcelain filter-crucible (e.g., of the Selas type): this is then heated in an electric muffle furnace at 1050–1150°C.

Procedure. To a neutral or slightly acid (hydrochloric) solution of a magnesium compound, containing not more than 0.1 g. of magnesium,* add 5 ml. of concentrated hydrochloric acid, and dilute to 150 ml. Add a few drops of methyl-red indicator to the cold solution, and then 10 ml. of the freshly prepared ammonium phosphate reagent (25 g. of A.R. (NH₄)₂HPO₄ dissolved in 100 ml. of water). Now add pure concentrated ammonia solution slowly while stirring the solution vigorously until the indicator turns yellow. Avoid scratching the sides of the beaker with the stirring-rod, for wherever there is contact, an adhering crystalline deposit forms quickly. Continue to stir the solution for 5 minutes, adding ammonia solution dropwise to keep the solution yellow, and finally add 5 ml. of concentrated ammonia solution in excess. Allow the solution to stand in a cool place for at least 4 hours or preferably overnight. The precipitate may be weighed either as MgNH₄PO₄·6H₂O or as Mg₂P₂O₇.

Weighing as MgNH₄PO₄·6H₂O. Filter through a sintered-glass or porous-porcelain crucible which has been washed with alcohol and ether as described below and weighed. Wash with small portions of dilute ammonia solution (1 : 9; ca. 1·5M) until a few ml. of the filtrate, when acidified with dilute nitric acid and tested with silver nitrate solution, gives no test for chloride. Now wash with three 10-ml. portions of rectified spirit (95 per cent ethyl alcohol), draining well after each washing; this serves to remove most of the adhering water. Finally, wash with five 5-ml. portions of anhydrous ether, draining after each washing. Then draw air through the crucible for 10 minutes, wipe the outside of the cold crucible with a clean linen cloth, and allow to stand in the air or in a desiccator for 20 minutes. Weigh as MgNH₄PO₄·6H₂O.

Weighing as Mg₂P₂O₇. Filter through a Selas porous filter-crucible, taking great care to remove all the precipitate from the beaker and stirring-rod, wash with cold 1·5M-ammonium hydroxide solution until the washings give no turbidity with dilute nitric acid and silver nitrate solution. Dry the filter crucible in an air oven at 100–150°C. for an hour, and then heat it gradually in an electric muffle furnace at 1000–1100°C, and maintain it at this temperature until constant weight is attained. If an electric furnace is not available, place the porcelain filter crucible inside a nickel crucible (Fig. II, 37, 4) (or use the ignition dish supplied with the crucible), and then heat gradually to the full heat of a Meker, Fisher, or equivalent burner. Heat for 25–30-minute periods until constant weight is attained. Weigh as Mg₂P₂O₇.

Alternatively, but less satisfactorily, the precipitate may be filtered through a quantitative filter-paper. Wash the precipitate on the paper with cold 1·5M-ammonium hydroxide solution until the washings give no turbidity with dilute nitric acid and silver nitrate solution. Dry the precipitate at 100°C. and place it in a previously ignited and weighed platinum crucible (1). Char the paper slowly without allowing it to ignite, and burn off the carbon at as low a temp-

* About 0·6 g. of A.R. magnesium sulphate, accurately weighed, is a convenient quantity of magnesium salt to employ for this estimation.
perature as possible with free access of air (gradually increase the flame, but do not heat the crucible to more than the faintest red), and then ignite to constant weight in an electric muffle furnace at 1050-1100° C. or, less desirably, over a Meker or Fisher high-temperature burner.

Calculate the percentage of magnesium in the compound. The factor for converting \( \text{Mg}_2\text{P}_2\text{O}_7 \) to Mg is 0.21851.

**Note.** 1. For elementary students it is sufficient to dry the filter with the precipitate in the steam-oven (or at 100° C.), and to incinerate the filter-paper apart from the precipitate (Section II, 36C) as low a temperature as possible; the paper should not be allowed to take fire. After the volatile carbonaceous matter has been burnt off, the residue may be ignited strongly with the lid of the crucible displaced, to allow circulation of the air, until the residue is as white as possible. The main precipitate is added, and the whole ignited to constant weight as described above.

If there is time for a second precipitation, or if a pure magnesium salt is not used and consequently the purity of the precipitate may be suspect, it is advisable to carry out a second precipitation. In this case the first precipitate must always be collected on a quantitative filter-paper: a little 1.5M-ammonium hydroxide solution should be used to assist the transfer of most of the precipitate to the filter-paper. Dissolve the precipitate on the filter-paper in approximately 50 ml of warm dilute hydrochloric acid (1 : 10), and wash the paper thoroughly with hot very dilute hydrochloric acid (1 : 100) into the beaker used for the initial precipitation. Dilute to 125-150 ml, add a few drops of methyl red indicator, 0.3 g. of A.R. diammonium hydrogen phosphate, and again precipitate the magnesium ammonium phosphate by the addition of concentrated ammonia solution dropwise (preferably from a burette) and with constant stirring until the solution is yellow, followed by a further 5 ml of the ammonia solution. Allow the solution to stand for at least 4 hours or, better, overnight. Weigh the precipitate as \( \text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O} \) or as \( \text{Mg}_2\text{P}_2\text{O}_7 \) as detailed above.

For other methods for the determination of magnesium, see Section IV, 46.

**IV. 12. Determination of nickel as the dimethylglyoxime complex.**—

**Discussion.** The nickel is precipitated by the addition of an alcoholic solution of dimethylglyoxime \[ \text{CH}_3\cdot\text{C}((\text{NOH})\cdot\text{C}((\text{NOH})\cdot\text{CH}_3, \text{referred to in what follows as } \text{H.Dmg}) \] to a hot, slightly acid solution of the nickel compound, and then adding a slight excess of ammonia solution. The precipitate is washed and weighed as nickel dimethylglyoxime after drying at 100-120° C. (compare Section I, 62A):

\[
\text{NiSO}_4 + 2\text{H.Dmg} = \text{Ni(Dmg)}_2 + \text{H}_2\text{SO}_4
\]

The precipitate is soluble in free mineral acids (even as much as is liberated by reaction in neutral solution), in alcoholic solutions containing more than 50 per cent of alcohol by volume, in hot water (0-6 mg. per 100 ml.), and in concentrated ammoniacal solutions of cobalt salts, but is insoluble in dilute ammonia solution, in solutions of ammonium salts, and in dilute acetic acid–sodium acetate solutions. Excessive amounts of ammonium hydroxide, cobalt, or copper retard the precipitation. Better results are obtained in the presence of cobalt, manganese, or zinc by adding sodium or ammonium acetate to precipitate the complex (compare Section IV, 90D); ferric iron must, however, be absent.
Dimethylglyoxime forms sparingly soluble salts with palladium, platinum, and ferrous iron, whilst gold is reduced. These elements, and indeed all the elements of the hydrogen sulphide group, should be absent. Ferric iron, aluminium, and chromic chromium are rendered inactive by the addition of a soluble tartrate or citrate, with which these elements form complex ions.

Dimethylglyoxime is almost insoluble in water, and is added in the form of a 1 per cent solution in rectified spirit or absolute alcohol; 1 ml. of this solution is sufficient for the precipitation of 0·0025 g. of nickel. As already pointed out, the reagent is added to a hot feebly acid solution of a nickel salt, and the solution is then rendered faintly alkaline. This procedure gives a more easily filterable precipitate than does direct precipitation from cold or from ammoniacal solutions. Only a slight excess of the reagent should be used, since dimethylglyoxime is not very soluble in water or in very dilute alcohol and may precipitate; if a very large excess is added (such that the alcohol content of the solution exceeds 50 per cent), some of the precipitate may dissolve.

Procedure. A. Nickel in a nickel salt. Weigh out accurately 0·3–0·4 g. of pure (preferably A.R.*) nickel ammonium sulphate NiSO₄·(NH₄)₂SO₄·6H₂O into a 400-ml. beaker provided with a clock-glass cover and stirring-rod. Dissolve it in water, add 5 ml. of dilute hydrochloric acid (1 : 1) and dilute to 200 ml. Heat to 70–80° C., add a slight excess (30–35 ml.) of the dimethylglyoxime reagent, and immediately add dilute ammonia solution dropwise and with constant stirring until precipitation takes place and then in slight excess (alternatively, 3–4 g. of sodium acetate may be used to effect precipitation).† Allow to stand on the steam-bath for 20–30 minutes, and test the solution for complete precipitation when the red precipitate has settled out. Allow the precipitate to stand for 1 hour, cooling at the same time. Filter the cold solution through a Gooch, sintered-glass or porous-porcelain crucible, previously heated to 110–120° C. and weighed after cooling in a desiccator. Wash the precipitate with cold water until free from chloride, and dry it at 100–120° C. for 45–60 minutes. Allow to cool in a desiccator and weigh. Repeat the drying until constant weight is attained. Weigh as Ni(C₄H₇O₂N₂)₂, which contains 20·32 per cent of Ni.

Calculate the percentage of nickel in the salt.

B. Nickel in nickel steel. Weigh out accurately about 1 g. of the drillings or borings of the nickel steel † (or sufficient of the sample to contain 0·03–0·04 g. of nickel) into a 100–150-ml. beaker or porcelain basin, dissolve it in the minimum volume of concentrated hydrochloric acid (about 20 ml. should suffice), and boil with successive additions of concentrated nitric acid (ca. 5 ml.) to ensure complete oxidation of the iron to the ferric state. Dilute somewhat, filter, if necessary, from any solid material, and wash the paper with hot water; dilute the filtrate (or solution) to 250 ml. in a 400-ml. beaker. Add 5 g. of citric or tartaric acid, neutralise the solution with dilute ammonium hydrox-

* This is obtainable from the Mallinckrodt Chemical Works, U.S.A. Alternatively, sufficient of a nickel salt to contain about 0·05 g. of nickel may be used.
† The sodium acetate method cannot be used in the presence of ferric iron; ferrous iron does not interfere. † Ridsdale’s “Nickel Steel, No. 22a” (one of the Analysed Samples for Students) or the Bureau of Analysed Samples “Nickel Steel, No. 222” (a British Chemical Standard) is suitable. Both steels contain about 4 per cent of nickel.
Gravimetric Analysis

ide solution, * and then barely acidify (litmus) with dilute hydrochloric acid. Warm the solution to 60–80°C, add a slight excess of a 1 per cent alcoholic solution of dimethylglyoxime (25–30 ml.), immediately followed by dilute ammonia solution until the liquid is slightly ammoniacal, stir well, and allow to stand on the steam-bath for 20–30 minutes. Allow the solution to stand at least 1 hour and cool to room temperature during this time. Filter off the precipitate through a weighed filter-crucible; test the filtrate for complete precipitation with a little dimethylglyoxime solution, and wash the precipitate with cold water until free from chloride. Dry the precipitate at 110–120°C for 45–60 minutes, and weigh as Ni(C₄H₇O₂N₂)₂.

Calculate the percentage of nickel in the steel.

For other methods for the determination of nickel, see Section IV, 32.

SYSTEMATIC GRAVIMETRIC ANALYSIS

IV, 13. General discussion.—In the succeeding sections a brief account will be given of a number of selected methods for the gravimetric determinations of the various elements and radicals. It is believed that these will suffice to meet the needs of the student during the whole period of his training; for a more detailed study, particularly of the limitations of some of the various methods, reference must be made to other treatises.†

It has been considered expedient, following Hillebrand and Lundell, to treat the elements and radicals in the following order:

(a) Elements that give precipitates with hydrogen sulphide in acid solution: lead, silver, mercury, bismuth, cadmium, copper, arsenic, antimony, tin, molybdenum, selenium, tellurium, gold, palladium, platinum (thallium). Of these the sulphides of lead, silver, mercury, bismuth, cadmium, copper, and palladium are insoluble in acids and in solutions of alkali sulphides.

(b) Elements that give precipitates with hydrogen sulphide in alkaline solution (or with ammonium sulphide): aluminium, beryllium, chromium, iron, nickel, cobalt, zinc, manganese, vanadium, uranium, thorium, cerium, titanium, zirconium, thallium. Of these, iron, nickel, cobalt, zinc, manganese, vanadium, uranium, and thallium form sulphides that are soluble in acids, whilst the following elements form hydroxides or basic compounds: aluminium, chromium, beryllium, thorium, cerium, zirconium, and titanium.

(c) The alkaline-earth elements (calcium, strontium, and barium) and magnesium.

* If a precipitate appears or if the solution is not clear when it is rendered ammoniacal, more tartaric or citric acid must be added until a perfectly clear solution is obtained upon adding dilute ammonia solution. Any insoluble matter should be filtered off and washed with hot water containing a little ammonia solution.

The alkali elements: sodium, potassium, and lithium (ammonium).

Tungsten.

The anions in the empirical order: chloride, bromide, iodide, thiocyanate, cyanide, fluoride, chlorate, perchlorate, iodate, sulphate, sulphide, sulphone, thiosulphate, phosphate, phosphite, hypophosphite, oxalate, borate, silicate, fluosilicate, ferrocyanide, ferricyanide, nitrite, nitrate, and carbonate.

IV, 14. LEAD

Discussion. Lead may be estimated in the following forms:

A. Lead sulphate, PbSO₄. This provides a separation from the numerous elements which form soluble sulphates. Calcium, strontium, barium, mercury, tungsten, silver, bismuth, antimony, and silica all interfere to a greater or less extent. Hydrochloric and nitric acids exert a solvent action upon lead sulphate, hence if these are present, the solution must be evaporated twice with sulphuric acid until dense white fumes are evolved. Lead sulphate is slightly soluble in dilute sulphuric acid, although with the extremely dilute acid, the solubility is less than in water (0.0040 g. per litre at 18° C.), owing to the common-ion effect; it is almost insoluble in alcohol. A satisfactory wash solution is a dilute solution of sulphuric acid that has been saturated with lead sulphate at the laboratory temperature.

At a red heat it is easily reduced by carbonaceous matter, with loss of lead by volatilisation. For this reason the precipitate is best collected in a filtering-crucible, and dried at 500–600° C.

B. Lead chromate, PbCrO₄. This determination is more accurate than A, but is limited in its applicability because of the general insolubility of chromates.

C. Lead molybdate, PbMoO₄. This is an excellent method, since the substance has a high molecular weight, is less soluble than the sulphate, and suffers no change upon ignition. Substances which form insoluble molybdates (e.g., the alkaline-earth metals, copper, and cadmium), which are easily hydrolysed (e.g., tin or titanium), and which form insoluble compounds with lead (e.g., chromates, arsenates, or phosphates) must be absent.

D. Lead salicylaldoxime, Pb(C₇H₆O₅N). Lead may be precipitated in strongly ammoniacal solution (pH 9-3 or higher) with salicylaldoxime as the lead salicylaldoxime complex Pb(C₇H₆O₅N); it may thus be separated from copper, nickel, cobalt, bismuth, iron, magnesium, manganese, and mercury, the salicylaldoximates of which are not sufficiently soluble in ammoniacal solution (see Section I, 62E).

E. Lead iodate, Pb(IO₃)₃. Lead iodate is sufficiently insoluble in very dilute nitric acid to make possible its use in the gravimetric and volumetric determination of the element. It may thus be separated from moderate amounts of aluminium, manganese, zinc, cadmium, calcium, strontium, and magnesium; titanium, zirconium, thorium, silver, mercury, bismuth, and appreciable quantities of iron interfere.

F. Lead dioxide, PbO₂. This excellent electrolytic method is described in Section IV, 79.

A. Determination of lead as sulphate. Procedure. Weigh out accurately about 0.3 g. of the lead salt * into a 10-cm. porcelain basin, dissolve it in about 20 ml. of water, add 2 ml. of pure concentrated sulphuric acid, evaporate the mixture as far as possible on the water-

* A.R. lead nitrate is suitable. If the substance is insoluble in water, dissolve it in the minimum quantity of nitric acid.
bath, then on a sand-bath, wire-gauze, or low-temperature hot-plate until thick white fumes of sulphuric acid are freely evolved. This ensures the complete removal of nitric acid and conversion of the lead salt into the sulphate.* Cool, dilute carefully with 40 ml. of water (the final solution should contain about 4 ml. of concentrated sulphuric acid in 100 ml. of solution), mix thoroughly, and allow to stand for at least an hour. Filter off the precipitate of lead sulphate through a weighed porcelain or silica Gooch crucible or through a porous-porcelain filtering-crucible. Wash the precipitate three times with 3 per cent (by volume) sulphuric acid saturated with lead sulphate (compare Section IV, 57A). Dry the crucible and contents at 100°C. for 1 hour, and then place it inside a nickel crucible (Fig. II, 31, 4) and heat gradually to a dull red heat (500-600°C.) until constant weight is obtained. Alternatively, the precipitate, collected on a sintered-glass or porous-porcelain filtering-crucible and washed as above, may be washed with rectified spirit until free from sulphate (1), and then dried at 130°C. to constant weight. Weigh as PbSO₄.†

Calculate the percentage of lead in the sample.

Note. 1. For the rapid weighing of the lead sulphate, the alcohol washing is followed by several washings with small volumes of anhydrous ether, and the precipitate is sucked dry at the pump for 10 minutes. The outside of the crucible is then wiped with a clean linen cloth, left in a vacuum desiccatior for 10 minutes, and weighed.

B. Determination of lead as chromate. Procedure (compare Section III, 109). Weigh out 0.3 g. of the lead salt (1), dissolve it in 150 ml. of water, and add dilute acetic acid to the solution until it is distinctly acid. Heat to boiling, add from a pipette 4 per cent potassium chromate solution in slight excess (10 ml. will usually suffice). Boil gently for 5-10 minutes (or until the precipitate settles); the supernatant liquid must be coloured slightly yellow. Filter through a Gooch, sintered-glass or porous-porcelain filtering-crucible, wash thoroughly with a hot, dilute solution of sodium acetate or with hot water. Dry at 120°C. to constant weight. Weigh as PbCrO₄.

Note. 1. A.R. lead nitrate is suitable for practice in this estimation. If the solution is neutral or basic, add acetic acid until it is distinctly acid. If the solution contains nitric acid, add sufficient sodium acetate (5-10 g.) to replace the nitric acid by acetic acid.

C. Determination of lead as molybdate. Procedure. Weigh out 0.3 g. of the lead salt, dissolve it in 200 ml. of water, and add 4 drops of concentrated nitric acid. Heat to boiling, and slowly add from a burette or pipette, with stirring, a 2.5 per cent aqueous solution of ammonium para-molybdate. When precipitation appears to be complete, boil for 1 minute, allow the precipitate to settle, and add a few drops of the precipitant to the supernatant liquid. If a precipitate forms, repeat the process until the ammonium molybdate is present in slight excess. When precipitation is complete, add dilute ammonia solution (1:2) dropwise until the solution is neutral or slightly alkaline to litmus. Acidify with a few drops of acetic acid, and allow to stand

* For work demanding the highest accuracy, allow to cool, wash down the sides of the dish, and repeat the evaporation.
† The conversion factors for all the determinations described in this and the following Sections are collected in the Appendix (Section A, 2).
Quantitative Inorganic Analysis

for a few minutes. Decant the supernatant liquid through a weighed porcelain or silica (Vitreosil) filter-crucible, and wash the precipitate 3 or 4 times by decantation with 75-ml. portions of 2 per cent ammonium nitrate solution. Transfer the precipitate to the filter, and wash until the washings give no test for molybdenum (e.g., no brown precipitate with potassium ferrocyanide solution). Place the filter-crucible inside a nickel crucible (Fig. II, 37, 4) or upon a crucible-ignition dish, and gradually heat to dull redness. Maintain the crucible at dull redness for 10 minutes, cool in a desiccator, and weigh. Repeat the heating, etc., until constant weight is attained. Weigh as PbMoO₄.

D. Determination of lead as the salicylaldoximate. Procedure. To a solution (ca. 25 ml.) of lead nitrate or lead acetate containing about 0.1 g. of Pb, add 10 ml. of a freshly prepared 1 per cent salicylaldoxime solution (for preparation, see Section I, 62E), dilute to 50 ml. and add 12.5 ml. of concentrated ammonia solution. Stir the resulting precipitate for 1 hour and allow to settle. Decant the supernatant liquid through a sintered-glass crucible (porosity No. 4), wash the precipitate by decantation until free from salicylaldoxime (as shown by the absence of a colour with ferric chloride solution), dry at 105°C. for 1 hour, and weigh as Pb(C₇H₇O₂N).

E. Determination of lead as iodate. Procedure. The solution may contain up to 0.3 g. of Pb (I) in 150 ml. of water, and should preferably be neutral. Add 4 ml. of concentrated nitric acid, heat to boiling, and introduce 25-30 ml. of 6 per cent iodic acid solution slowly and with constant stirring. Continue stirring for 2 minutes after the iodic acid reagent has been added, and keep at 60-70°C. for 30 minutes. Cool to the laboratory temperature, filter through a sintered-glass crucible (porosity No. 3), wash the precipitate with 75 ml. of 0.2 per cent iodic acid in 1 per cent v/v nitric acid, then with three 2-ml. portions of ice-cold water, and finally twice with a little dry acetone. Draw air through the precipitate (water-pump) for 5 minutes. Dry at 140°C. to constant weight (about 1 hour). Weigh as Pb(IO₃)₂.

The lead may also be determined volumetrically as follows. Dissolve the precipitate in hot 10 per cent sodium hydroxide solution (2), and wash the filter with 2 per cent sodium hydroxide solution. Cool the solution, add 4 g. of pure potassium iodide, then a large excess of concentrated hydrochloric acid, and titrate with standard 0.1N-sodium thiosulphate solution.

Notes. 1. About 0.45 g., accurately weighed, of dry A.R. lead nitrate may be employed for practice in this determination.
2. A protective layer of lead chloride is formed with hydrochloric acid.

IV, 15.

SILVER

Discussion. This element is usually determined as silver chloride, AgCl. The theory of the process has been given under Chloride (Section IV, 5). Lead, cuprous, palladous, mercurous, and thallous ions interfere, as do cyanides and thiosulphates. If a mercurous (or cuprous or thallous) salt is present, it must be oxidised with concentrated nitric acid before the precipitation of silver; this process also destroys cyanides and thiosulphates. If lead is present, the solution must be diluted so that it contains not more than 0.25 g. of the substance in 200 ml., and the hydrochloric acid must be added very slowly.

Silver may also be determined electrolytically; for details see Section IV, 83.
Determination of silver as chloride. Procedure. The solution (200 ml.) should contain about 0.1 g. of silver (1) and about 1 per cent by volume of nitric acid. Heat to about 70° C., and add approximately 0.2N pure hydrochloric acid slowly and with constant stirring until no further precipitation occurs; avoid a large excess of the acid. Do not expose the precipitate to too much bright light. Warm until the precipitate settles, allow to cool to about 25° C., and test the supernatant liquid with a few drops of the acid to be sure that precipitation is complete. Allow the precipitate to settle in a dark place for several hours or, preferably, overnight. Pour the supernatant liquid through a weighed Gooch, sintered-glass or porous-porcelain crucible, wash the precipitate by decantation with 0.1N-nitric acid, transfer the precipitate to the crucible, and wash again with 0.01N-nitric acid until free from chloride. Dry the precipitate first at 100° C. and then at 130–150° C., allow to cool in a desicator and weigh. Repeat the heating, etc., until constant weight is obtained (2). Weigh as AgCl.

Notes. 1. For example, from 0-2 g. of A.R. silver nitrate. 2. See last footnote in Section IV, 5.

IV, 16. MERCURY

Discussion. Mercury may be estimated in the following forms:

A. Mercuric sulphide, HgS. The precipitation of mercury in hydrochloric acid solution by hydrogen sulphide as mercuric sulphide is an accurate procedure in the absence of copper, cadmium, tin, zinc, and thallium; the latter metals complicate reactions which are based upon the behaviour of pure mercuric sulphide. Unless the experimental conditions detailed below are strictly followed, the precipitate is liable to be contaminated with a little sulphur, which must be removed by extraction with carbon disulphide. Oxidising agents (nitric acid, chlorine, ferric chloride, etc.) must be absent.

B. Mercury zinc thiocyanate, Hg\([Zn(CNS)\_4]\). This method is based upon the precipitation of mercury from mercuric compounds in neutral or acid solutions as mercuric zinc thiocyanate with a reagent which contains 39 g. of ammonium thiocyanate and 29 g. of zinc sulphate per litre. For quantitative precipitation not more than 5 per cent of free acid should be present in the solution before the addition of the precipitating agent. If a larger quantity of acid is present, it must be neutralised with sodium hydroxide solution: ammonia solution should not be used, because an excessive quantity of ammonium salts exerts a solvent action upon the precipitate. Cadmium, cobalt, copper, bismuth, manganese, and mercurous compounds must be absent, since they give insoluble thiocyanates with the reagent; small quantities of nickel do not interfere.

C. Copper ethylenediamine mercuri-iodide \([\text{Cu en}_2][\text{HgI}_4]\); ethylenediamine method. This is a rapid method for the determination of mercury, but numerous elements interfere.

For further discussion, see Section I, 620.

D. Mercuric para-periodate, Hg\(_5\)(IO\(_6\))\(_2\). Mercury may be determined by precipitation with sodium periodate as mercuric para-periodate Hg\(_5\)(IO\(_6\))\(_2\): moderate amounts of copper, cadmium, aluminium, nickel, zinc, and magnesium do not interfere, but iron must be absent, as it is precipitated as ferric periodate. Chlorides and other halides must be absent because they prevent complete precipitation of mercury. The maximum possible acidity for complete precipitation is 0.15N-nitric acid or 0.1N-sulphuric acid, and under these conditions a large excess of periodate is required.
Quantitative Inorganic Analysis

A. Determination of mercury as sulphide. Procedure. Weigh out accurately about 0.15 g. of the mercuric salt (1), dissolve it in 100 ml. of water, and add a few ml. of dilute hydrochloric acid. Saturate the cold solution with washed hydrogen sulphide (2), allow the precipitate to settle, and filter through a weighed Gooch, sintered-glass or porous-porcelain crucible. Wash the precipitate with cold water (3), and weigh it, as HgS, after drying at 105–110°C. (4).

Notes. 1. A.R. mercuric chloride is suitable. Alternatively, the solution should contain not more than 0.1 g. of mercuric mercury per 100 ml., and should be free from oxidising agents.
2. The colour of the mercuric sulphide precipitate will become perfectly black as soon as the liquid is saturated with the gas.
3. If the presence of sulphur is suspected, the precipitate is washed with hot water, alcohol, carbon disulphide, or alcohol + ether, and then dried at 105–110°C.
4. A rapid method for weighing the precipitate, collected in a sintered-glass or porous-porcelain crucible, is as follows. After washing the mercuric sulphide with cold water, wash it five or six times with rectified spirit, followed by several times with small volumes of anhydrous ether, and then suck the precipitate dry on the pump for 10 minutes. Wipe the outside of the crucible dry with a clean linen cloth and leave in a vacuum desiccator for 10 minutes. Weigh as HgS.

B. Determination of mercury as mercuric zinc thiocyanate. Procedure. Weigh out accurately about 0.2 g. of the mercuric salt (e.g., A.R. mercuric chloride) into a 250-ml. beaker, and dissolve it in 100 ml. of cold water containing 2 drops of concentrated hydrochloric acid. Add 25 ml. of the ammonium thiocyanate–zinc sulphate reagent (see Discussion). Stir vigorously with a previously moistened glass rod for 2–3 minutes, but avoid touching the walls of the beaker. The initially clear liquid gradually becomes turbid during the stirring, and a white crystalline precipitate slowly forms. Allow the contents of the beaker to stand for at least 2 hours. Filter the precipitate on a weighed sintered-glass or porous-porcelain crucible; transfer the precipitate to the crucible with the aid of a wash-liquid composed of 5 ml. of the precipitating reagent and 450 ml. of water. (The precipitate is slightly soluble in water, but practically insoluble in the special wash-liquid.) Finally, wash the precipitate five times with the special wash-liquid, and then once with a little water to remove the adhering wash-liquid. Dry the crucible and precipitate in an electric oven maintained at 105 ± 2°C until constant in weight. Weigh as Hg[Zn(CNS)₂].

C. Determination of mercury by the ethylenediamine method. Procedure. The neutral or faintly ammoniacal mercury solution should occupy a volume of 80–500 ml., and contain not more than about 0.2 g. Hg. Treat with excess (say, 2–3 g.) of KI in the form of a 2 per cent solution, heat nearly to boiling and precipitate with a boiling, concentrated aqueous solution of copper ethylenediamine nitrate [Cu en₄(NO₃)₂] or of the corresponding sulphate (Section I, 620). Allow to cool to room temperature and filter off the dark blue-violet, crystalline complex [Cu en₄][HgI₄] on a weighed crucible (Gooch, sintered-glass, or porous-porcelain). Wash three to six times with a solution containing 0.2 g. of KI and 0.2 g. of [Cu en₄(NO₃)₂]₂H₂O (or the corresponding sulphate) in 200 ml. of water. To remove the water adhering to the wall of the crucible, wash three or four times with 2-ml. portions of 95 per cent
alcohol and finally three or four times with 2-ml. portions of anhydrous ether. Suck the precipitate dry at the pump for 10 minutes, and dry the precipitate for 10 minutes (or to constant weight) in a vacuum desiccator. Weigh as $[\text{Cu en}_2[HgI_4]]$.

For the determination of mercury in aqua regia solution (up to 0.3 g. Hg in 100–200 ml.), render the solution faintly alkaline with ammonia solution, add a large excess of potassium iodide (say, 3–4 g. KI in the form of a 2 per cent solution), heat to boiling and precipitate as above. When precipitation is complete, dilute with distilled water (one quarter of the total volume), allow to cool slowly to room temperature, and complete the determination as already detailed.

D. Determination of mercury as mercuric para-periodate. Procedure. For practice in this determination, dissolve about 0.2 g., accurately weighed, of A.R. mercury in nitric acid of sp. gr. 1.2, and evaporate the solution just to dryness. Dissolve in 150 ml. of 0.15N-nitric acid or 0.1N-sulphuric acid, heat to boiling, and add slowly and with constant stirring a solution of 2 g. of sodium or potassium periodate in 50 ml. of water. Allow to cool, collect the precipitate on a sintered-glass or porous-porcelain crucible, wash with warm water, and dry at 100°C. to constant weight. Weigh as Hg$_5$(IO$_4$)$_2$.

The mercury may also be determined volumetrically as follows. Transfer the precipitate quantitatively (for experimental details, see Section IV, 32D) to a filter-flask, add a solution of 2–3 g. of pure potassium iodide in 10–15 ml. of water, and stir until the periodate has dissolved. Acidify with 10 ml. of 2N-hydrochloric acid, and titrate the liberated iodine with 0.1N-sodium thiosulphate, using starch as indicator. The reaction is:

$$\text{Hg}_5(\text{IO}_4)_2 + 34\text{KI} + 24\text{HCl} = 5\text{K}_2[\text{HgI}_4] + 8\text{I}_2 + 24\text{KCl} + 12\text{H}_2\text{O}$$

IV, 17. BISMUTH

Discussion. Bismuth may be satisfactorily determined in the following forms:

A. Bismuth oxyiodide, BiOI. The cold bismuth solution, weakly acid with nitric acid, is treated with an excess of potassium iodide when BiI$_3$ and some K[BiI$_4$] are formed:

$$\text{Bi(NO}_3)_3 + 3\text{KI} = \text{BiI}_3 + 3\text{KNO}_2$$
$$\text{BiI}_3 + \text{KI} = \text{K}[\text{BiI}_4]$$

Upon dilution and boiling, bismuth oxyiodide is formed, and is weighed as such after suitable drying.

$$\text{BiI}_3 + \text{H}_2\text{O} = \text{BiOI} + 2\text{HI}$$
(black)

$$\text{K}[\text{BiI}_4] + \text{H}_2\text{O} = \text{BiOI} + \text{KI} + 2\text{HI}$$
(yellow)

A large excess of potassium iodide should be avoided, since the complex salt is not so readily hydrolysed as the tri-iodide. This is an excellent method, because the oxyiodide is precipitated in a form which is very convenient for filtration and weighing.

B. Bismuth pyrogallate, Bi(C$_6$H$_5$O$_3$)$_3$. The precipitation of bismuth with pyrogallol is quantitative only if the acidity (hydrochloric, sulphuric, or nitric acid) does not exceed 0.1N. The method is an excellent one for the determination of bismuth in the presence of lead, cadmium, and zinc. Antimony, which forms a similar complex, must, of course, be absent.
C. Bismuth oxide, Bi₂O₃, through the cupferron complex. The bismuth in hydrochloric or nitric acid solution is precipitated as the cupferron complex (see Section I, 62B), and the latter is converted by ignition into, and weighed as, Bi₂O₃. This procedure separates bismuth from cadmium, lead, arsenic, mercury, antimonial, and zinc ions.

D. Bismuth “oxinate”, Bi(O₂H₂ON)₃. This method uses oxine as the precipitating agent. For the advantages and limitations of this versatile reagent, see Section I, 62C. Halogens must be absent, as there is a tendency for compounds of the general formula (C₆H₄ON)₃BiX₃ (where X = halogen) to be precipitated.

E. Bismuth phosphate, BiPO₄. The precipitation of bismuth as phosphate is a good method for its determination. Under the correct experimental conditions a dense crystalline precipitate is obtained, which may be collected on a porous-porcelain filter-crucible, ignited, and weighed as BiPO₄. The procedure serves to separate bismuth from silver, copper, cadmium, mercury, and the aluminium, zinc, and calcium groups.

F. Metallic bismuth. The electrolytic method for the determination of the element is described in Section IV, 85.

A. Determination of bismuth as oxyiodide. Procedure. The cold bismuth nitrate solution, containing 0.1-0.15 g. of Bi (1), must be slightly acid with nitric acid (2), and occupy a volume of about 20 ml. Add finely powdered solid potassium iodide, slowly and with stirring, until the supernatant liquid above the black precipitate of bismuth tri-iodide is just coloured yellow (due to K[BiI₄]). Dilute to 200 ml. with boiling water, and boil for a few minutes. The black tri-iodide is converted into the copper-coloured precipitate of the oxyiodide. The supernatant liquid should be colourless; if this is yellow, a further 100 ml. of water should be added, and the boiling continued until colourless. Add a few drops of methyl orange indicator, and then sodium acetate solution (25 g. per litre) from a burette until the solution is neutral. Filter off the precipitate through a weighed Gooch, sintered-glass, or porous-porcelain crucible, wash with hot water, and dry at 105-110°C to constant weight. Weigh as BiOI.

Notes. 1. A suitable solution for practice can be obtained by dissolving about 0.15 g. of pure bismuth (the A.R. product is obtainable, inter alia, from the Mallinckrodt Chemical Works, U.S.A.), accurately weighed, in the minimum volume of 1:4 nitric acid.

2. Chloride and bromide should be absent. If the solution is strongly acid with nitric acid, it should be evaporated to dryness on the water-bath, and dissolved in a little dilute nitric acid.

B. Determination of bismuth as pyrogallate. Procedure. The solution (150 ml.) should be weakly acid with nitric acid and contain 0.1-0.2 g. of Bi. Treat the solution with dilute ammonia solution until a permanent turbidity is obtained; render the solution clear by the cautious addition of a little dilute nitric acid. Heat to boiling, and add a slight excess of a solution of pure pyrogallol (Section I, 62N) in air-free water. A yellow, finely crystalline precipitate is immediately formed. Boil for a short time, test for completeness of precipitation with a little of the reagent, dilute slightly, and filter through a weighed sintered-glass or porous-porcelain crucible after the precipitate settles out. Wash with 0.05N-nitric acid, and finally with water. Dry to constant weight at 105°C. Weigh as Bi(C₆H₃O₇)₃.

The following alternative method has been recommended. Add 1 g.
of pure pyrogallol to the solution (150 ml.) containing about 0.1 g. of Bi and heated to 70° C. Then add 0.5N-ammonium hydroxide solution dropwise until a distinct turbidity forms. Heat the resulting solution to boiling, add 2 drops of thymol-blue indicator, and then more of the ammonia solution until the solution is basic. Heat on a water-bath for 10 minutes, filter on a sintered-glass or porous-porcelain filter-crucible, wash, and dry to constant weight at 105° C. Weigh as Bi(C₆H₅O₇).  

**C. Determination of bismuth as oxide after precipitation as the cupferron complex. Procedure.** Treat the aqueous bismuth nitrate solution (200 ml.) with freshly prepared 6 per cent aqueous cupferron solution until there is present at least three times as much cupferron as bismuth (i.e., <0.3 g. per 0.1 g. Bi). Heat the solution to boiling, add ammonia solution until the liquid is alkaline (litmus-paper), followed by dilute nitric acid until it is just acid. Filter the precipitate through a quantitative filter-paper, and wash with 0.1 per cent cupferron solution containing a few drops of dilute nitric acid. Ignite in a crucible in the usual manner (Section II, 36), and finally with free access of air over the full flame of a Bunsen burner to constant weight. Weigh as Bi₂O₃.

**D. Determination of bismuth with "oxine." Procedure.** The solution of bismuth nitrate (100 ml.) should contain sufficient tartaric acid to prevent precipitation in the following stages. Add a drop or two of phenolphthalein, and then dilute ammonia solution until the indicator is just pink. Acidify with acetic acid, and add 1–2 g. of ammonium or sodium acetate for each 0.05 g. of Bi expected to be present. Heat to 60–70° C., treat rapidly with a saturated alcoholic solution of oxine (excess is without influence), then heat almost to boiling, and allow to cool. Filter off on a weighed sintered-glass or porous-porcelain crucible, wash with hot water, and dry to constant weight at 130–140° C. Weigh as Bi(C₉H₆O₅N)₃.

**E. Determination of bismuth as phosphate. Procedure.** The solution (100 ml.) may contain up to 0.1 g. of Bi and should be free from chloride. Add concentrated ammonia solution until a slight permanent precipitate is obtained; dissolve this precipitate in 2 ml. of dilute nitric acid (1:1). Heat to boiling and add, whilst stirring constantly, 30 ml. of 10 per cent diammonium hydrogen phosphate solution from a burette. Dilute to 400 ml. with boiling water, and allow to stand 10–15 minutes on a water-bath or hot plate. Decant through a weighed porous-porcelain filter-crucible and wash the precipitate with 3 per cent ammonium nitrate solution containing a few drops of nitric acid per litre. Dry and ignite gently upon a crucible-ignition dish or inside a larger crucible (Fig. II, 3); 4. Weigh as BiPO₄.

**IV, 18. CADMIUM**

**Discussion.** Cadmium may be determined in the following forms:

- **A. Cadmium molybdate, CdMoO₄.** The method is of limited application, since all metals other than magnesium and the alkali metals must be absent.

- **B. Cadmium β-naphthaquinoline complex ([C₁₈H₁₉N₄]H₂CdCl₂.** This method permits of the separation of cadmium from relatively large quantities of zinc, iron, chromium, aluminium, cobalt, nickel, manganese, and magnesium, and also from antimony and tin if ammonium oxalate or large amounts of sodium tartrate are used.
C. Cadmium quinaldinate, \( \text{Cd}(C_{6}H_{5}O_{2}N)_{2} \). Quinaldinic acid or its sodium salt precipitates cadmium quantitatively from acetic acid or neutral solutions. The precipitate is collected on a Gooch type of crucible, and dried at 125°C. A determination may be completed in about 90 minutes. For the limitations of the method, see Section I, 620.

D. \( [\text{Cd}(C_{6}H_{5}O_{2}N)_{2}](\text{CNS})_{3} \); pyridine method. If a hot neutral or faintly acid solution of a cadmium salt is treated with ammonium thiocyanate and pyridine, dipyridine cadmium thiocyanate is quantitatively precipitated. This precipitate is collected, and washed, \textit{inter alia}, with alcohol and ether containing a little pyridine; it may be dried simply by leaving in a vacuum desiccator for 15-20 minutes. A determination can thus be completed in less than an hour. The limitations of the method are discussed under Copper (Section IV, 19E). If the solution is weakly acid, ammonium thiocyanate may be added, followed by pyridine, until a precipitate just forms, the latter dissolved by warming, and a further 1 ml. of pyridine added.

E. Cadmium anthranilate, \( \text{Cd}(C_{7}H_{7}O_{2}N)_{2} \). The applications of anthranilic acid for the precipitation of cadmium and other elements are discussed in Section I, 62L. The solution should contain no free acid, no interfering elements, and no excessive amounts of neutral salts: acid solutions should be evaporated to dryness and the residue dissolved in the appropriate volume of water (160 ml. for up to 100 mg. of Cd).

F. Cadmium ammonium phosphate monohydrate, \( \text{CdNH}_{4}\text{PO}_{4}\cdot\text{H}_{2}\text{O} \), and cadmium pyrophosphate, \( \text{Cd}_{2}\text{P}_{2}\text{O}_{7} \). The solution should be free from elements which yield precipitates of phosphates in neutral solution and should also contain little or no ammonium salts: the latter prevent quantitative precipitation. If a neutral solution of a cadmium salt is treated with a large excess of diammonium hydrogen phosphate \( (\text{NH}_{4})_{2}\text{HPO}_{4} \), an amorphous or flocculent precipitate is first obtained; this becomes crystalline upon standing for at least 12 hours. The precipitate may be weighed as \( \text{CdNH}_{4}\text{PO}_{4}\cdot\text{H}_{2}\text{O} \) after drying at 100-105°C, or as \( \text{Cd}_{2}\text{P}_{2}\text{O}_{7} \), after ignition in the usual way.

G. Metallic cadmium. This excellent electrolytic method is described in Section IV, 50.

A. Determination of cadmium as molybdate. Procedure. Weigh out accurately 0.4-0.5 g. of the cadmium salt (1), dissolve it in 100 ml. of water, render the solution just alkaline with ammonia solution, and then feebly acid with acetic acid. Treat the boiling solution dropwise and with constant stirring (2) with a solution of ammonium molybdate (3) in slight excess (4), and maintain the mixture at about 90°C until the precipitate has settled. Allow to stand for at least 2 hours, but preferably overnight. Filter off the precipitate of cadmium molybdate upon a weighed sintered-glass or porous-porcelain crucible of fine porosity, or upon a Gooch crucible covered with a layer of ground asbestos, wash with hot water, and dry at 120°C to constant weight. Weigh as \( \text{CdMoO}_{4} \).

Notes. 1. A.R. cadmium iodide is a suitable salt to employ for practice in this determination.

2. The precipitate adheres very tenaciously to the glass if this is touched with the stirring-rod during precipitation. Touching of the sides of the glass vessel with the stirring-rod should therefore be avoided.

3. This solution is prepared by stirring up 15 g. of A.R. molybdenum trioxide with 200 ml. of water, adding a few drops of phenolphthalein, and then concentrated ammoniacal solution with constant stirring until the oxide is dissolved. Acetic acid is then added until the pink colour disappears, but the reaction is acid to litmus. Filter and dilute to 500 ml. 1 ml. of this reagent will precipitate 0.02 g. of Cd.
4. Add a drop of the supernatant solution to a saturated solution of pyrogallol in chloroform; a brown coloration is produced if excess of molybdate is present.

B. Determination of cadmium as the β-naphthaquinoline complex. Procedure. The cadmium salt solution, containing about 0.15 g. of Cd, should occupy a volume of about 50 ml. and be 2N with regard to sulphuric acid. Add 50 ml. of 10 per cent sodium tartrate solution, followed successively by a 2-5 per cent solution of β-naphthaquinoline in 0.5N-sulphuric acid, a few drops of dilute sulphuric acid, and then 0.2N-potassium iodide in excess. After 20 minutes, filter the precipitate of the cadmium complex through a weighed Gooch, sintered-glass, or porous-porcelain crucible, wash with a solution containing 10 ml. of 0.2N-potassium iodide, 10 ml. of 2-5 per cent β-naphthaquinoline in 0.5N-sulphuric acid, 80 ml. of water, and 1-2 drops of dilute sulphurous acid, and finally suck as free as possible from the wash liquor. Dry the precipitate to constant weight at 130° C. Weigh as [(C₉H₅N)₂H]₂CdI₄·

C. Determination of cadmium as quinaldinate. Procedure. The solution (150 ml.) should be neutral or weakly acid with acetic acid, and should contain 0.1-0.15 g. of Cd. Heat the solution to boiling, and remove the source of heat. Add the reagent (a 3.3 per cent solution of quinaldinic acid or of the sodium salt in water) dropwise with vigorous stirring until present in slight excess. Then neutralise carefully with dilute ammonia solution, and allow the white curdy precipitate to settle. When cold, wash with cold water by decantation, filter through a sintered-glass or porous-porcelain crucible, wash thoroughly with cold water, and dry at 125° C. to constant weight. Weigh as Cd(C₁₁H₁₃O₂N)₂·

D. Determination of cadmium by the pyridine method. Procedure. The solution (75-100 ml.) should contain about 0.1 g. of Cd (1) and be neutral or very feebly acid. Add 0.5-1.0 g. of A.R. ammonium thiocyanate, stir, heat to boiling, and treat the solution with 1 ml. of pure pyridine dropwise and with stirring. The complex slowly separates as the solution cools. Filter the cold solution through a weighed sintered-glass or porous-porcelain crucible, transfer the precipitate to the crucible with the aid of Solution 1. Wash four to five times with Solution 2, then twice with 1-m! portions of Solution 3, and finally five to six times with small volumes (ca. 1 ml.) of Solution 4. (For further experimental details, see under Copper, Section IV, 19E, and Zinc, Section IV, 34D.) Dry the precipitate in a vacuum desiccator (Fig. 2-10) for 10-15 minutes and weigh. Repeat the drying until constant weight is attained. Weigh as [Cd(C₅H₅N)₂](CNS)₂·

Solution 1. 100 ml. of water containing 0.3 g. of NH₄CNS and 0.5 ml. of pyridine.
Solution 2. 73 ml. of water, 25 ml. of 95 per cent alcohol, 0.1 g. of NH₄CNS, and 2 ml. of pyridine.
Solution 3. 10 ml. of absolute alcohol and 1 ml. of pyridine.
Solution 4. 15 ml. of absolute (sodium dried) ether and 2 drops of pyridine.

Note. 1. For practice in this determination the student may employ about 0.3 g., accurately weighed, of A.R. cadmium sulphate or of A.R. cadmium iodide.
E. Determination of cadmium as anthranilate. Procedure. The solution may contain up to 0.1 g. of Cd in a volume of 150 ml. Render it neutral with 3 per cent sodium carbonate solution (3 g. Na₂CO₃ per 100 ml. of water), heat to boiling, and add 25 ml. of 3 per cent sodium anthranilate solution. Allow to cool to room temperature during 1 hour, filter through a sintered-glass or porous-porcelain filter-crucible, wash with 50–75 ml. of the diluted reagent (1:20), then with alcohol, and dry to constant weight at 105–110° C. Weigh as Cd(C₇H₆O₇N₃)₂.

F. Determination of cadmium as the ammonium phosphate monohydrate or as the pyrophosphate. Procedure. The solution may contain about 0.2 g. of Cd in 100 ml. of water (1). Add a ten to fifteen-fold excess of A.R. diammonium hydrogen phosphate (NH₄)₂HPO₄ (say, 3 g. of the salt dissolved in 50 ml. of water) with stirring. Allow to stand overnight, when the amorphous precipitate will become crystalline. Filter through a porous-porcelain crucible (2), wash with about 25 ml. of water, then with 50 per cent alcohol, and dry at 100–105° C. to constant weight. Weigh as CdNH₄PO₄·H₂O.

Alternatively, place the crucible upon a crucible-ignition dish or upon a pad of asbestos inside a nickel crucible (compare Fig. II, 31, 4), and ignite at red heat (800–900° C.) for about 90 minutes. Weigh as Cd₃P₂O₇.

Notes. 1. For practice in this determination, the student may weigh out accurately about 0.4 g. of A.R. cadmium sulphate, 3CdSO₄·8H₂O, and dissolve it in 100 ml. of water.
2. A sintered-glass crucible may be used if weighing only as the ammonium phosphate monohydrate is required.

IV, 19. COPPER

Discussion. Copper may be determined in the following forms:

A. Cuprous thiocyanate, Cu₂(CNS)₂. This is an excellent method, since most thiocyanates of the metals are soluble. Separation may thus be effected from bismuth, cadmium, arsenic, antimony, tin, iron, nickel, cobalt, manganese, and zinc. The addition of 2–3 g. of tartaric acid is desirable for the prevention of hydrolysis when bismuth, antimony, or tin are present. Excessive amounts of ammonium salts or of the thiocyanate precipitant should be absent, as should also oxidising agents and high acidity. Lead, mercury, the precious metals, selenium, and tellurium interfere and contaminate the precipitate.

B. Copper benzoinoxime, Cu(C₁₄H₁₁O₂N). α-Benzoinoxime (cupron) is a specific reagent for the determination of copper in ammoniacal solutions (compare Section I, 62D). A green, heavy, and readily filterable precipitate is obtained: this is insoluble in water, dilute ammonia solution, acetic acid, tartaric acid, and alcohol, is slightly soluble in concentrated ammonia solution, and readily soluble in mineral acids. Precipitation is quantitative in ammoniacal tartrate solutions: separation can thus be effected from iron and other metals whose hydroxides are not precipitated in tartrate solutions. Separation can also be made from cadmium, zinc, cobalt, and nickel, which are not precipitated in ammoniacal solutions.

C. Copper salicylaldolime, Cu(C₆H₄O₂N). In this method silver, mercuric, arsenious, nickel, cobalt, and zinc ions do not interfere provided the solution contains sufficient acetic acid; the copper complex alone is insoluble in acetic acid (compare Section I, 62E). Ferric iron is carried down with copper.
Gravimetric Analysis

salicylaldoxime and interferes seriously. In neutral or in very faintly acid solution nickel and cobalt are precipitated, but the other ions remain in solution. An excellent method for the separation of copper and nickel is thus available (see Section IV, 32B).

D. Copper quinaldinate, Cu(C₁₅H₁₀O₅)₂H₂O. Quinaldic acid or its sodium salt is a specific reagent for copper if precipitation is made in sulphuric acid solution and iron and zinc are absent (compare Section I, 62M). With this reagent, a determination of copper may be completed in 2 hours.

E. [Cu(C₅H₅N)₂](CNS)₂; pyridine method. If a neutral or faintly acid copper solution is treated with ammonium thiocyanate and pyridine, dipyridine copper dithiocyanate is quantitatively precipitated. This precipitate is collected and washed, inter alia, with alcohol and ether containing a little pyridine, and then dried simply by leaving in a vacuum desiccator for 10–20 minutes. A determination can be completed in less than 1 hour. This rapid method is applicable in the absence of cadmium, nickel, cobalt, zinc, and manganese (see Section I, 62K). Large quantities of ammonium salts must be absent, as these exert a solvent action upon the precipitate. If the solution is strongly acid, it must be evaporated to dryness and the residue dissolved in water.

F. Copper ethylenediamine mercuri-iodide [Cu en₂][HgI₂]; ethylenediamine method. This, like E, is a rapid method for the determination of copper. Owing to the small conversion factor (0.07126) the procedure is valuable for the determination of small amounts of copper.

For further discussion, see Section I, 62O.

G. Metallic copper. The electrolytic method is one of the best for the determination of copper. Comparatively large quantities (up to 5 g.) can be handled (see Section IV, 78 for details).

A. Determination of copper as cuprous thiocyanate. Procedure. Weigh out accurately about 0.4 g. of the copper salt (1) into a 250-ml. beaker, and dissolve it in 50 ml. of water. Add a few drops of dilute hydrochloric acid, and then a slight excess (2–3 ml.) of freshly prepared saturated sulphurous acid solution. Dilute the cold liquid to about 150 ml., heat to boiling, and add freshly prepared 10 per cent ammonium thiocyanate solution, slowly and with constant stirring, from a burette until present in slight excess. The precipitate of cuprous thiocyanate should be white; the mother liquor should be colourless and smell of sulphur dioxide. Allow to stand for several hours, but preferably overnight. Filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), and wash the precipitate ten to fifteen times with a cold solution prepared by adding to every 100 ml. of water 1 ml. of a 10 per cent solution of ammonium thiocyanate and 5–6 drops of saturated sulphurous acid solution, and finally several times with 20 per cent alcohol to remove ammonium thiocyanate (2). Dry the precipitate to constant weight at 110–120° C. (3). Weigh as Cu₂(CNS)₂.

Notes. 1. A.R. copper sulphate pentahydrate is suitable for practice in this determination. 0.4 Gram of this contains about 0.1 g. of Cu.

2. Alternatively, but less desirably, the precipitate may be washed with cold water until the filtrate gives only a slight reddish coloration with ferric chloride, and finally with 20 per cent alcohol.

3. The precipitate, collected in a sintered-glass or porous-porcelain crucible, may be weighed more rapidly as follows. Wash the cuprous thiocyanate five or six times with rectified spirit, followed by a similar treatment with small volumes of anhydrous ether, then suck the precipitate dry at the pump.
for 10 minutes, wipe the outside of the crucible with a clean linen cloth and leave it in a vacuum desiccator for 10 minutes. Weigh as Cu$_2$(CNS)$_2$.

**B. Determination of copper with α-benzoinoxime. Procedure.** Treat the neutral solution, which should be free from ammonium salts and contain not more than 0.05 g. of copper, with dilute ammonia solution until a clear blue solution is obtained. Heat to boiling and precipitate the copper by the addition, dropwise, of a 2 per cent alcoholic solution of the reagent. Precipitation is complete when the blue colour of the solution disappears. Filter the heavy green precipitate on a weighed sintered-glass or porous-porcelain crucible, wash with hot 1 per cent ammonia solution, then with warm alcohol, and finally with hot water. Dry to constant weight at 105–115° C. Weigh as Cu(C$_7$H$_5$O$_7$N). It is recommended that completeness of washing be tested for by washing the dry precipitate with warm alcohol followed by hot water. Dry again to constant weight at 105–110° C.

**C. Determination of copper with salicylaldoxime. Procedure.** Add 2N-sodium hydroxide to the copper solution (100 ml.), containing 0.05–0.1 g. of Cu, until a slight permanent precipitate is formed, and dissolve this by the addition of a little dilute acetic acid.* Add the salicylaldoxime reagent (for preparation, see Section I, 62E) in slight excess at room temperature. Filter off the precipitated complex on a weighed sintered-glass or porous-porcelain crucible, wash with water until the washings give no colour with ferric chloride, and dry to constant weight at 100–105° C. (about 1 hour). Weigh as Cu(C$_7$H$_5$O$_7$N)$_2$. Decomposition occurs above 115° C.

**D. Determination of copper as quinaldinate. Procedure.** Acidify the solution (ca. 150 ml.), containing up to 0.1 g. of copper, with 2–5 ml. of 2N-sulphuric acid, heat to boiling, and add the reagent (for preparation, see Section I, 62M) slowly and with stirring until present in slight excess. The green crystalline precipitate of copper quinaldinate separates out immediately. Stir the precipitate vigorously and allow to stand for 5–10 minutes. Wash with hot water by decantation, then transfer to a weighed sintered-glass or porous-porcelain crucible and wash with hot water until the excess of the reagent is removed. Dry at 110–115° C. to constant weight. Weigh as Cu(C$_5$H$_6$O$_2$N)$_2$.H$_2$O.

**E. Determination of copper by the pyridine method. Procedure.** The solution (100 ml.) should contain not more than 0.1 g. of Cu (1) and be neutral or very faintly acid. Add pure pyridine dropwise until the colour of the solution is practically azure-blue (1–2 ml. should suffice), then add 0.5 g. of solid A.R. ammonium thiocyanate, and stir vigorously. After a few minutes, collect the precipitate on a weighed sintered-glass or porous-porcelain crucible; transfer the precipitate to the crucible with the aid of Solution 1. Wash the precipitate six to eight times with Solution 2, then wash the walls of the crucible two or three times with 1-5-ml. portions of Solution 3 (use a 2-ml. pipette for this purpose), and finally several times with small volumes (1–2 ml.) of Solution 4. It is important to suck the precipitate almost dry between each washing; it is advisable also to stir the precipitate with a thin glass rod during the washing with Solutions 3 and 4. Dry the crucible and precipitate in a vacuum desiccator (Fig. II, 10, 4) for 5–20 minutes, according to its weight. Weigh as [Cu(C$_5$H$_5$N)$_2$](CNS)$_2$.

* Quantitative precipitation of copper commences at pH 2.6.
Gravimetric Analysis

Solution 1. 100 ml. of water containing 0.3 g. of \( \text{NH}_4\text{CNS} \) and 0.3 ml. of pyridine.

Solution 2. 80 ml. of 95 per cent alcohol, 19.2 ml. of water, 0.8 ml. of pyridine, and 0.05 g. of \( \text{NH}_4\text{CNS} \).

Solution 3. 10 ml. of absolute alcohol + 2 drops of pyridine.

Solution 4. 20 ml. of absolute (sodium dried) ether + 2 drops of pyridine.

Note. 1. For practice in this determination, the student may employ ca. 0.25 g., accurately weighed, of A.R. copper sulphate.

F. Determination of copper by the ethylenediamine method. Procedure. The solution should be neutral or very faintly acid and should contain up to 0.10 g. of Cu in a volume of 100–1000 ml. The experimental details for a volume of 100 ml. will be given. Treat the solution dropwise with an aqueous solution of ethylenediamine until the characteristic coloration of the \( [\text{Cu en}_2]^{++} \) ion appears; add a little more of the reagent, followed by 1–2 g. of solid ammonium nitrate and 2 g. of potassium iodide. Heat to boiling, add a hot concentrated solution of potassium mercuri-iodide (1) to precipitate the complex. Allow to cool slowly with frequent stirring of the solution. When cold, filter off the precipitated complex \( [\text{Cu en}_2][\text{HgI}_4] \) through a weighed crucible (Gooch, sintered-glass, or porous-porcelain); transfer the precipitate to the crucible with the aid of a wash-liquid containing 0.1 g. of mercuric chloride, 2 g. of potassium iodide, 1 g. of ammonium nitrate, and 2–3 drops of ethylenediamine per 100 ml., and wash it several times with the solution. Wash the walls of the crucible four times with 2-ml. portions of 95 per cent alcohol (rectified spirit), followed by three to four times with 2-ml. portions of anhydrous ether, and then suck the precipitate dry at the pump for 10 minutes. Dry the outside of the crucible with a clean linen cloth, leave it in a vacuum desiccator for 10 minutes, and weigh. Repeat the final drying in the desiccator until the weight is constant. Weigh as \( [\text{Cu en}_2][\text{HgI}_4] \).

Note. 1. The potassium mercuri-iodide solution is prepared by treating aqueous mercuric chloride with a slight excess of potassium iodide solution.

IV, 20.

ARSENIC

Discussion. Arsenic may be determined in the following forms:

A. Arsenic trisulphide, \( \text{As}_2\text{S}_3 \). The arsenic must be present in the tervalent state. Arsenic in the tervalent state (ensured by the addition of, for example, ferrous sulphate, cuprous chloride, pyrogallol, or phosphorous acid) may be separated from other elements by distillation from a hydrochloric acid solution, the temperature of the vapour being held below 108° C.; arsenic trichloride alone (also germanium chloride, if present) volatilises and is collected in water or in hydrochloric acid.

B. Magnesium pyroarsenate, \( \text{Mg}_2\text{As}_2\text{O}_7 \). Here the arsenic must be present in the quinquevalent state (e.g., as arsenate). Phosphates and other substances which give a precipitate with magnesia mixture must be absent, as must also organic matter, for this reduces the substance, and arsenic is volatilised.

C. Ammonium uranyl arsenate, \( \text{NH}_4\text{UO}_2\text{AsO}_4\cdot2\text{H}_2\text{O} \), and subsequent weighing as uranous uranate, \( \text{U}_3\text{O}_8 \). The addition of a uranyl salt solution to an arsenate solution containing excess of ammonium ions results in the precipitation of ammonium uranyl arsenate, which is soluble in mineral acids but insoluble in
Acetic acid. Upon igniting the precipitate, the arsenic is completely volatilised, leaving a moss-green residue which consists mainly of $\text{U}_3\text{O}_8$; this residue is dissolved in concentrated nitric acid, and the resultant uranyl nitrate upon cautious evaporation and subsequent ignition yields pure black $\text{U}_3\text{O}_8$, and is weighed in this form.

If the solution contains arsenite, the latter must first be oxidised to arsenate with 0.1N-potassium bromate in hydrochloric acid solution at 70°C. in the usual way (Section III, 137). A method is thus available for the determination of arsenite and arsenate in admixture. The arsenite is first determined with standard potassium bromate solution, and the total arsenate in the resulting liquid is then determined by precipitation as the uranium salt.

A. Determination of arsenic as trisulphide. Procedure. Pass a rapid stream of washed hydrogen sulphide through a solution of the arsenious arsenic (1) in 9N-hydrochloric acid at 15-20°C. Allow to stand for an hour or two, and filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain) (2). Wash the precipitate with 8N-hydrochloric acid saturated with hydrogen sulphide, then successively with alcohol, carbon disulphide (to remove any free sulphur which may be present), and alcohol. Dry at 105°C. to constant weight, and weigh as $\text{As}_2\text{S}_3$.

Notes. 1. A suitable solution for practice in this estimation is prepared by dissolving about 0.3 g. of A.R. arsenious oxide, accurately weighed, in 9N-hydrochloric acid.

2. Sometimes a film of arsenious sulphide adheres to the glass vessel in which precipitation was carried out; this can be dissolved in a little ammonia solution and the sulphide re-precipitated with the acid washing liquor.

B. Determination of arsenic as magnesium pyroarsenate. Procedure. The solution must contain all the arsenic as arsenate, and have a volume of not more than 100 ml. per 0.1 g. of arsenic. Add 5 ml. of concentrated hydrochloric acid slowly and with constant stirring to the arsenate solution (100 ml.) (1). Add a few drops of methyl-red indicator, followed by 10–15 ml. of magnesia mixture (2) for each 0.1 g. of As present; the magnesia mixture must be added dropwise and with continuous stirring. Cool the solution in ice water, and add pure concentrated ammonia solution slowly and with constant stirring until the solution is alkaline. Stir the liquid for a few minutes, and add 10 ml. of concentrated ammonia solution. Allow the solution to stand at room temperature for at least 4 hours, but preferably overnight. Filter the precipitate through a weighed silica (Vitreosil) or porous-porcelain filter-crucible, wash with cold 1:25 ammonia solution until free from chloride, and then remove as much as possible of the liquid by suction. Dry the precipitate at 100°C. for 1–2 hours, place the crucible inside a nickel crucible (Fig. II, 31, 4), or upon a crucible ignition dish, and apply heat slowly at first until no more ammonia is evolved, and finally at the full temperature of a Meker-type burner for 10 minutes (3). Cool in a desiccator and weigh. Repeat the heating, etc., until constant weight is attained. Weigh as $\text{Mg}_2\text{As}_2\text{O}_7$ (4).

Notes. 1. A suitable solution for practice is prepared by dissolving about 0.5 g., accurately weighed, of pure sodium arsenate $\text{Na}_2\text{HAsO}_4\cdot12\text{H}_2\text{O}$ (the A.R. product is obtainable, inter alia, from the Mallinckrodt Chemical Works, U.S.A.) in 100 ml. of water.
2. The magnesia mixture is prepared as follows. Dissolve 25 g. of magnesium chloride $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 50 g. of ammonium chloride in 250 ml. of water. Add a slight excess of ammonia solution, allow to stand overnight, and filter if a precipitate is present. Acidify with dilute hydrochloric acid, add 2 ml. excess of concentrated hydrochloric acid, and dilute to 500 ml.

3. The best results are obtained by conducting the final ignition in an electrically heated muffle furnace at 800-900° C.

4. The following procedure permits of the weighing as magnesium ammonium arsenate $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$. Treat the concentrated arsenate solution with 3-5 g. of ammonium chloride and 10-15 ml. of magnesia mixture. Add hydrochloric acid dropwise until the precipitate which has formed is dissolved. Add 1 drop of phenolphthalein to the cold solution, stir, then enough 2-5 per cent ammonia solution to turn the solution red, followed by an amount of concentrated ammonia solution equal to one-third of the volume of the solution. At this stage the total volume of the solution should not exceed 60-70 ml. for each 0·1 g. of As present. Cool in ice water for 1-2 hours, filter through a weighed crucible * (sintered-glass or porous-porcelain), wash with 2·5 per cent ammonia solution, followed by 95 per cent alcohol (five or six times), and small volumes of anhydrous ether (five or six times). Dry in a vacuum desiccator for 10 minutes or to constant weight. Weigh as $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$, which contains 25·89 per cent arsenic.

C. Determination of arsenic by precipitation as ammonium uranyl arsenate and weighing as uranous uranate. Procedure. The solution (150 ml.) should contain about 0·06 g. of As as arsenate. Add 30 ml. of 4N-ammonia solution, acidify with acetic acid, heat to boiling, and add 50 ml. (excess) of approximately 0·1N-uranyl acetate solution. Allow to stand several hours, but preferably overnight; during this period the pale-yellow granular precipitate will become coarser. Filter through a fine quantitative filter-paper, wash free from soluble salts, and transfer the filter and precipitate to a weighed silica or, better, a Main-Smith crucible. Heat in a fume chamber provided with a good draught until all the carbon has burnt off—the arsenic is simultaneously volatilised. Moisten the residue with a few drops of concentrated nitric acid, and ignite to constant weight over an ordinary Bunsen burner. Weigh as $\text{U}_3\text{O}_6$.

IV, 21. ANTIMONY

Discussion. Antimony may be determined in the following forms:

A. Antimony trisulphide, $\text{Sb}_2\text{S}_3$. This method is of limited application, since no other elements that are precipitable by hydrogen sulphide in acid solution can be present, and the sulphide must be dried and finally heated in an atmosphere of carbon dioxide at 280-330° C. Arsenic can be separated by removal by distillation as arsenic trichloride; tin can be removed by precipitation in the presence of oxalic and tartaric acids or of phosphoric acid.

B. Antimony tetroxide, $\text{Sb}_2\text{O}_4$. Instead of weighing the antimony as the trisulphide after the procedure described in Method A, the wet sulphide (or sulphide dried at 100° C) may be converted by controlled oxidation with fuming nitric acid into the higher oxide, and subsequently heated at 820-850° C., and weighed as $\text{Sb}_2\text{O}_4$. Since this process is an inconvenient one and the oxide is very easily reduced, it will not be described in detail.

* Wash the crucible several times with alcohol (95 per cent), followed by anhydrous ether, wipe the outside, leave in a vacuum desiccator for 5 minutes and weigh.
C. Antimony pyrogallate, \( \text{Sb} \left( \text{C}_{6}\text{H}_{6}\text{O}_{3} \right) \). Antimonious salts in the presence of tartrate ions may be quantitatively precipitated with a large excess of aqueous pyrogallol as the dense antimony pyrogallate. The method allows of a simple separation from arsenic; the latter element may be determined in the filtrate from the precipitation of antimony by direct treatment with hydrogen sulphide.

The volumetric methods described in Chapter III are simpler, quite as accurate, and more rapid; they are therefore to be preferred.

A. Determination of antimony as trisulphide. Procedure. Quickly heat the solution of the antimony compound in 1 : 4-hydrochloric acid (100 ml.) (1) contained in a conical flask to boiling and immediately pass a rapid stream of washed hydrogen sulphide; maintain the solution at 90–100° C. Shake the flask gently at intervals after the sulphide has turned red, and keep the precipitate, as far as possible, below the surface of the solution. As the precipitate darkens in colour, reduce the gas stream. Continue the passage of gas until the precipitate is crystalline and black in colour (total time required for precipitation is 30–35 minutes). Dilute the solution with an equal volume of water, mix, and heat again whilst the gas is slowly passed into the suspension for some minutes. When the solution is clear, cool, and filter through a filter-crucible (Gooch, sintered-glass, or porous-porcelain) that has been heated at 280–300° C. and weighed. Wash the precipitate a few times with water to remove acid, and then with alcohol; draw air through the crucible to dry the precipitate as far as possible. Place the crucible and contents in a wide glass tube passing through the centre of an air-bath (Section II, 12F) or through an electrically heated tube furnace. Heat for 2 hours at 100–130° C. in a current of carbon dioxide (this will completely dry the precipitate), and then heat for a further 2 hours at 280–300° C. (this process will convert any \( \text{Sb}_2\text{S}_3 \) present into \( \text{Sb}_2\text{S}_5 \) and will volatilise the sulphur). Cool in a slow stream of carbon dioxide, then place in a desiccator for 20–30 minutes, and weigh as \( \text{Sb}_2\text{S}_5 \).

Note. 1. A solution, suitable for practice in this determination, may be prepared by dissolving 0·5 g., accurately weighed, of A.R. anhydrous potassium antimonyl tartrate or of pure tartar emetic in 150 ml. of 1 : 4-hydrochloric acid.

C. Determination of antimony as antimonious pyrogallate. Procedure. The solution should contain the antimony (0·1–0·2 g.) in the antimonious condition. Add a slight excess over the calculated quantity of Rochelle salt (sodium potassium tartrate) to avoid the formation of basic salts upon dilution. Dissolve approximately five times the theoretical quantity of pure pyrogallol (Section I, 62N) in 100 ml. of air-free water, add this all at once to the antimony solution, and dilute to 250 ml. After 30–60 seconds the clear mixture becomes turbid, and then a dense, cloudy precipitate forms which separates out rapidly. Allow to stand for 2 hours, filter through a weighed sintered-glass or porous-porcelain crucible, wash several times with cold water to remove the excess of pyrogallol (50 ml. is usually sufficient), dry at 100–105° C. to steady weight. Wash again with cold water, dry at 100–105° C. and weigh; repeat the operation until the weight is constant. Weigh as \( \text{Sb} \left( \text{C}_{6}\text{H}_{6}\text{O}_{3} \right) \).
IV, 22.

Discussion. Tin may be determined in any of the following ways:

A. Tin dioxide, SnO₂. The method depends upon the oxidation of the tin to the quadrivalent state, precipitation with ammonium hydroxide, followed by ignition to stannic oxide, SnO₂. This procedure is satisfactory when applied to solutions containing tin alone, but it cannot be used directly in the presence of many other elements.

Tin is, however, frequently estimated as the dioxide in alloys (e.g., in brass or gun-metal). The alloy is treated with nitric acid, when a precipitate of hydrous stannic oxide is formed; the formula for this may be written, for simplicity, as H₂SnO₅, metastannic acid:

\[ 3\text{Sn} + \text{H}_3\text{O} + 4\text{HNO}_3 = 3\text{H}_2\text{SnO}_5 + 4\text{NO} \]

The precipitate possesses colloidal character and exhibits powerful adsorption properties for certain ions, for example, iron, lead, copper, nickel, and zinc. It is advisable to use macerated filter-paper in the subsequent filtration and also to wash the precipitate with dilute nitric acid in order to avoid peptisation. The precipitate is ignited at the highest temperature of a Meker-type burner to stannic oxide:

\[ \text{H}_2\text{SnO}_5 = \text{SnO}_2 + \text{H}_2\text{O} \]

Owing to the ready reduction of the oxide to the metal, the carbon of the filter-paper must be burnt off as low a temperature as possible and the flame gases excluded from the crucible.

The precipitate should be white, but rarely is because of the presence of impurities. The amount of impurity may be determined by adding to the pure weighed oxide fifteen times its weight of pure ammonium iodide and heating for 15 minutes in an electric oven at 425-475°C, or until no further fumes are evolved. The tin is volatilised quantitatively as stannic iodide:

\[ \text{SnO}_3 + 4\text{NH}_4\text{I} = \text{SnI}_4 + 4\text{NH}_3 + 2\text{H}_2\text{O} \]

The residue is treated with 2-3 ml. of concentrated nitric acid, cautiously evaporated, ignited, and the residual metallic oxides weighed; the loss in weight gives the weight of pure stannic oxide present in the precipitate. The treatment with nitric acid is necessary, for the other metals are converted into iodides and/or oxyiodides, which are only slowly converted into the oxides by heating in air.

B. Precipitation with cupferron and weighing as stannic oxide, SnO₂. This process permits of the precipitation of tin in the presence of aluminium, chromium, cobalt, nickel, and manganese. In the presence of 5 ml. of 48 per cent hydrofluoric acid per 200-400 ml. of solution which is 0.5N in acid, tin is not precipitated by hydrogen sulphide, whereas copper, lead, tervalent arsenic, and antimony are thus precipitated; many separations are therefore possible by this method. The addition of several grams of tartaric acid and of sodium acetate is desirable if antimony is present.

C. Precipitation with phenylarsionic acid and weighing as stannic oxide, SnO₂. This method is applicable in the presence of zinc, copper, and other elements commonly associated with tin in alloys, etc. (compare Section I, 327). Zirconium and thorium seriously interfere and must be absent.

The volumetric methods described in Chapter III are more rapid and equally accurate; they are therefore generally preferred.

A. Determination of tin as dioxide. Procedure. Weigh out accurately 0.5-1.0 g. of the alloy (1) into a 150-ml. beaker covered with a
clock-glass or Fisher “speedvap” beaker-cover. Add 15 ml. of concentrated nitric acid mixed with 10 ml. of water while keeping the beaker covered. When the vigorous action is over, evaporate the solution during a period of at least 1 hour on a water-bath to a volume of 5–10 ml., but not to dryness. This digestion ensures the quantitative precipitation of the stannic acid. Dilute to about 50 ml., and heat on the water-bath for 30 minutes (to dissolve soluble salts). Add a Whatman accelerator or one-quarter of a Whatman ashless tablet, and stir with the hot suspension for 5 minutes. Filter through a Whatman No. 42 or 542 filter-paper into a 150-ml. beaker; if the first portion of the filtrate is not clear, pass it through a second time, and add more macerated filter-paper if the precipitate persists in running through. Wash the precipitate at least ten times with hot 1 per cent nitric acid. Fold up the filter, place it in a weighed porcelain crucible, dry and char the filter at as low a temperature as possible, burn off the carbon at a very low red heat to avoid reduction, and finally ignite the residue for 30 minutes at the full heat of a Mörké type of burner whilst keeping the crucible in a standing position, preferably in an asbestos or “uralite” shield, to permit the free access of air. (If reduction occurs, the precipitate may be moistened with a drop or two of nitric acid and ignited again.) Allow to cool in a desiccator and weigh. Repeat the ignition, etc., until constant weight is attained. Weigh as SnO₂.

If the residue is appreciably coloured, the amount of impurities may be determined as described in the Discussion.

Note. 1. Ridsdale’s “Gun-metal, No. 6e” (one of the Analysed Samples for Students) is suitable. Alternatively 0.15–0.2 g. of A.R. tin may be used.

B. Determination of tin with cupferron. Procedure. Remove metals such as copper, lead, tervalent arsenic, and antimony, if present, by precipitation with hydrogen sulphide in the presence of hydrofluoric acid (see Discussion), and boil off the excess of hydrogen sulphide. The solution should contain 0.1–0.3 g. of Sn and occupy a volume of 200–500 ml. Add 5–10 ml. of concentrated hydrochloric acid, 4 g. of boric acid, 2–5 ml. of concentrated sulphuric acid, followed, whilst stirring, with a liberal excess of filtered 10 per cent aqueous cupferron solution. Stir vigorously for 30–45 minutes. The tin complex first separates in a white form (emulsion), rapidly assumes a curdy appearance, passes through a stage when it resembles plastic sulphur, and finally becomes compact and brittle, and may be crushed to a fine powder with a glass rod. Filter upon a Whatman No. 41 or 541 filter-paper, wash with cold water, dry in a weighed crucible, expel the organic matter by gentle ignition, and then ignite to constant weight. Weigh as SnO₂.

C. Determination of tin with phenylarsonic acid, C₆H₅AsO(OH)₂. Procedure. Treat a weight of the sample containing about 0.1 g. of Sn (1) with 10 ml. of 1:1 nitric acid, heat gently to complete oxidation and until excess of nitric acid has been removed; take care not to dehydrate the metastannic acid. Add concentrated hydrochloric acid dropwise until complete solution is just obtained, dilute to 150–200 ml. with water, and adjust the acidity to 5 per cent of hydrochloric acid by volume (2). Heat the solution, and add 35 ml. of a saturated aqueous solution of phenylarsonic acid (3). Allow to stand several hours, and filter through a quantitative filter-paper (4). Wash the
Gravimetric Analysis

precipitate with 4 per cent ammonium nitrate solution until free from chlorides (or sulphates). Ignite the precipitate and paper in a weighed crucible over a small flame until all the carbon is burnt off, and then heat in an electric furnace at 1075–1100°C to constant weight (5). Weigh as SnO₂.

Notes. 1. For practice in this determination, the student may use either A.R. tin or Ridsdale’s “Brass, No. 5e” or “Gun-metal, No. 6e.”
2. If bismuth is absent, sulphuric acid (7·5 per cent by volume) may be used.
3. The saturated aqueous solution is approximately 10 per cent.
4. The addition of a little macerated filter-paper (Section II, 29) aids the filtration.
5. If an electric furnace is not available, a Meker or Fisher high-temperature burner may be used.

IV, 28. MOLYBDENUM

Discussion. Molybdenum may be determined in the following forms:

A. Lead molybdate, PbMoO₄. Precipitation as lead molybdate is usually made by the slow addition of a solution of lead acetate to a hot, dilute acetic acid–ammonium acetate solution containing the molybdenum. The method is applicable in the presence of copper, mercury, cobalt, nickel, manganese, zinc, and magnesium. Alkali salts are not objectionable except sulphates, which must be absent when the alkaline earths are present. A great excess of the precipitant should be avoided if chlorides are present. Free mineral acids prevent complete precipitation, and elements such as iron, chromium, vanadium, silicon, tin, and titanium interfere.

B. Precipitation with α-benzoinoxime and weighing as molybdic oxide, MoO₃. Precipitation as the α-benzoinoxime complex is made by the addition of excess of an alcoholic solution of the reagent to a solution of the molybdenum compound containing 5 per cent by volume of sulphuric acid. The precipitate cannot be weighed as such, but must be ignited to molybdic oxide. The only other elements that give precipitates in mineral acid solution with the reagent are tungsten, palladium, sexivalent chromium, quinquevalent vanadium, and tantalum. Chromium and vanadium do not interfere if they are reduced to the tervalent and quadrivalent states respectively with sulphurous acid. Tungsten may be determined in the ignited precipitate by extracting with the minimum volume of warm 1:3 ammonia solution, filtering, acidifying the ammoniacal solution with hydrochloric acid, and then adding a little cinchonine solution; the solution is allowed to stand overnight, the precipitate filtered off, washed, ignited at 525°C, and weighed. The weight of tungstic oxide is deducted from that of the molybdic oxide.

C. Molybdenum “oxinate”, MoO₂(C₆H₄ON)₂. Molybdates yield sparingly soluble orange-yellow molybdyl “oxinate” with oxine solution; the pH of the solution should be between the limits 3·3–7·6. The complex differs from other “oximates” in being insoluble in organic solvents and in many concentrated inorganic acids. The freshly precipitated compound dissolves only in concentrated sulphuric acid and in hot solutions of caustic alkalis. This determination is of particular interest, as it allows a complete separation of molybdenum and rhenium.

For the volumetric determination of molybdenum, the precipitate is brought into solution by repeated digestion with 2–4N-sodium hydroxide solution, the alkaline solution is slowly introduced with constant stirring into 25–50 ml. of concentrated hydrochloric acid, the solution diluted to 50–100 ml., and
then titrated with standard 0.1N-potassium bromate (Section III, 138; Procedure A).

1 ml. \( N-KBrO_3 = 0.01199 \text{ g. Mo} \)

**A. Determination of molybdenum as lead molybdate.** Procedure. Weigh out accurately about 0.4 g. of ferro-molybdenum (1), dissolve it in 10 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid, evaporate to 2–3 ml., dilute to 50 ml., and transfer to a separating-funnel. Dissolve 5 g. of sodium hydroxide in 200 ml. of water in the original beaker, heat to boiling, and run in the solution from the separating funnel dropwise and with constant stirring. Rinse out the funnel twice with boiling water, and add the washings to the main filtrate. Filter off the precipitated ferric hydroxide and wash with hot water. Dissolve the precipitate in the minimum volume of dilute hydrochloric acid, and re-precipitate by slowly pouring into a solution of about 4 g. of sodium hydroxide in 100 ml. of water. Filter off the precipitate, wash with hot water, and add the filtrate and washings to the main filtrate. Acidify with acetic acid, add 50 ml. of a 50 per cent solution of ammonium acetate, and make up to 500 ml. in a measuring-flask. Remove 250 ml. of the solution (2), heat to boiling, and maintain near the boiling point with a small flame; add from a burette a solution of lead acetate (containing 4 g. of the salt and 1 ml. of glacial acetic acid per 100 ml.) dropwise and with constant stirring. When a slight excess of the precipitant has been added, the milky solution clears appreciably. When this occurs, boil for 2–3 minutes whilst the solution is stirred, allow to settle, and add a few drops of the reagent to see if precipitation is complete. A large excess of precipitant should be avoided. Digest on the steam-bath for 15–30 minutes. Decant the clear solution through a weighed Gooch or porous-porcelain crucible, wash by decantation three or four times with 75–ml. portions of hot 2–per cent ammonium nitrate solution, transfer the precipitate to the filter, and wash until the soluble salts have been removed. Dry and ignite the precipitate at a dull red heat (ca. 600°C) as described in Section IV, 140. Weigh as PbMoO₄.

**Notes.** 1. The Bureau of Analyzed Samples “Ferro-Molybdenum, No. 231” (a British Chemical Standard) is suitable.
2. If molybdenum is being determined in a simple salt, e.g., in A.R. molybdic acid or molybdic anhydride, commence at this point. The solution should contain about 0.1 g. of Mo in 200 ml. and may be prepared as follows. Dissolve 0.15 g., accurately weighed, of A.R. molybdic acid or anhydride, in 50 ml. of dilute ammonia solution, acidify with acetic acid, add 25 ml. of a 50 per cent solution of ammonium acetate, and dilute to 200 ml.

**B. Determination of molybdenum with α-benzoinoxime (cupron).** Procedure. Prepare a solution containing 10 ml. of concentrated sulphuric acid in a volume of 200 ml. and not more than 0.15 g. of hexavalent molybdenum. If vanadates or chromates are present, add sufficient freshly prepared sulphurous acid to reduce them, and heat to boiling: continue the boiling until the odour of sulphur dioxide can no longer be detected. Cool to 5–10°C, stir, and slowly add 10 ml. of a solution of the reagent (2 g. of α-benzoinoxime in 100 ml. of alcohol) and 5 ml. extra for each 0.01 g. of Mo present (from two to five times the theoretical amount is required). Continue the stirring, add just sufficient bromine water to tint the solution a pale yellow, and then add
4–5 ml. more of the reagent. Allow the mixture to stand for 10–15 minutes at 10–15° C. with occasional stirring, and filter through a Whatman No. 40 or 540 filter-paper. Wash the precipitate with 200 ml. of a cold, freshly prepared wash solution (containing 10 ml. of the reagent, and 2 ml. of concentrated sulphuric acid diluted to 200 ml.). Transfer the paper and washed precipitate to a weighed platinum crucible, char the paper at a low temperature without inflaming, and then ignite to constant weight at 500–525° C. Weigh as MoO₃.

As an additional check, or if contamination of the precipitate is suspected, treat the ignited residue with 5 ml. of concentrated ammonia solution, digest, and filter through a small quantitative filter-paper. Wash well with dilute ammonia solution (1:99). Ignite the filter-paper and contents in the original crucible, allow to cool and weigh. The difference in weight represents the MoO₃ present.

C. Determination of molybdenum with oxine. Procedure. Neutralise the solution of alkali molybdate, containing up to 0·1 g. of Mo, to methyl red, and then acidify with a few drops of 2N-sulphuric acid. Add 5 ml. of 2N-ammonium acetate, dilute to 50–100 ml., and heat to boiling. Precipitate the molybdenum by the addition of 3 per cent solution of oxine in dilute acetic acid (for preparation, see Section IV, 37B; Note 2) until the supernatant liquid becomes perceptibly yellow. Boil gently and stir for 3 minutes, filter through a filter-crucible (sintered glass or porous porcelain), wash with hot water until free from the reagent, and dry to constant weight at 130–140° C. Weigh as MoO₃(C₇H₆ON)₂.

IV, 24. SELENIUM AND TELLURIUM

Discussion. The gravimetric estimation depends upon the separation and weighing as elementary selenium or tellurium (or as tellurium dioxide). Alkali selenites and selenious acid are reduced in hydrochloric acid solution with sulphur dioxide, hydroxylamine hydrochloride, and hydrazine sulphate or hydrate. Alkali selenates and selenic acid are not reduced by sulphur dioxide alone, but are readily reduced by a saturated solution of sulphur dioxide in concentrated hydrochloric acid. In working with selenium it must be remembered that appreciable amounts of the element may be lost on warming strong hydrochloric acid solutions of its compounds: if dilute acid solutions (concentration <6N) are heated at temperatures below 100° C., the loss is negligible.

With tellurium, precipitation of the element with sulphur dioxide is slow in dilute hydrochloric acid solution and does not take place at all in the presence of excess of acid; moreover, the precipitated element is so finely divided that it oxidises readily in the subsequent washing process. Satisfactory results are obtained by the use of a mixture of sulphur dioxide and hydrazine hydrochloride as the reducing agent, and the method is applicable to both tellurites and tellurates. Another method utilises excess of sodium hypophosphite in the presence of dilute sulphuric acid as the reducing agent.

Two processes for the gravimetric estimation of mixtures of selenium and tellurium are described. Selenium and tellurium occur in practice either as the impure elements or as selenides or tellurides. They may be brought into solution by mixing intimately with 2 parts of sodium carbonate and 1 part of potassium nitrate in a nickel crucible, covering with a layer of the mixture, and then heating gradually to fusion. The cold melt is extracted with water, and filtered. The elements are then determined in the filtrate.
A. Determination of selenium.  Procedure A.  The selenium must be present in the quadrivalent state, and the selenium content of the solution must not exceed 0·25 g. per 150 ml. Saturate the cool (15–20° C.) selenium solution containing at least 28 per cent by volume of hydrochloric acid (3-4N) with sulphur dioxide, allow to stand until the red selenium settles out, filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), wash well successively with cold concentrated hydrochloric acid, cold water until free from chloride, alcohol, and ether. Dry the precipitate for 3–4 hours at 30–40° C. to remove ether, and then to constant weight at 100–110° C. Weigh as Se.

Note. A simpler method of drying and weighing the precipitated selenium is to treat the well-washed precipitate, collected in a sintered-glass or porous-porcelain crucible, five or six times with small volumes of rectified spirit and then similarly with anhydrous ether. The precipitate is sucked dry at the pump for 10 minutes, the crucible wiped with a clean linen cloth, left in a vacuum desiccator for 10 minutes, and weighed.

Procedure B. Both selenites and selenates may be analysed by the following method. To the solution (ca. 25 ml.) of the substance containing not more than 0·3 g. of Se, add 50 ml. of concentrated hydrochloric acid which has been saturated in the cold with sulphur dioxide. Separation of red selenium occurs almost at once. Allow to stand for 2 hours, heat on a hot-plate (fume cupboard) to drive off sulphur dioxide and much of the hydrochloric acid, and to convert the selenium into the grey form. Dilute with water to about 50 ml., and boil gently for some time to dissolve any soluble matter from the selenium. Collect the precipitate on a filter-crucible (Gooch, sintered-glass, or porous-porcelain), wash with water until free from chloride, then with alcohol, and dry at 100–110° C. to constant weight.* Weigh as Se.

B. Determination of tellurium.  Procedure A.  The solution should contain not more than 0·2 g. of Te in 50 ml. of 3N-hydrochloric acid (ca. 25 per cent by volume of hydrochloric acid). Heat to boiling, add 15 ml. of a freshly prepared, saturated solution of sulphur dioxide, then 10 ml. of a 15 per cent aqueous solution of hydrazine hydrochloride, and finally 25 ml. more of the saturated solution of sulphur dioxide. Boil until the precipitate settles in an easily filterable form; this should require not more than 5 minutes. Allow to settle, filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), and immediately wash with hot water until free from chloride. Finally wash with alcohol (to remove all water and prevent oxidation), and dry to constant weight at 105° C.* Weigh as Te.

In the alternative method of reduction, which is particularly valuable for the determination of small amounts of tellurium, the procedure is as follows. Treat the solution containing, say, up to about 0·01 g. of Te in 90 ml. with 10 ml. of 1 : 3-sulphuric acid, then add 10 g. of sodium hypophosphite, and heat on a steam-bath for 3 hours. Collect and weigh the precipitated tellurium as above.

Procedure B. Dissolve the material (elementary tellurium, oxides, or tellurites) in concentrated hydrochloric acid or in 10 per cent potassium hydroxide solution, using 2 ml. per 0·2 g. of oxide. If alkaline, just acidify the solution with hydrochloric acid, and dilute to 200 ml.

* Alternatively use the rectified spirit–anhydrous ether method given in Note A.
Gravimetric Analysis

with boiling water. Add a slight excess of dilute ammonia solution, and just acidify with acetic acid. Allow to cool, when the crystalline dioxide will separate out. Collect the precipitate on a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), wash with hot water, and dry at 105°C, to constant weight. Weigh as TeO₂.

C. Determination of mixtures of selenium and tellurium. Procedure A. Dissolve the mixed oxides (not exceeding 0.25 g. of each) in 100 ml. of concentrated hydrochloric acid, and add with constant stirring 50 ml. of cool concentrated hydrochloric acid which has been saturated with sulphur dioxide at the ordinary temperature. Allow the solution to stand until the red selenium has settled, filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), and complete the determination as described in A, Procedure A. Preserve the filtrate, hydrochloric acid, and water washings. Concentrate the latter on a water-bath below 100°C. (above 100°C tellurium is lost as chloride) to 50 ml., and estimate the tellurium as described under B, Procedure A.

Procedure B. Dissolve the mixed oxides (not exceeding 0.25 g. of each) in 40 ml. of concentrated hydrochloric acid. Add 10 ml. of 25 per cent hydroxylamine hydrochloride, and heat at 90°C for 4 hours. Filter off the black selenium through a weighed filter-crucible, wash with water, then with alcohol, and dry to constant weight at 110°C. Determine the tellurium in the filtrate exactly as detailed in B, Procedure A.

IV, 25. PLATINUM

Discussion. Platinum may be determined in either of the following forms:

A. Metallic platinum. The platinum solution is treated with formic acid, best at pH 6, and the precipitated platinum weighed.

B. Ammonium chloroplatinate, \((\text{NH}_4)_2[\text{PtCl}_4]\), and subsequent weighing as platinum. If platinum alone is present in hydrochloric acid solution, it may be precipitated as ammonium chloroplatinate by the addition of a half-saturated solution of ammonium chloride, washed, carefully ignited, and weighed as Pt.

A. Determination as metallic platinum. Procedure. In this estimation any excess of nitric and/or hydrochloric acid present must be removed. Evaporate the solution of platinum, containing no other platinum metals (ruthenium, rhodium, palladium, osmium, and iridium) and gold, to a syrup on the steam-bath so as to remove as much hydrochloric acid as possible. If nitric acid was present, dissolve the residue in 5 ml. of water, heat on the water-bath for a few minutes, add 5 ml. of concentrated hydrochloric acid, and again evaporate to a syrupy consistency. Dissolve the residue in water, and dilute so that the solution does not contain more than 0.5 g. of Pt in 100 ml. For each 100 ml. of solution, add 3 g. of anhydrous sodium acetate and 1 ml. of formic acid. Heat on the boiling water-bath for several hours. Filter through a quantitative filter-paper. Add a little more sodium acetate and formic acid to the filtrate and digest in order to ensure complete precipitation. Wash the precipitate with water until free from chloride, dry and ignite the filter-paper in contact with the precipitate (Section II, 36A) to constant weight. Weigh as metallic Pt.

B. Determination of platinum by precipitation as ammonium chloroplatinate. Procedure. Only hydrochloric acid may be present in this
Quantitative Inorganic Analysis

estimation. The solution should be free from gold (which may be removed by the cautious addition of sulphurous acid to the solution or of hydroquinone to the solution 1·2N with respect to hydrochloric acid) and the other platinum metals (see, however, below). If nitric acid is present, it must be removed by several evaporations with concentrated hydrochloric acid. Dissolve the residue in 5 ml. of concentrated hydrochloric acid and 20 ml. of hot water, and then add gradually an equal bulk of half-saturated ammonium chloride solution. Allow to stand for some hours, or overnight. Filter off the precipitate, wash it with the ammonium chloride solution, and finally twice with cold water. Transfer the filter-paper and precipitate to a Main-Smith crucible (Section II, 66B), heat extremely slowly at first (otherwise loss may occur), and ultimately raise to a bright red heat. Heat to constant weight and weigh as Pt.

If other metals of the platinum group are present, the above procedure does not give satisfactory results. It is necessary to proceed as follows. Rinse back the precipitate of ammonium chloroplatinate into the precipitating-vessel, and wash the filter thoroughly with hot water. Slightly acidify the liquid (150 ml. for 1 g. of Pt) with hydrochloric acid, boil vigorously and keep stirred by means of a glass tube through which a brisk current of chlorine is passed (the operation must be performed in the fume chamber). When the precipitate has dissolved (after a few minutes), stop the current of chlorine and wash the tube with hot water. The solution now contains chloroplatinic acid. Then add just enough ammonium chloride solution to combine with the platinum (6 ml. of a 10 per cent solution for 1 g. of platinum), and evaporate (hot-plate) to 20 ml. Allow to cool, and dilute with an equal bulk of saturated ammonium chloride solution. After a few hours, filter off the coarsely crystalline precipitate, wash with half-saturated ammonium chloride solution, then with a little cold water, ignite cautiously, and weigh as Pt.

IV, 26. PALLADIUM

Discussion. Palladium may be determined in one of the following forms:

A. Palladous cyanide, Pd(CN)₂, and subsequent weighing as the metal. This is quite a good method, particularly when large quantities of palladium are involved, because of the comparative compactness of the precipitate.

B. Palladium dimethylglyoxime, Pd(C₄H₇O₂N₂)₂. This is one of the best methods for the estimation of the element. Gold must be absent, for it precipitates as the metal even from cold solutions. The other platinum metals do not, in general, interfere. Moderate amounts of platinum cause little contamination of the precipitate, but with large amounts a second precipitation is desirable. The precipitate is decomposed by digestion on the water-bath with a little aqua regia, and diluted with an equal volume of water; the resulting solution is largely diluted with water, and the palladium re-precipitated with dimethylglyoxime.

An objection to the precipitation of palladium with dimethylglyoxime is the voluminous character of the precipitate. Hence if much palladium is present, an aliquot part of the solution should be used, or the palladous cyanide method applied.

C. Palladium 1 : 2-cyclohexanedione dioxime, Pd(C₆H₅O₂N₂)₂. 1 : 2-cyclo-Hexanenedione dioxime (nioxime) yields a highly insoluble yellow compound, Pd(C₆H₅O₂N₂)₂, with palladium salts at pH values between 1 and 5; it can be filtered from the hot solution after a brief digestion period. The reagent, unlike dimethylglyoxime, is soluble in water, and hence the palladium precipitate is unlikely to be contaminated with excess of reagent. The pre-
Gravimetric Analysis

Cipitate is rather bulky, so that determinations are conducted with quantities not exceeding 20–30 mg. Common anions do not interfere, nor do beryllium, aluminium, lanthanum, uranium (VI), and the alkaline-earth ions. Amounts of platinum (up to that of the palladium) do not interfere; aurous ion at 60° C. is partially reduced to metallic gold.

It may be mentioned that palladium may also be precipitated with α-nitroso-β-naphthol (brown precipitate; subsequently ignited to and weighed as the metal) or with salicylaldoxime (the precipitate, after drying at 110° C., is weighed as Pd(C₇H₆O₂N)₂). Both procedures may be used for separating palladium from platinum.

A. Determination of palladium as palladous cyanide. Procedure. This estimation must be carried out in a fume cupboard provided with a good draught. Nearly neutralise the solution containing up to 0.3 g. of Pd with sodium carbonate, and add an excess of mercuric cyanide solution. Heat on the water-bath until the odour of hydrocyanic acid has disappeared, and allow the light-yellow precipitate to settle. Filter the precipitate through a quantitative filter-paper. Wash the precipitate first by decantation and then on the filter with cold water. Dry and ignite in a weighed crucible to constant weight, using the full heat of a Meker type of burner. Weigh as Pd.

B. Determination of palladium with dimethylglyoxime. Procedure. The solution should contain not more than 0.1 g. of Pd in 250 ml., be 0.25N with respect to hydrochloric or nitric acid, and be free from nickel and gold. Add, at room temperature, a 1 per cent solution of dimethylglyoxime in 95 per cent alcohol. Use 2–5 ml. of the reagent for every 10 mg. of palladium. Allow the solution to stand for 1 hour, and then filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain). Test the filtrate with a little of the reagent to make sure that precipitation is complete. Wash the orange-yellow precipitate of palladium dimethylglyoxime thoroughly, first with cold water and then with hot water. Dry at 110° C. to constant weight. Weigh as Pd(C₄H₇O₂N₂)₉.

C. Determination of palladium with 1 : 2-cyclohexanedione dioxime. Procedure. The solution (volume about 200 ml.) may contain 5–30 mg. of palladium: the pH may vary from 1 to 5. Heat the solution to 60° C., add slowly from a graduated pipette with stirring 0.50 ml. of a 0.8 per cent aqueous solution of nioxime (1) for each milligram of Pd present. Digest the solution with occasional stirring for 30 minutes at 60° C., filter through a sintered-glass or porous-porcelain crucible, and wash well with hot water. Dry at 110° C. to constant weight, and weigh as Pd(C₆H₄O₂N₂)₉.


IV, 27. GOLD

Discussion. Gold is nearly always determined as the metal. The reducing agents generally employed are sulphur dioxide, oxalic acid, and ferrous sulphate. No free nitric acid must be present in the solution; if this is the case, the nitric acid must be removed by repeated evaporation with concentrated hydrochloric acid, and the solution diluted with water. With sulphurous acid, small amounts of the platinum metals (particularly platinum)
Quantitative Inorganic Analysis

may be carried down with the precipitate. It is therefore usually necessary to re-dissolve the solid in dilute aqua regia and to re-precipitate the gold; oxalic acid gives a better separation from the platinum metals in the second precipitation, although the precipitate is somewhat finely divided. Ferric sulphate gives satisfactory results for gold alone, but difficulties are introduced if the platinum metals are subsequently to be determined. Oxalic acid is slow in its action, and yields a precipitate which is difficult to filter.

The best results are obtained with hydroquinone as the reducing agent. Precipitation in hot 1·2N-hydrochloric acid solution is rapid, the gold is readily filtered, and occlusion of the platinum metals is negligible. Precipitation in the cold is complete in 2 hours. Palladium in the filtrate can be precipitated directly with dimethyl-glyoxime, whilst platinum in the filtrate may be determined either by evaporating to dryness in order to destroy organic matter and then digesting with a little aqua regia or by reduction with sodium formate and formic acid.

Gold may also be separated from hydrochloric acid solutions of the platinum metals by extraction with ether or with ethyl acetate (compare Section I, 71); except in special cases these methods do not offer any special advantages over the reduction to the metal.

Determination of gold as the metal. Procedure A. The solution should contain not more than 5 ml. of concentrated hydrochloric acid per 100 ml. of solution, not more than 0·5–1 g. of Au, and be free from lead, selenium, tellurium, and the alkaline earths. Add 25 ml. of a freshly prepared saturated sulphur dioxide solution, and digest for 1 hour on the steam-bath in order to coagulate the precipitate. Add 5–10 ml. more of the sulphur dioxide solution, and allow to cool. If the cold solution smells strongly of sulphur dioxide, the precipitation of gold is complete. Some of the metal is finely divided, and it is therefore advisable to treat the filter-paper with a suspension of macerated filter-paper prepared from a Whatman accelerator or ashless tablet. Pour the supernatant liquid through a Whatman No. 42 or 542 filter-paper, preferably containing some filter-paper pulp, and transfer as little as possible of the precipitate to the paper unless one precipitation is thought sufficient; this will only be the case if very small amounts of platinum or palladium are present. Wash well by decantation with hot dilute hydrochloric acid (1:99). Transfer the filter to the beaker, and re-dissolve the gold in dilute aqua regia; use 8 ml. of concentrated hydrochloric acid, 2 ml. of concentrated nitric acid, and 10 ml. of water for each gram or less of gold. Filter from the paper-pulp, and wash thoroughly with hot dilute hydrochloric acid (1:99). Evaporate the filtrate to dryness on the water-bath, add 2–3 ml. of concentrated hydrochloric acid, and evaporate to dryness again; repeat this operation twice in order to eliminate all the nitric acid. Treat the residue with 3 ml. of concentrated hydrochloric acid, 5 drops of concentrated sulphuric acid, and 75 ml. of water, disregard the small amount of gold which may separate, add 25 ml. of a saturated solution of oxalic acid, and boil for a minute or two. If no further visible precipitation of gold occurs, digest the solution on the water-bath for at least 4 hours. Filter off the gold through a filter-paper (as described above), and wipe the inside of the beaker with small pieces of quantitative filter-paper to ensure that all the metal is transferred from the beaker; wash well with 1:99 hydrochloric acid. Transfer the filter to a weighed porcelain or silica crucible, burn off the paper carefully, and ignite to constant weight. Weigh as Au.
Procedure B. Treat the dilute solution of the gold, containing only a little free hydrochloric acid, with a large excess of a clear ferrous sulphate solution, cover the beaker, and heat on the water-bath for several hours. Filter off the precipitated gold through a filter-paper, and complete the estimation as under Procedure A.

Procedure C. The solution must be free from nitric acid, be about 1·2N with respect to hydrochloric acid (ca. 5 ml. of concentrated hydrochloric acid in 50 ml. of water), and contain up to 0·2 g. of Au in 50 ml. Heat the solution to boiling, add excess of 5 per cent aqueous hydroquinone solution (3 ml. for every 25 mg. of Au), and boil for 20 minutes. Allow to cool, and filter either through a weighed porous-porcelain crucible or through a Whatman No. 42 or 542 filter-paper (Section II, 28); wash thoroughly with hot water. The small particles of gold remaining in the bottom of the beaker (easily seen with a small flash lamp) are best removed with pieces of ashless filter-paper. Ignite the porous-porcelain crucible to constant weight. If filter-paper is used, transfer to a weighed porcelain or silica crucible, and complete the estimation as described in Procedure A.

IV, 28.

ALUMINIUM

Discussion. Aluminium may be determined in the following forms:

A. Aluminium oxide, $\text{Al}_2\text{O}_3$. Full details of this determination (precipitation with ammonia solution) are given in Section IV, 9. A more readily filterable precipitate may be obtained by precipitation in weakly acid solution with a mixture of equal volumes of a 25 per cent aqueous solution of potassium iodide and a saturated solution of potassium iodate. The mixture removes the acid produced by hydrolysis, and causes the reaction to proceed from left to right:

$$2\text{AlCl}_3 + 6\text{H}_2\text{O} \rightleftharpoons 2\text{Al(OH)}_3 + 6\text{HCl} \ldots \ldots (1)$$

$$6\text{HCl} + \text{KIO}_3 + 5\text{KI} = 3\text{H}_2\text{O} + 3\text{I}_2 + 6\text{KCl}$$

The weakly acid solution (200–300 ml. containing up to 0·2 g. of Al) is treated with an excess of the KI–KIO$_3$ mixture; iodine separates immediately. After 10 minutes the iodine is removed by the addition of sodium thiosulphate solution with stirring from a burette, and several ml. excess of the thiosulphate solution are added. The mixture is heated on a water-bath for 45 minutes with frequent stirring. The hydrated aluminium oxide is filtered off, washed with hot water or with 2 per cent ammonium nitrate solution, ignited, and weighed. The method may be applied also to the precipitation of chromium and iron as hydroxides from dilute, weakly acid solutions of their tervalent salts.

Sodium thiosulphate may also be employed to remove the acid formed by hydrolysis of the aluminium salt (equation (1)):

$$6\text{HCl} + 3\text{Na}_2\text{S}_2\text{O}_3 = 3\text{H}_2\text{O} + 6\text{NaCl} + 3\text{S} + 3\text{SO}_2$$

The mixture of aluminium hydroxide and sulphur, which is precipitated, can be readily filtered and washed. Here the dilute solution is neutralised with ammonium carbonate until a slight precipitate forms, which is dissolved in a little hydrochloric acid. Excess (say, 2 g.) of sodium thiosulphate dissolved in a small volume of water is added, the solution heated to boiling, and boiled until all traces of sulphur dioxide are expelled. 1:1 Ammonia solution is added until its odour is barely perceptible after blowing away the vapours, and the mixture boiled for 2 minutes. The precipitate is filtered off, washed, and ignited in the usual way.
Quantitative Inorganic Analysis

Precipitation of aluminium hydroxide can also be brought about by bases other than ammonia, e.g., phenylhydrazine, pyridine, aniline, etc. Of these phenylhydrazine is sometimes employed for the separation of aluminium from divalent iron in a form suitable for immediate ignition and weighing as the oxide. (Phenylhydrazine also precipitates, best from solution of the sulphates, chromic, titanium, zirconium, and thorium; beryllium is incompletely precipitated; ceric and ferric salts are partially reduced and incompletely precipitated.) For the determination of aluminium the dilute sulphuric acid solution, free from elements of Group II and other interfering elements, is made slightly alkaline (methyl orange) with ammonium hydroxide solution, then just enough acid is added to hold the other elements in solution, and the solution is diluted to 100–200 ml. The whole is then heated, any iron present is reduced by the addition of a little saturated ammonium bisulphite solution, or sodium hydrosulphite:

$$2\text{FeCl}_3 + \text{NH}_4\text{HSO}_3 + \text{H}_2\text{O} = 2\text{FeCl}_2 + \text{NH}_4\text{HSO}_4 + 2\text{HCl}$$

the solution quickly neutralised with ammonia solution, and 6–7 ml. of 1 : 1 hydrochloric acid added. 1–3 ml. of pure phenylhydrazine (preferably dissolved in 10–20 ml. of 60 per cent alcohol) are then added according to the amount of aluminium to be precipitated, followed by one Whatman "accelerator": the solution is boiled for 5 minutes and kept hot for at least 30 minutes more until the flocculent precipitate settles. The supernatant liquid will be alkaline to methyl orange but acid to litmus. If the precipitate has a brownish colour, this is due to the colouring matter contained in the phenylhydrazine and not to ferric hydroxide. The precipitate is filtered after a short time whilst still warm, washed with a solution of phenylhydrazine sulphite,* and ignited to Al$_2$O$_3$ in the usual manner. It may be mentioned that the filtrate cannot be used for the determination of other elements because of the difficulty of destroying organic matter.

B. Basic aluminium succinate and subsequent ignition to the oxide, Al$_2$O$_3$. Aluminium can be precipitated as the dense basic succinate by boiling an acid solution containing succinic acid with urea. The hydrolysis of the urea forms ammonia gradually in a homogeneous solution, resulting in a pH of 4·2–4·6:

$$\text{CO(NH}_2)_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{NH}_3$$

The dense precipitate is easily filtered and washed, and exhibits much less tendency to adsorption of other salts than does the precipitate obtained by precipitation as the hydroxide. Upon ignition, the basic succinate is readily converted into alumina.

This method permits the separation of aluminium from large amounts of ferrous iron, nickel, cobalt, manganese, zinc, calcium, barium, and magnesium. For the separation of aluminium and iron, the latter must be maintained in the ferrous state by the addition of phenylhydrazine; for zinc and aluminium, the precipitate contains a little zinc which can be removed by volatilisation at 1000–1100° C. in a current of hydrogen introduced through a silica Rose crucible cover and inlet tube.

C. Basic aluminium benzoate and subsequent ignition to the oxide, Al$_2$O$_3$. Aluminium may be precipitated by ammonium benzoate solution, best at pH 3·5–4, which is attained in the presence of ammonium acetate solution, as the granular basic benzoate: upon ignition, the precipitate is converted into alumina. Separation may thus be made from cobalt, nickel, zinc, * Prepared by adding a cold saturated solution of sulphurous acid to a few ml. of phenylhydrazine until the crystalline sulphite first formed dissolves in the excess, and then adding phenylhydrazine drop-wise and with vigorous shaking until the odour of sulphur dioxide is no longer perceptible. Use 6–10 ml. of this solution in 100 ml. of hot water.
Gravimetric Analysis 449

manganese, calcium, and magnesium, provided that the amounts of these elements do not exceed that of the aluminium: for larger quantities, double precipitation is recommended.

D. Aluminium 8-hydroxy-quinolate, Al(C₆H₅ON)₃. Details of this method are given in Section III, 188A. This procedure separates aluminium from beryllium (see, however, Section IV, 29), the alkaline earths, magnesium, and phosphate. For the gravimetric determination a 2 or 5 per cent solution of oxine in 2N-acetic acid may be used; 1 ml. of the latter solution is sufficient to precipitate 0·003 g. of Al. For practice in this determination, about 0·4 g. of A.R. ammonium alum, accurately weighed, may be used. This is dissolved in 100 ml. of water. The precipitated aluminium oxinate is collected on a weighed filter-crucible (Gooch, sintered-glass, or porcelain), well washed with cold water, dried to constant weight at 130–140° C., and weighed as Al(C₆H₅ON)₃.

B. Determination of aluminium as the basic succinate and ignition to aluminium oxide. Procedure. The solution should contain about 0·1 g. of Al and be acid with hydrochloric acid. Add dilute ammonia solution until the solution becomes slightly turbid, remove the turbidity with dilute hydrochloric acid, and add 1–2 drops in excess. Add a solution of 5 g. of A.R. succinic acid in 100 ml. of water, followed by 10 g. of ammonium chloride and 4 g. of urea; dilute to 500 ml. with distilled water. Heat the solution to boiling and continue the boiling for 2 hours after the solution has become turbid (ca. 45 minutes).* Allow the precipitate to settle for a few minutes, add a Whatman "accelerator," filter, and wash ten times with a 1 per cent succinic acid solution made neutral to methyl red with ammonia solution. If any precipitate adheres to the sides of the beaker, dissolve it in a little dilute hydrochloric acid, add a drop of methyl red or phenol red indicator, and then dilute ammonia solution until just alkaline; filter off the precipitate of aluminium hydroxide on a separate small filter-paper, and wash it with a 2 per cent solution of ammonium nitrate. Place both papers and precipitates in a silica or, preferably, a platinum crucible, and ignite to constant weight at 1200° C. (compare Section IV, 9). Weigh as Al₂O₃.

C. Determination of aluminium as the basic benzoate and subsequent ignition to the oxide. Procedure. To the slightly acid solution (usually with hydrochloric acid) containing about 0·1 g. of Al in a volume of 250–300 ml., add 1 g. of ammonium chloride, 20 ml. of 10 per cent ammonium acetate solution, 20 ml. of 10 per cent ammonium benzoate solution, and a few drops of bromophenol-blue indicator. Heat to 80° C., add sufficient dilute hydrochloric acid to dissolve any precipitated aluminium benzoate (any benzoic acid which separates out in the cold will dissolve during the heating) and introduce dilute ammonia solution from a burette, slowly and with shaking, until the indicator just commences to change colour and precipitation just begins. Boil the solution for 1–2 minutes, whereupon further precipitation takes place and a granular precipitate is formed. Usually at this point the solution becomes faintly acid again: continue the addition of dilute ammonia solution from a burette until the indicator acquires the red-blue colour characteristic of pH 3·5–4. Boil the solution gently for

* The boiling period (after the appearance of a turbidity) may be reduced to 1 hour by first partially neutralising the hot solution to bromo-phenol blue or to methyl orange by the drop-wise addition of dilute ammonia solution: a very faint opalescence will appear.
2–3 minutes, and digest on a water-bath for 30 minutes, by which time the precipitate will have settled out. Filter through a quantitative filter-paper, and wash ten times with a hot wash liquor containing 1.0 g. of ammonium benzoate and 2.0 ml. of glacial acetic acid per 100 ml. (pH ca. 3.8). Ignite to constant weight as under B, and weigh as \( \text{Al}_2\text{O}_3 \).

**BERYLLIUM**

*Discussion.* Until about 1927 beryllium was nearly always determined by precipitation as the hydroxide \( \text{Be(OH)}_2 \) with ammonia solution in the presence of ammonium chloride or nitrate, and subsequently weighing as the oxide \( \text{BeO} \). The method was not entirely satisfactory owing to the gelatinous nature of the precipitate, its tendency to adhere to the sides of the vessel, and its liability to adsorption and related effects. Beryllium hydroxide was usually separated with aluminium hydroxide, which it resembles in many respects; two methods for the separation of beryllium and aluminium are given below.

It has been shown (L. Moser, 1927) that the hydroxide may be obtained in an easily filterable and compact form by precipitation from neutral solutions by heating with ammonium nitrite and methyl alcohol at 70° C., a current of air being passed through the solution. This method provides a separation from all metals of the later analytical groups, excepting barium, which should previously be removed as sulphate; cadmium and thallium also do not interfere.

Beryllium may also be conveniently estimated by precipitation with tannin in ammoniacal solution. Elements such as aluminium, chromium, ferric iron, thorium, zirconium, and titanium are precipitated by tannin from acetic acid solution; beryllium is not precipitated under these conditions, hence a good method of separation from these elements is available. If ferric iron is present, slight reduction to the ferrous state occurs; this is prevented by the addition of a few drops of 10-volume hydrogen peroxide solution prior to precipitation with tannin.

Beryllium may be quantitatively separated from aluminium (and also from iron) by means of oxine. An acetic acid solution containing ammonium acetate is used; the aluminium and iron are precipitated as oxinates, and the beryllium in the filtrate is then precipitated with ammonia solution. It has been stated (Stevens and Carron, 1946) that the oxine method of separation from aluminium and from iron leads to small losses of beryllium. Excellent results are obtained by first removing the iron by the cupferron method, destroying the excess of cupferron, and precipitating the beryllium and aluminium phosphates with ammonium phosphate solution at pH of about 6.2 (methyl-red indicator). The mixed phosphates, unlike the oxides, are readily decomposed upon fusion with anhydrous sodium carbonate in a platinum crucible; upon digesting the product with water and allowing to stand overnight, the hydrated beryllia remains quantitatively in the residue, whilst the alumina (also phosphoric oxide and silica) remain in solution as the sodium salts. The beryllia is filtered off, washed, ignited, and weighed as \( \text{BeO} \).

In all these methods the element is weighed as beryllia, which is somewhat hygroscopic. The ignited residue must be cooled in a desiccator over concentrated sulphuric acid or phosphorus pentoxide, preferably in a tared and stoppered weighing-bottle, and weighed as quickly as possible—usually after 25 minutes.

**A. Determination of beryllium by precipitation with ammonia solution.** *Procedure.* The beryllium solution (200 ml.), prepared with
nitric acid or hydrochloric acid and containing about 0.1 g. of Be, must
be almost neutral and contain no other substance precipitable by
ammonia solution. Heat to boiling, and add dilute ammonia solution
slowly and with constant stirring until present in very slight excess.
Add a Whatman accelerator or one-half of a Whatman ashless tablet,
boil for 1 or 2 minutes, and filter on a Whatman No. 41 or 541
filter-paper. Transfer as much of the precipitate as possible by rinsing
with hot 2 per cent ammonium nitrate solution. Remove any pre-
cipitate adhering to the walls of the beaker by dissolving in the mini-
imum volume of hot very dilute nitric acid, heating to boiling, and
precipitating as before. Filter through the same paper, and wash
thoroughly with the ammonium nitrate solution. Place the paper and
precipitate in a weighed silica, platinum, or Main-Smith crucible, dry,
heat at a low temperature until the carbon has been destroyed, and finally
ignite with a Meker type of burner (at approximately 1000° C.). Allow
to cool in a desiccator over concentrated sulphuric acid or phosphoric
oxide, and weigh rapidly after 25 minutes. Repeat the ignition until
constant weight is attained. Weigh as BeO.

A'. Determination of beryllium by hydrolysis with ammonium nitrite.
Procedure. Neutralise the feebly acid solution, containing about 0.1 g.
of BeO per 100 ml., cautiously with sodium carbonate, and remove the
resultant slight opalescence with a few drops of dilute acid. Heat the
solution to 70° C., pass a current of air through it, and add, with stirring,
50 ml. of 6 per cent ammonium nitrite solution and 20 ml. of methyl
alcohol for each 0.1 g. of BeO expected to be present. Any acid-forming
oxides of nitrogen are thus removed as methyl nitrite. The solution
becomes cloudy after a few minutes. Complete the precipitation by
boiling gently for 30 minutes. Add a further 10 ml. of methyl alcohol,
and, after 10 minutes, filter through a Whatman No. 41 or 541
filter-paper, wash thoroughly with hot water, dry, and ignite as in A.
Weigh as BeO.

A''. Determination of beryllium by means of tannin. Procedure. The solution (300–400 ml.) should be weakly acid, free from all cations
other than those of alkali metals, and contain at most 0.1 g. of BeO.
Add 20–30 g. of ammonium nitrate, heat to boiling, and treat with 10
per cent aqueous tannin solution (use ten times as much tannin as
there is BeO present) with constant stirring, followed by ammonia
solution, dropwise, until precipitation is complete, (the solution should
be just basic to litmus-paper). The precipitate is bulky but not gelatin-
ous, is readily filtered, and shrinks to a relatively small volume on
suction. Filter on a Whatman No. 40 or 540 filter-paper resting
upon a Whatman filter-zone (hardened, No. 51), and apply suction.
Wash with hot water. If alkali metals are present, wash the precipitate
back into the beaker, dissolve in a little hydrochloric or sulphuric acid,
and precipitate the boiling solution with ammonia solution as before.
Filter, dry the paper, and precipitate at 100–130° C., transfer to a
weighed silica, platinum, or Main-Smith crucible, ignite, add a few
drops of concentrated nitric acid (to remove any organic matter which
may be present), ignite strongly, allow to cool in a desiccator, and
rapidly weigh as BeO.

B. Determination of beryllium in the presence of Al, Cr, Fe, Th, and
V by means of tannin. Procedure. The solution should be neutral,
occupy a volume of 300–400 ml. (depending upon the amount of alumin-
Quantitative Inorganic Analysis

ium, etc., present, but this should not exceed 0.1 g.), and contain 30-40 g. of ammonium acetate, and 20-25 g. of ammonium nitrate. Treat with 15-20 ml. of 2N-acetic acid, boil, and precipitate by the addition, with stirring, of excess of 10 per cent aqueous tannin solution or of a 3 per cent solution of tannin in saturated ammonium acetate solution. Filter the tannin adsorption-complex on a filter-paper with suction as in A', and wash with dilute ammonium nitrate solution. Rinse back the precipitate into the beaker by means of a stream of hot water from a wash bottle, and dissolve it by the addition of dilute sulphuric acid to the hot liquid. Nearly neutralise the resulting solution with ammonia solution, and repeat the precipitation as before with ammonium acetate, ammonium nitrate, and acetic acid. After the precipitate has settled, decant the clear supernatant liquid through the filter used for the first filtration, wash the precipitate by decantation with hot ammonium nitrate solution, transfer it completely to the filter, and wash with the hot ammonium nitrate solution until the washings are sulphate-free (test with barium chloride and hydrochloric acid). Precipitate the beryllium in the filtrate and washings by the addition of more tannin solution (if necessary), followed by excess of ammonia solution. Complete the determination as in A'. Weigh as BeO.

If ferric iron is present, add a few drops of 10-volume hydrogen peroxide before precipitating with tannin solution to minimise the chance of any ferrous iron being formed.

If titanium and/or zirconium are present, precipitation may be effected in the presence of more concentrated acid because the tannin complexes of these metals are less soluble; only one precipitation is necessary. The procedure is as follows. To the cold solution (300 ml.) add ammonia solution until it produces an incipient cloudiness, then add ammonium acetate (10 g.), ammonium nitrate (20 g.), and 80 per cent acetic acid (25 ml.). Heat the solution to boiling, and precipitate the titania and/or zirconia by the addition, with stirring, of 10 per cent aqueous tannin solution in ten-fold excess of the weight of the combined oxides. Boil for a few minutes, filter, wash the precipitate with 10 per cent acetic acid and a little ammonium nitrate. Determine the beryllium in the filtrate and washings as above.

Note. If any one of the above metals is present alone with the beryllium it may be determined by igniting the tannin complex, produced in acetic acid solution, to the oxide in the usual way.

B'. Determination of beryllium in the presence of aluminium by means of oxine. Procedure. Precipitate the aluminium from an ammonium acetate-acetic acid solution (Section IV, 28B), and keep the filtrate. Heat the filtrate to boiling, and add a very slight excess of dilute ammonia solution. Filter off the precipitated beryllium hydroxide (preferably after the addition of macerated filter-paper in the form of a Whatman accelerator or one-third of an ashless tablet), which is coloured yellow or brown by adsorbed oxine, through a Whatman No. 41 or 541 filter-paper, wash thoroughly with a hot dilute solution of ammonium acetate containing a few drops of ammonia solution, and complete the determination as in A.

IV, 30.

CHROMIUM

Discussion. Chromium may be determined in one of the following forms:

A. Chromic oxide, Cr₂O₃. The chromium must be present in solution as a chromic compound. It can be precipitated as the hydroxide exactly as
Gravimetric Analysis

453
described under Aluminium in Section IV, 9 by means of the smallest possible excess of ammonia solution (the precipitate is appreciably soluble in excess of ammonia solution) in the presence of excess of ammonium salts. It is important to adjust the pH of the solution because of the amphoteric character of hydrated chromic oxide; the colour of the solution prevents the use of internal indicators, so that electrometric methods must be used; however, the indicator (methyl red) may be used "externally."

The KI-KIO₃ method (Section IV, 28) gives a more easily filterable precipitate:

\[
2\text{CrCl}_3 + 6\text{H}_2\text{O} \rightleftharpoons 2\text{Cr(OH)}_3 + 6\text{HCl}
\]

The basic benzoate method (Sections IV, 28C and IV, 8) may also be used. Good results are obtained by precipitation based upon the slow hydrolysis of potassium cyanate; this yields a granular precipitate of chromic hydroxide which is readily filtered and washed. This procedure will accordingly be described in detail.

A disadvantage of the chromic oxide method is that the results obtained are frequently a few tenths of a per cent too high on account of the formation of small amounts of chromic chromate, \(\text{Cr}_2(\text{CrO}_4)_3\). For highly accurate results the precipitate should be ignited and allowed to cool in hydrogen.

B. Mercurous chromate, \(\text{Hg}_2\text{CrO}_4\), and subsequent weighing as \(\text{Cr}_2\text{O}_3\). The chromium must be present as chromate, and the solution should be free from chloride and large amounts of sulphate. Upon ignition, mercurous chromate is converted into chromic oxide. Numerous cations interfere, hence the method has a very limited application.

C. Barium chromate, \(\text{BaCrO}_4\). The chromium must be present as chromate. The method is of limited application because of the general insolubility of chromates. Chlorides do not interfere, but sulphates must, of course, be absent. For further properties of barium chromate, see Section IV, 45B.

To convert a chromic salt into a chromate, treat the chromic solution contained in a porcelain dish with several ml. of bromine water, followed by freshly prepared potassium hydroxide solution until alkaline. Warm until the odour of bromine disappears.

To convert a chromate into a chromic salt, acidify the solution with hydrochloric acid, and either add excess of freshly prepared saturated sulphurous acid and boil until all the sulphur dioxide has been removed or add concentrated hydrochloric acid and a little alcohol, and boil until the odour of acetaldehyde can no longer be detected and the solution is green. For practice in this operation, determination A may be carried out with A.R. potassium dichromate, previously dried at 180-200° C. for 1 hour. 0·5 Gram of the salt is accurately weighed out into a 600-ml. beaker, dissolved in about 150 ml. of water, 5 ml. of concentrated hydrochloric acid and 15 ml. of ethyl alcohol added, and the whole heated until the solution is green and no longer smells of alcohol or of acetaldehyde. The solution is diluted to 300 ml., and the chromium precipitated as the hydroxide.

A. Determination of chromium as hydroxide by hydrolysis of potassium cyanate. Procedure. Weigh out accurately sufficient of the chromic salt to contain about 0·15 g. of Cr (1), and dissolve it in 200 ml. of cold water. Add 5 g. of ammonium chloride and 1 g. of potassium cyanate, and stir the solution until the solid has dissolved. Heat the solution slowly to boiling, when a fine granular precipitate separates gradually. Allow the precipitate to settle, decant the turbid liquor through a Whatman No. 41 or 541 filter-paper (a), and wash the
precipitate once by decantation with hot 2·5 per cent ammonium nitrate solution rendered faintly ammoniacal. Heat the filtrate to boiling, add a few drops of alizarin-S indicator (2) followed by concentrated hydrochloric acid until the solution is permanently yellow, and then add ammonia solution until the indicator is just red. Collect the small precipitate which is formed upon a separate filter (b), and wash it with hot ammonium nitrate solution. Wash the main bulk of the precipitate by decantation with ammonium nitrate solution, filter off on paper (a), and wash with the same solution. Dissolve the film of precipitate which adheres firmly to the beaker in a few drops of hydrochloric acid, re-precipitate it in the presence of alizarin-S by means of ammonia solution in very slight excess, and filter it upon the second filter (b). Ignite both filters in a weighed platinum crucible; when the carbon has burnt off, ignite for 10 minutes at the maximum heat of a Méker type of burner, and weigh as \( \text{Cr}_2\text{O}_3 \).

Notes. 1. For practice, the student may employ about 2 g., accurately weighed, of A.R. chrome alum \( \text{K}_2\text{SO}_4\cdot\text{Cr}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O} \) for this estimation.
2. The alizarin-S indicator is prepared by dissolving 1 g. of the solid in 1 litre of water, and filtering from any insoluble matter present.

B. Determination of chromium by precipitation as mercurous chromate. Procedure. The solution (1) should be neutral or faintly acid, and contain about 0·1 g. of Cr as chromate (or dichromate) in 100 ml. To the cold solution add a decided excess of mercurous nitrate solution (2), whereby a brown amorphous precipitate of basic mercurous chromate is formed. Heat the solution to boiling, stirring frequently, until the precipitate is converted into the bright red and crystalline mercurous chromate, which settles out quickly; if the precipitation is complete, the supernatant liquid will be colourless. Allow to cool, filter off the precipitate through a Whatman No. 40 or 540 filter-paper, and wash it thoroughly with a cold 2·5 per cent aqueous solution of mercurous nitrate. Dry the filter and precipitate at 100° C. Transfer the filter and precipitate to a weighed porcelain or platinum crucible, heat gently at first and afterwards with the full Méker flame in an oxidising atmosphere until constancy of weight is attained. Weigh as \( \text{Cr}_2\text{O}_3 \). Owing to the poisonous nature of the mercury fumes, the whole operation concerned with the ignition of the precipitate must be carried out in a fume cupboard provided with a good draught.

Notes. 1. A suitable solution for practice may be prepared by dissolving 0·5–0·6 g. of A.R. potassium dichromate, accurately weighed, in 250 ml. of water.
2. Prepare the mercurous nitrate solution as follows. Moisten 3–4 g. of A.R. mercurous nitrate in a test-tube with 2 drops of concentrated nitric acid, add 10 ml. of water, and warm until the salt dissolves. Dilute the solution somewhat before use.

C. Determination of chromium as barium chromate. Procedure. The solution should contain about 0·1 g. of Cr as chromate, be neutral or weakly acid with acetic acid, and occupy a volume of 200–300 ml. Add a 10 per cent solution of barium acetate dropwise from a burette and with constant stirring to the boiling solution (1) until present in slight excess. Place the beaker on a water-bath until the precipitate settles; test for completeness of precipitation by adding a little more
Gravimetric Analysis

of the reagent. Allow to cool, filter with gentle suction through a weighed Gooch, sintered-glass, or porous-porcelain crucible, wash with hot water until 1 ml. of the washings gives no precipitate with a little dilute sulphuric acid. Complete the determination as described in Section IV, 45B. Weigh as $\text{BaCrO}_4$.

Note. 1. A solution for practice may be prepared by dissolving about 0.5 g. of A.R. potassium dichromate, accurately weighed, in 300 ml. of water, adding ammonia solution until neutral, and then 1 ml. of 6N-acetic acid.

IV, 31. IRON

Discussion. Iron may be determined in the following forms:

A. Ferric oxide, $\text{Fe}_2\text{O}_3$. The precipitation of iron as ferric hydroxide by ammonia solution, etc., and its conversion into ferric oxide, in which form it is weighed, is fully described in Section IV, 8. Precipitation with ammonia solution yields a gelatinous precipitate which is somewhat difficult to wash and to filter; this difficulty is partly overcome by the use of macerated filter-paper.

There are, however, three methods of precipitation which yield ferric hydroxide in a relatively dense and granular form, which is easily washed and filtered. These are:

(i) The potassium cyanate method. This has already been discussed under Chromium, Section IV, 30.

(ii) The hexamethylenetetramine method. This is based upon the slow hydrolysis of hexamethylenetetramine in acid solution:

$$2\text{FeCl}_3 + 6\text{H}_2\text{O} \rightleftharpoons 2\text{Fe(OH)}_3 + 6\text{HCl}$$

$$(\text{CH}_2)\text{N}_4 + 10\text{H}_2\text{O} \rightleftharpoons 6\text{HCHO} (\text{formaldehyde}) + 4\text{NH}_4\text{OH}$$

Separation of ferric iron is effected from manganese, zinc, cobalt, and nickel, but not from aluminium, chromium, and titanium, which are precipitated. If calcium is present, there is no risk of co-precipitation as carbonate, as when ammonia solution is used, for the latter reagent frequently contains traces of carbonate.

(iii) The hydrazine hydrate method. This procedure is particularly valuable in the separation of ferric iron from manganese. Precipitation must be carried out in neutral or slightly alkaline solution, for in acid solution reduction to the ferrous state occurs.

Full experimental details for each of these methods will be given.

Attention is directed to the fact that if ignition is carried out in a platinum crucible at a temperature above 1100° C. some reduction to triferric tetroxide $\text{Fe}_3\text{O}_4$ may occur, and at temperatures above 1200° C. some of the oxide may be reduced to the metal and alloy with the platinum. This accounts in part for the contamination of the platinum crucible by iron which sometimes occurs in analytical work. No magnetic oxide of iron is produced if Main-Smith crucibles (Section II, 38B) are employed for the ignitions.

B. Ferric cupferron and subsequent weighing as ferric oxide. Cupferron, the ammonium salt of nitrosophenylhydroxylamine, $\text{C}_9\text{H}_8\text{N(NO)}\text{ONH}_4$, precipitates iron, vanadium, titanium, and zirconium from strongly acid solutions, thus affording a separation from aluminium, chromium, beryllium, phosphorus, boron, manganese, zinc, nickel, cobalt, and sexivalent uranium (compare Section I, 62B). Copper and thorium must be precipitated from weakly acid solutions. Several metals (e.g., lead, silver, mercury, bismuth, tungsten, and cerium) interfere, but most of these may usually be removed by other methods—for example, by hydrogen sulphide in acid solution. The precipitate cannot be weighed as such, but must be ignited to the oxide.
The ignition must be very carefully carried out in the early stages in order to avoid mechanical losses, for wet precipitates tend to liquefy and effervesce, whilst dry precipitates give off considerable volatile matter. The precipitate is rather bulky, and the amount of material taken should therefore be such as to yield 0·1-0·2 g. of ferric oxide.

C. Ferric 8-hydroxyquinolinate (oxinate). Although subject to interference by numerous elements, this determination is of interest, as it provides a method of producing a crystalline ferric complex, which can be collected upon a filter-crucible and weighed after drying at 135°C. Co-precipitation of aluminium may be prevented by maintaining the pH at 3·5-4·0 by the use of a buffer solution containing ammonium acetate and tartaric acid. The experimental details given below refer to a solution of a ferric salt free from interfering elements.

Treat 25 ml. of the ferric solution (containing about 0·03 g. of Fe) with dilute ammonia solution until a faint precipitate persists, and dissolve the precipitate in the minimum volume of ca. N-hydrochloric acid. Then add a solution of 3 g. of ammonium acetate in 125 ml. of water, followed by oxine solution (2 per cent in N-acetic acid) from a burette with constant stirring until an excess is present: 12-15 ml. are required. Digest the dark precipitate at 80-90°C (water-bath) for 30 minutes, filter through a sintered-glass crucible (porosity No. 3), wash successively with 1 per cent acetic acid and water, and dry to constant weight at 130-140°C. Weigh as Fe(C₉H₆O₇N)₃.

A. Determination of iron as hydroxide by hydrolysis of potassium cyanate. Procedure. The solution (200 ml.) should contain 0·15-0·20 g. of Fe in the ferric state. Add a few drops of concentrated hydrochloric acid, and heat to boiling (1). Add a concentrated aqueous solution containing 2 g. of potassium cyanate to the boiling solution as rapidly as possible, with vigorous stirring (2). Boil the solution for 2-3 minutes, and allow the precipitate to settle. Wash well by decantation with hot water, filter off, and complete the determination as in Section IV, 30A. It is better to ignite the wet filter-paper and precipitate in a Main-Smith crucible. Weigh as Fe₂O₃.

Notes. 1. If the yellowish solution darkens during heating, add more hydrochloric acid to bring back the solution to the original colour.
2. The cyanate solution cannot be added all at once, for frothing will then be excessive. It is important that the ferric hydroxide sol stage be passed through as quickly as possible.

A'. Determination of iron as hydroxide by means of hexamethylenetetramine. Procedure. The solution (200 ml.) should be faintly acid and contain about 0·1 g. of Fe in the ferric state. To the cold solution add 20 g. of ammonium chloride, followed by excess of a 10 per cent aqueous solution of hexamethylenetetramine with stirring. Allow the precipitate to settle, decant the mother liquor through a Whatman No. 41 or 541 filter-paper, wash the precipitate by decantation with hot water, transfer to the filter (1), and again wash with hot water. Ignite the precipitate and weigh as Fe₂O₃.

Note. 1. If a tenacious film of the precipitate adheres to the beaker, dissolve it in a few drops of concentrated hydrochloric acid, and re-precipitate with ammonia solution.

A". Determination of iron as hydroxide by means of hydrazine hydrate. Procedure. The solution (100 ml.) should contain about
Gravimetric Analysis

0·1 g. of Fe in ferric state. Add 8 g. of ammonium chloride, a few drops of methyl-red indicator and neutralise with ammonia solution (methyl red turns yellow). Then add in one operation a slight excess of hydrazine hydrate solution (1), and boil for a short time. Filter through a Whatman No. 41 or 541 filter-paper, wash with hot water containing 1 g. of ammonium chloride and 1 ml. of hydrazine hydrate per 100 ml., and then with hot water. Dry and ignite in the usual way. Weigh as Fe2O3.

Note. 1. Prepared by adding 4 ml. of hydrazine hydrate (poisonous) to 100 ml. of water.

B. Determination of iron with cupferron. Procedure. The solution (1) (150–200 ml.) should contain about 0·1 g. of Fe in the ferric state and be strongly acid with hydrochloric acid or sulphuric acid. To the cooled solution (ca. 10° C.) add a freshly prepared, filtered 5 per cent aqueous cupferron solution (2) slowly and with constant and vigorous stirring until no further formation of a brown precipitate takes place. The formation of a white precipitate of nitrosophenylhydroxylamine indicates when the reagent is present in excess. Do not warm, since the reagent is rapidly decomposed in hot acid solution. Add a Whatman accelerator (or a third of a Whatman ashless tablet), stir for 2–3 minutes, and without further delay filter through a Whatman No. 41 or 541 filter-paper, preferably supported upon a Whatman filter-cone. Wash several times with 10 per cent by volume of hydrochloric acid containing 1·5 g. of cupferron per litre, then twice with 5N-ammonia solution to remove excess of cupferron, and finally once with water. Ignite the precipitate with the paper in a weighed porcelain, silica, or platinum crucible (best in a Main-Smith crucible, Section II, 36B) very gently at first until all the organic matter is destroyed, and then strongly to constant weight. Weigh as Fe2O3.

Notes. 1. A suitable solution for practice may be prepared by weighing out accurately 0·8–0·9 g. of A.R. iron alum, dissolving it in 150 ml. of water, and adding 25 ml. of concentrated hydrochloric acid.

2. Only freshly prepared solutions should be employed, because the solution only keeps for a day or two. The dry reagent should be kept in a cool, dark place, and preferably with a bag of ammonium carbonate suspended in the bottle.

IV, 32. NICKEL

Discussion. Nickel may be determined in one of the following forms:

A. Nickel dimethylglyoxime, Ni(C₂H₅O₂N₂)₂. Full details of this estimation are given in Section IV, 12.

B. Nickel salicylaldoxime, Ni(C₇H₆O₃N)₂. The complex is precipitated in neutral or very faintly acid solutions (best at pH = 7) in contrast to that of copper (Section IV, 19C), which is formed in the presence of acetic acid. The experimental details are similar to those already given for copper, except that the solution must be neutral or very faintly acid. Experimental details for the separation of copper and nickel with salicylaldoxime are given below. Ferric iron interferes, and should therefore be absent.

C. [(Ni(C₂H₅N)₄)(CN)₃] ; pyridine method. This is a rapid method, similar in advantages and limitations to those described for copper (Section IV, 19E), cobalt (Section IV, 33D), and zinc (Section IV, 34D). A determination may be completed in about 30 minutes.
D. Nickel dicyandiamidine, Ni(C₂H₄ON₄)₂. When a solution of a nickel salt is made strongly alkaline with ammonia solution and treated with sodium or potassium hydroxide solution and dicyandiamidine sulphate, a yellow or orange precipitate of the nickel dicyandiamidine complex, Ni(C₂H₄ON₄)₂, is obtained. This may be weighed after drying at 120–130°C. It is usually preferable to dissolve the precipitate in excess of standard 0·1N-hydrochloric acid and to titrate the excess of standard acid with standard 0·1N-sodium hydroxide solution in the presence of methyl red as indicator:

\[ \text{Ni(C}_2\text{H}_4\text{ON}_4)_2 + 4\text{HCl} \rightleftharpoons 2(\text{C}_2\text{H}_4\text{ON}_4\text{HCl}) + \text{NiCl}_2 \]

1 ml. 0·1N-HCl = 0·001467 g. Ni

This provides an excellent method for the volumetric determination of nickel. Moderate amounts of iron, aluminium, chromium, zinc, cobalt, titanium, and zirconium do not interfere, but copper (which gives a red precipitate, Cu(C₂H₄ON₄)₂) must be absent. Cobalt gives a red-violet coloration and, if present in high concentration, should be converted into the cobaltic state by oxidation with hydrogen peroxide in ammoniacal solution or its co-precipitation prevented by the addition of sucrose. The addition of hydrazine sulphate is said to prevent the precipitation of manganese as the hydrated dioxide.

Nickel may be determined in nickel steel by first removing the iron as chloride by ether extraction (Section I, 73B) or by the basic acetate method (Section I, 61B).

E. Metallic nickel. Experimental details of the electrolytic method are given in Section IV, 81.

B. Determination of nickel in the presence of copper with salicylaldoxime. Procedure. Treat the solution, free from mineral acid and containing both nickel (not more than 0·03 g.) and copper (about 0·03 g.), with 1 g. of sodium acetate and 10 ml. of glacial acetic acid per 100 ml. of solution.† Add excess of salicylaldoxime reagent over the quantity required to precipitate both metals, and stir the solution vigorously during the addition. Filter off the precipitated copper complex on a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), wash well with cold water, and dry at 100–105°C to constant weight. Weigh as Cu(C₇H₅O₂N)₂. Calculate the weight of copper present. Add dilute ammonia solution to the filtrate and washings (diluted to 350–400 ml.) until the solution is very faintly acid or alkaline. Stir thoroughly to coagulate the precipitate of nickel salicylaldoxime. Filter through a weighed, sintered-glass or porous-porcelain crucible, wash with cold water until the washings give no coloration with ferric chloride solution, and dry at 100°C to constant weight. Weigh as Ni(C₇H₅O₂N)₂. Calculate the weight of nickel present.

C. Determination of nickel by the pyridine method. Procedure. The solution (100 ml.) should contain about 0·1 g. of nickel (1) and be neutral in reaction. Stir in 0·5–1·0 g. of A.R. ammonium thiocyanate, heat to boiling, add 1–2 ml. of pure pyridine, and immediately remove the flame. Stir for 2–5 seconds until the precipitate commences to separate in sky-blue prisms. (The precipitate separates immediately or after standing a short time, according to the quantity of nickel present.) When cold, filter through a weighed, sintered-glass or porous-porcelain crucible, and use Solution 1 to assist in the transfer of the precipitate.

---

* Dicyanodiamidine or guanyl urea, \( H₂N-C(=NH)-NHCONH₂ = C₂H₄ON₂ \).
† The best pH range for the precipitation of copper in the presence of nickel is 2·6–3·1.
to the crucible. Wash four to five times with Solution 2, then twice with 1-ml. portions of Solution 3, and finally five or six times with 1-ml. portions of Solution 4. Dry in a vacuum desiccator at room temperature for 10 minutes and weigh. Repeat the drying until the weight is constant. Weigh as \([\text{Ni}(C_6H_5N)_4](\text{CNS})_2\) (2).

**Solution 1.** 100 ml. of water containing 0·4 g. of NH₄CNS and 0·6 ml. of pyridine.

**Solution 2.** 61·5 ml. of water, 37·0 ml. of 95 per cent alcohol, 0·1 g. of NH₄CNS, and 1·5 ml. of pyridine.

**Solution 3.** 10 ml. of absolute alcohol and 0·5 ml. of pyridine.

**Solution 4.** 20 ml. of absolute (sodium dried) ether and 2 drops of pyridine.

**Notes.** 1. For practice in this estimation, the student may employ 0·3 g., accurately weighed, of A.R. nickel sulphate or pure nickel ammonium sulphate.

2. For further experimental details, see under Copper and Zinc.

**D. Determination of nickel with dicyandiamidine sulphate. Procedure. A. Nickel in a nickel salt.** Weigh out accurately about 0·4 g. of pure nickel ammonium sulphate, NiSO₄(NH₄)₂SO₄·6H₂O, into a 250-ml. beaker, dissolve it in a little water, add 6 ml. of concentrated ammonia solution, followed by 50 ml. of 3–4 per cent aqueous dicyandiamidine sulphate solution. Cool, and add 20 per cent potassium hydroxide solution (about 5 ml. are required) with constant stirring until the solution acquires an orange colour. The orange (yellow) complex soon separates. Allow to stand for a few hours, or overnight. Filter through a sintered-glass crucible (porosity No. 3), wash with 2 per cent ammonia solution, then with a little alcohol, and dry to constant weight at 120–130°C. Weigh as Ni(C₆H₅N₄)₂. The precipitate is slightly hygroscopic so that rapid weighing is desirable.

It is preferable to employ the volumetric method. Filter off the precipitate through a sintered-glass crucible: use the rubber-ring adapter shown in Fig. 11, 31, 3, to support the crucible. Wash the precipitate with 2 per cent ammonia solution to remove free potassium hydroxide solution, and then with rectified spirit until free from ammonia solution (test with mercurous nitrate paper). Remove the crucible from the rubber adapter, invert it, place it centrally over the rubber ring and apply suction: upon directing a stream of water from a wash-bottle on to the sintered-glass disc, the precipitate is completely transferred to the filter-flask. Introduce 50 ml. of 0·1N-hydrochloric acid and a few drops of methyl-red indicator into the flask, swirl the liquid gently until the precipitate dissolves, and titrate the excess of acid with 0·1N-sodium hydroxide. Calculate the percentage of nickel in the salt.

\[1 \text{ml. } 0·1N-\text{HCl} = 0·001467 \text{ g. Ni}\]

**B. Nickel in nickel steel (compare Section IV, 12B).** Weigh out accurately about 1 g. of the nickel steel, dissolve it in about 10 ml. of concentrated hydrochloric acid, and add about 3 ml. of concentrated nitric acid to oxidise the ferrous iron. Boil the solution to complete the oxidation and remove nitrous fumes. Dilute to 200 ml., add a dilute solution of sodium carbonate from a burette, slowly and with stirring, until a slight opalescence persists. Just dissolve the precipitate by the addition of glacial acetic acid (ca. 3 ml.), then dilute
with a further 500 ml. of water, heat to the boiling point, introduce 6 ml. of 30 per cent sodium acetate solution and boil for 1 minute only. Add a Whatman "accelerator," allow the precipitate to settle for 3 minutes, filter, and wash the precipitate three times with 5 per cent sodium acetate solution. Set the combined filtrate and washings (F) aside. Puncture the apex of the filter with a glass rod, and wash the precipitate into the original beaker with warm dilute hydrochloric acid (1 : 1). Re-precipitate exactly as before by neutralisation of the acid with sodium carbonate solution, addition of sodium acetate solution, etc. Combine the filtrate and washings from the re-precipitation with (F), and evaporate on a hot-plate to a volume of about 100 ml. Add 5 ml. of dilute ammonia solution, 1 g. of dicyandiamidine sulphate, and 1 g. of sodium potassium tartrate, and stir. When the solids have dissolved, precipitate the nickel dicyandiamidine complex by adding, with stirring, 20 ml. of 20 per cent potassium hydroxide solution. Complete the determination as detailed under A.

Calculate the percentage of nickel in the sample of nickel steel.

The following alternative procedure may be used to remove most of the iron in the solution prior to precipitation of the nickel complex. It is based upon the fact that ferric chloride is soluble in diethyl ether, whereas the chlorides of a number of other elements (including nickel) are insoluble or so slightly soluble as to cause little or no concern. First prepare the following solutions: (a) dilute concentrated hydrochloric acid with distilled water to a specific gravity of 1.10 (use a hydrometer); (b) saturate the diluted hydrochloric acid with alcohol-free ether by adding small portions of ether with cooling and shaking until a layer of ether remains on top of the acid (about 30 ml. of ether are required for 100 ml. of acid).

Weigh out accurately about 1 g. of the nickel steel, dissolve it in 10 ml. of concentrated hydrochloric acid, and oxidise the ferrous iron by adding 3 ml. of concentrated nitric acid. Evaporate the solution to a volume of 5 ml., cool, transfer to a 250-ml separatory funnel with the aid of 40–50 ml. (in small portions) of solution (a). Cool the solution to about 5° C., introduce 30 ml. of alcohol-free ether, cool to 5° C., stopper the funnel, and shake gently for several minutes to extract the ferric chloride. Allow to stand for 5 minutes and run off the aqueous layer into another 250-ml separatory funnel. Wash the residual ether layer with three 5-ml. portions of solution (b), and draw off the aqueous solution obtained after each washing to the second separatory funnel. Extract the aqueous layer in the latter with 15 ml. of ether, and draw off the aqueous layer into a 600-ml beaker: wash the ether layer with three 5-ml. portions of solution (b) and, as before, run off the aqueous phase (after settling) into the beaker. Evaporate the aqueous solution almost to dryness on a low-temperature hot-plate (caution 1), add 100 ml. of water, 1 g. of sodium potassium tartrate, 1 g. of dicyandiamidine sulphate, and 5 ml. of concentrated ammonia solution, and warm until dissolved. Precipitate the nickel dicyandiamidine complex with 20 ml. of 20 per cent potassium hydroxide solution, and allow to stand overnight. Filter and complete the determination as under A.

Calculate the percentage of nickel in the steel.
IV, 33. COBALT

Discussion. Cobalt may be separated in one of the following forms:

A. Cobalt α-nitroso-β-naphthol complex, weighed as CoSO₄ or as Co. α-Nitroso-β-naphthol gives a red precipitate with solutions of cobalt salts. There is some doubt as to the exact composition of the precipitate: the composition Co(C₁₀H₆O₃N)₂ has been assigned to it, but it is probably not pure. The complex is best converted into cobalt sulphate, CoSO₄, or into metallic cobalt, and weighed in either of these forms. For the limitations of the method, see Section I, 62F.

An important application is to the separation of nickel and cobalt: a double precipitation is desirable when nickel is present in large amount.

B. Cobalt anthranilate, Co(C₇H₄O₂N)₂. In the absence of numerous interfering elements (see Section I, 62L) cobalt can be precipitated in neutral or faintly acid solution by sodium anthranilate as the complex Co(C₇H₄O₂N)₂, which is weighed after drying at 105–110°C.

The procedure may be employed to determine the cobalt which remains after nickel has been precipitated with dimethylglyoxime. The filtrate is evaporated down with sulphuric acid until fumes of sulphur trioxide appear, the solution is diluted, the pH adjusted, and the cobalt precipitated as the anthranilate.

C. Cobalt phenylthiohydantoate complex. Phenylthiohydantoic acid precipitates cobalt in ammoniacal solution in the presence of citrate as a red-brown complex of somewhat indefinite composition. The precipitate may be ignited to the oxide “Co₃O₄” of uncertain composition, the latter fused with potassium pyrosulphate, and the cobalt in the aqueous extract determined by any of the other methods given in this Section. For the limitations and advantages of the method, see Section I, 62G.

D. [Co(C₇H₄N)₄](CNS)₆; pyridine method. If a dilute neutral solution of a cobalt salt is treated with ammonium thiocyanate and pyridine, tetra-pyridine cobalt dithiocyanate is quantitatively precipitated. The precipitate is collected and washed, inter alia, with alcohol and ether containing a little pyridine, and then dried by simply leaving in a vacuum desiccator for 5–15 minutes. A complete determination of cobalt may be carried out in about 30 minutes. The precipitate may be kept unchanged for several hours in a vacuum desiccator. The method can be applied in the presence of the alkali metals, magnesium, and the alkaline-earth metals, but copper, cadmium, nickel, manganese, and zinc must be absent. Large quantities of ammonium salts must be absent, since these exert a slight solvent action upon the precipitate. If the solution is strongly acid, it should be evaporated to dryness and the residue dissolved in water.

E. Metallic cobalt. The electrolytic method is discussed in Section IV, 82.

A. Determination of cobalt with α-nitroso-β-naphthol. Procedure. Dilute the solution containing not more than 0.1 g. of Co as chloride or as sulphate (1) to 200 ml., add sufficient concentrated hydrochloric acid to give a total of 5 ml. of the concentrated acid in the solution, and warm to about 80°C. Add the freshly prepared α-nitroso-β-naphthol reagent (for preparation, see Section I, 62F) until precipitation is considered complete: about 0.05 g. of α-nitroso-β-naphthol are required for each 0.01 g. of Co. Heat to gentle boiling with stirring until the precipitate coagulates or settles out. The supernatant liquid should be clear and yellow. Test whether precipitation is complete by adding a little more of the reagent to the clear solution. Allow to stand for 2–3 hours and decant the clear solution through a quantitative filter-paper (e.g.,
Whatman, No. 541). Wash the precipitate by decantation with a little warm (ca. 80° C.) dilute hydrochloric acid (1 : 2), finally transfer the precipitate to the filter-paper, and wash with hot water until free from acid. Dry the bulky precipitate at 100–110° C. for 1 hour; it will shrink considerably. Place the dried filter-paper and precipitate in a silica crucible provided with an interior-fitting serrated lid (Fig. II, 36, 2) just cover the precipitate with A.R. oxalic acid (this will prevent sudden decomposition of the complex and consequent mechanical loss during the ignition process) and heat gently until all the organic matter has burned off. Ignite the precipitate for a few minutes, allow to cool, treat with a few drops of concentrated nitric acid to oxidise any residual carbon and to convert the oxide into nitrate; heat carefully until the excess of nitric acid has been expelled. Finally, add enough sulphuric acid to convert the nitrate into sulphate, heat cautiously until the excess of acid has been expelled, and then for a few moments to very pale redness (450–500° C.). Allow to cool, moisten with a drop or two of water, and again heat cautiously as before to expel any free sulphuric acid. Allow to cool in a desiccator and weigh as cobaltous sulphate, CoSO₄.

In an alternative procedure, the cobalt is weighed as the metal. Transfer the dried precipitate and filter-paper to a Rose crucible (Fig. IV, 34, 1). Ignite the precipitate and filter-paper in the presence of oxalic acid as before: it is important to heat very slowly at first and subsequently to oxidise any residual carbon with a little concentrated nitric acid. Fit a Rose crucible-cover on to the crucible, and continue the ignition in a stream of pure hydrogen for at least 30 minutes. Withdraw the burner beneath the crucible and, after the crucible is almost at room temperature, momentarily stop the stream of hydrogen so as to extinguish the flame burning at the cover. Continue the passage of the stream of hydrogen until the crucible is at room temperature, and weigh as metallic cobalt. Repeat the treatment with hydrogen (heating period of 30 minutes in hydrogen) until constant weight is attained.

Note. 1. A suitable solution for practice in this determination may be prepared from 0.1 g., accurately weighed, of A.R. cobaltous sulphate (clear, uneffloresced crystals) or pure cobalt ammonium sulphate.

B. Determination of cobalt as the anthranilate. Procedure. The solution should contain not more than 0.10 g. of Co in 250 ml., the pH should be 4.5 or higher, and be free from high concentrations of sodium acetate or ammonium salts. Heat to boiling, add with stirring 15–20 ml. of 3 per cent sodium anthranilate solution, and continue the boiling for 5 minutes. Allow to stand for 10–15 minutes, filter on a sintered-glass or porous-porcelain crucible, wash with cold 0.15 per cent sodium anthranilate solution, followed by alcohol, and dry at 105–110° C. to constant weight. Weigh as Co(C₇H₇NO₂).
Filter the bulky precipitate through a Whatman No. 41 or 541 filter-paper, wash well with a 0.5 per cent ammonium citrate solution, and dry at 100-105°C. The material thus obtained is not pure cobaltous phenylthiohydantoate, and upon ignition it gives impure Co₃O₄; nevertheless, if it is ignited in a porcelain crucible over a Meker-type burner, fairly accurate results are obtained by calculating as if it were Co₃O₄. However, it is usually best to fuse the impure oxide with pure potassium pyrosulphate, dissolve the cooled melt in water, and determine the cobalt by methods A or B.

D. Determination of cobalt by the pyridine method. Procedure. The solution (75-100 ml.) should be neutral and contain about 0.1 g. of Co (1). Add 0.5-1.0 g. of A.R. ammonium thiocyanate, heat to boiling, treat with 1-2 ml. of pure pyridine, and remove the source of heat immediately. Stir for 5 seconds, and allow to cool to room temperature. The solution remains clear for a short time; as the solution cools, red, shiny crystals of the complex separate. (If the precipitate on the sides of the beaker exhibits the blue colour of the di-pyridine complex, this is washed with a little water into the solution when the blue colour immediately disappears. If stirring is continued for several minutes after the addition of the pyridine, the compound soon separates in the crystalline form.) Filter through a weighed, sintered-glass or porous-porcelain crucible; use Solution 1 to assist in the transfer of the precipitate to the crucible. Wash the precipitate five or six times with Solution 2, then twice with 1-ml. portions of Solution 3, and finally eight to ten times with small volumes (1-2 ml.) of Solution 4 (for further experimental details, see Sections IV, 19E, and IV, 34D). Dry in a vacuum desiccator at room temperature for 10 minutes, and weigh. Repeat the drying, etc., until the weight is constant. Weigh as [Co(C₅H₇N)₄]₆(OS₄)₂.

Solution 1. 100 ml. of water containing 0.5 g. of NH₄CNS and 0.7 ml. of pyridine.
Solution 2. 85-5 ml. of water, 13-0 ml. of 95 per cent alcohol, 0.1 g. of NH₄CNS and 1-5 ml. of pyridine.
Solution 3. 25 ml. of absolute alcohol and 2 ml. of pyridine.
Solution 4. 30 ml. of absolute (sodium dried) ether and 4 drops of pyridine.

Note. 1. For practice in this estimation, the student may employ 0.3 g., accurately weighed, of A.R. cobalt ammonium sulphate or of A.R. cobaltous sulphate. If the solution is weakly acid, add ammonium thiocyanate, then pyridine until a precipitate appears, warm until the precipitate dissolves, add 1-1.5 ml. of pyridine, and immediately remove the source of heat.

IV, 34. ZINC

Discussion. Zinc may be determined in any of the following forms:
A. Zinc ammonium phosphate, ZnNH₄PO₄, or zinc pyrophosphate, Zn₂P₂O₇.
The zinc is precipitated, with close adherence to the experimental conditions detailed below, as zinc ammonium phosphate, ZnNH₄PO₄·6H₂O, and weighed either as ZnNH₄PO₄ (after drying at 105°C) or as Zn₂P₂O₇ (after ignition at 900-1000°C). It has been stated that zinc pyrophosphate is slightly volatile at the high temperature required for its conversion from zinc ammonium phosphate; it is therefore probably best to weigh the zinc as the
ammonium phosphate. The method is of limited application because of the numerous elements which form sparingly soluble phosphates.

The precipitant is diammonium hydrogen phosphate, \((\text{NH}_4)_2\text{HPO}_4\), which exerts an important buffering action (due to \((\text{NH}_4)_2\text{HPO}_4/(\text{NH}_4\text{H}_2\text{PO}_4)\)):

\[
\begin{align*}
\text{ZnCl}_2 + (\text{NH}_4)_2\text{HPO}_4 &= \text{ZnNH}_4\text{PO}_4 + \text{NH}_4\text{Cl} + \text{HCl} \\
\text{HCl} + (\text{NH}_4)_2\text{HPO}_4 &= \text{NH}_4\text{H}_2\text{PO}_4 + \text{NH}_4\text{Cl}
\end{align*}
\]

It has been shown that the most satisfactory results are obtained over the pH range 6·4–6·9 (optimum pH is 6·6), and that when the pH exceeds 7·0 the precipitate is removed from the beaker with difficulty. A solution containing 5–10 g. of ammonium chloride, 10 ml. of 2N-sodium acetate, and 10 ml. of 10 per cent \((\text{NH}_4)_2\text{HPO}_4\) solution in 150 ml. has a pH of 7·5; this automatically falls to 6·4–6·9 when heated for 2 hours on the water-bath, hence this mixture is employed for precipitation.

Considerable quantities of alkali salts should be absent, for in their presence the precipitate is contaminated with zinc sodium (or potassium) phosphate. These may be removed by double precipitation; the precipitate is dissolved in the minimum volume of dilute hydrochloric acid and re-precipitated.

B. Zinc sulphide, \(\text{ZnS}\), and subsequent weighing either as \(\text{ZnS}\) or as \(\text{ZnNH}_4\text{PO}_4\). The zinc is precipitated as zinc sulphide under carefully controlled conditions. The pH of the solution should be maintained between 2 and 3; precipitation is only partial from more acid solutions; the zinc sulphide is gelatinous and difficult to filter when precipitated from solutions of pH greater than 3. The appropriate pH is attained by the use of such buffer mixtures as formate/formic acid or sulphate/hydrosulphate: the use of the latter will be described. The method may be used for the separation of zinc from moderate quantities of iron, aluminium, chromium, uranium, manganese, and nickel, but not from cobalt. The amounts of these metals co-precipitated with the zinc sulphide can be reduced to negligible proportions by the addition of a little gelatin or agar-agar, which causes the zinc sulphide to flocculate rapidly and thus filter more easily (compare barium sulphate, Section IV, 6). If the precipitation is carried out in the presence of a little acrolein (ca. 0·20 ml.), the amount of cobalt carried down is so reduced that one precipitation gives a satisfactory separation.

The zinc sulphide may be weighed as such after heating with excess of pure sulphur in a current of hydrogen, or it may be dissolved in 1 : 1 hydrochloric acid, the solution boiled until free of hydrogen sulphide, precipitated as \(\text{ZnNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}\) and weighed as \(\text{ZnNH}_4\text{PO}_4\) as under A.

C. Zinc quinaldinate, \(\text{Zn(C}_{14}\text{H}_{16}\text{O}_8\text{N})_{2}\cdot\text{H}_2\text{O}\). Quinaldic acid or its sodium salt precipitates zinc quantitatively from dilute acetic acid or slightly ammoniacal solutions. Iron, aluminium, chromium, beryllium, titanium, and uranium interfere in acid solution, but in the presence of alkali tartrate in alkaline solution only zinc precipitates; copper and cadmium must be absent. The reagent is expensive, but may be recovered (see Section I, 63M).

D. \([\text{Zn(C}_{3}\text{H}_{5}\text{N})_{2}]\text{(CNS)}_{2}\); pyridine method. This method is a very rapid one, but unless the various wash solutions are carefully prepared, low results will be obtained. The complex may be kept unchanged in a vacuum desiccator for 2–3 hours (see Section I, 62K). Large quantities of ammonium salts must not be present, as these exert a slight solvent action upon the precipitate. If the solution is strongly acid, it must be evaporated to dryness and the residue dissolved in water.

E. Zinc anthranilate, \(\text{Zn(C}_{7}\text{H}_{6}\text{O}_2\text{N})_{2}\). Sodium anthranilate precipitates zinc from neutral solution as \(\text{Zn(C}_{7}\text{H}_{4}\text{O}_2\text{N})_{2}\), which may be weighed after drying at 105–110° C. Numerous elements interfere (for discussion, see Section I, 62L). At present the main application would appear to be to
solutions containing no interfering elements, or as a final weighing form for zinc, subsequent to the separation of that element by conventional methods, e.g., as ZnS.

F. Zinc hydroxyquinaldinate, Zn(C₉H₇ON₂). Zinc may be precipitated by 8-hydroxyquinaldine (2-methyloxine) in acetic acid-acetate solution: it can thus be separated from aluminium and magnesium (see Section I, 62P). It can be weighed as Zn(C₉H₇ON₂)₂ after drying at 130–140°C. The co-precipitated reagent is volatile at 130°C.

G. Metallic Zinc. For details of the electrolytic determination see Section IV, 84.

A. Determination of zinc as the ammonium phosphate or as the pyrophosphate. Procedure. To the solution containing about 0·1 g. of Zn (1), add a drop or two of methyl-red indicator and neutralise, if necessary, by the addition of dilute ammonia solution (1 : 1). Dilute to 150 ml. Heat nearly to boiling and treat with 25 ml. of 10 per cent A.R. diammonium hydrogen phosphate solution added slowly from a pipette or burette. A flocculent precipitate of zinc phosphate first forms. Heat on a water-bath (30–60 minutes) until the flocculent precipitate changes to the crystalline zinc ammonium phosphate, which settles readily. Allow to stand until the solution is at room temperature, filter through a weighed crucible (Gooch, sintered-glass, or porous-porcelain), wash first with 1 per cent ammonium hydrogen phosphate solution, and then about 10 times (using a total volume of about 100 ml.) with cold water. (Measure the volume of the wash water used and apply a correction of 0·5 mg. of Zn for every 100 ml. employed to cover the solubility loss.) Dry to constant weight at 100–105°C. (about 1 hour). Weigh as ZnNH₄PO₄(2).

To weigh as the pyrophosphate, filter through a weighed porous-porcelain or Vitreosil filter-crucible (Section II, 33), and ignite slowly at 900°C in an electrically heated muffle furnace to constant weight. If a muffle furnace is not available, place the crucible within a larger nickel crucible (Fig. II, 51, 4), heat with a Meker type of burner slowly at first and then to redness until constant weight is attained. Weigh as Zn₂P₂O₇.

Notes. 1. A suitable solution for practice may be prepared by dissolving about 0·4 g., accurately weighed, of A.R. zinc sulphate in about 75 ml. of water. A better method is to prepare pure zinc ammonium sulphate ZnSO₄(NH₄)₂SO₄·6H₂O by mixing equimolecular amounts of A.R. zinc sulphate and A.R. ammonium sulphate dissolved in boiling water, and re-crystallising the product twice from hot water. The crystals are air dried, and 0·6 g., accurately weighed, is dissolved in 75 ml. of water.

2. A more rapid, but less accurate method of weighing the precipitate, collected on a sintered-glass or porous-porcelain crucible, is as follows. After washing with cold water, wash the zinc ammonium phosphate five or six times with small volumes of rectified spirit and then five times with small portions of anhydrous ether. Suck the precipitate dry at the pump for 10 minutes, wipe the outside of the crucible dry with a clean linen cloth, leave in a vacuum desiccator for 10 minutes, and weigh as ZnNH₄PO₄·H₂O, which contains 38–28 per cent of Zn.

B. Determination of zinc as sulphide. Procedure. The zinc solution may contain up to 0·25 g. of Zn in a volume of about 250 ml.; it should be free from chloride, which tends to raise the pH required for the complete precipitation of zinc sulphide, and is therefore undesirable.
Quantiﬁcative Inorganic Analysis

Add 6–8 g. of A.R. ammonium sulphate, stir until dissolved, and render the solution just acid to methyl orange. Fit the conical flask with a two-hole rubber stopper carrying an inlet tube extending well down into the flask and an outlet tube flush with the bottom of the stopper. Pass a rapid stream of hydrogen sulphide through the solution for 30 minutes at room temperature. Add 5–10 ml. of a 0.02 per cent solution of gelatin (ash content less than 0.1 per cent) with rapid stirring, and allow the precipitate to settle. After standing for 15 minutes, ﬁlter through a porous-porcelain ﬁlter-crucible and wash with water containing a little hydrogen sulﬁde.

Weighing as ZnS. Dry the crucible at 110–120°C, cover the precipitate with a layer of pure sulphur (which has been re-crystallised from carbon bisulphide), support the crucible upon a crucible-ignition dish, place a perforated Rose crucible-cover on the crucible (Fig. IV, 34, 1), pass a stream of hydrogen through it (the wash bottle contains concentrated sulphuric acid), and heat the crucible at ﬁrst over a small ﬂame until the excess of sulphur has disappeared, and ﬁnally so that the bottom of the crucible glows very faintly for a few minutes. Allow the crucible to cool in hydrogen, and weigh as ZnS after leaving in a desiccator for 15 minutes.

Weighing as ZnNH₄PO₄. Dissolve the precipitated zinc sulﬁde in 25–35 ml. of 1 : 1 hydrochloric acid, followed by a little water. Boil the solution to remove hydrogen sulﬁde, and almost neutralise with ammonia solution. Complete the estimation as in A. Weigh as ZnNH₄PO₄.

C. Determination of zinc as quinaldinate. Procedure. The solution may contain not more than 0.1 g. of Zn, and should be acidiﬁed with 2–5 ml. of acetic acid (to pH 3–4). Heat to boiling and add 3 per cent sodium quinaldinate solution with stirring until precipitation is complete; an excess of 25 per cent should be used. Allow to cool to room temperature. Wash the precipitate by decantation with cold water, collect it on a sintered-glass or porous-porcelain crucible, wash with a little alcohol, and dry at 105–110°C. to constant weight. Weigh as Zn(C₁₀H₈O₂N)₂.H₂O.

D. Determination of zinc by the pyridine method. Procedure. The solution (75 ml.) should contain about 0.05 g. of zinc (1) and be neutral or very faintly acid. To the cold solution add 1 g. of solid A.R. ammonium thiocyanate, followed by 1 ml. of pure pyridine. Shake vigorously, when a white crystalline precipitate will separate. (Precipitation may also be carried out in hot solution; the complex separates in comparatively large crystals on cooling.) Allow to stand for 15 minutes, and stir frequently. Filter through a weighed sintered-glass or porous-porcelain crucible, and transfer the precipitate to the crucible with the aid of Solution 1. Wash the precipitate four times with Solution 2, then wash the walls of the crucible with 1-ml portions of Solution 3 (use a 1- or 2-ml. pipette for this process), and ﬁnally ﬁve to six times with 1–2 ml. volumes of Solution 4. It is important to suck well on the pump between each washing; it is also advantageous to
stir the precipitate with a thin glass rod when washing with Solutions 3 and 4. Dry the crucible and precipitate in a vacuum desiccator (preferably of the type shown in Fig. II, 16, 4, B) for 15 minutes, and weigh. Repeat the drying process until the weight is constant. Weigh as $[\text{Zn(C}_6\text{H}_5\text{N)}_2\text{(CNS)}_2]_2$.

Solution 1. 100 ml. of water containing 0·3 g. of $\text{NH}_4\text{CNS}$ and 0·5 ml. of pyridine.

Solution 2. 85·5 ml. of water, 13 ml. of 95 per cent alcohol, 0·1 g. of $\text{NH}_4\text{CNS}$, and 1·5 ml. of pyridine.

Solution 3. 10 ml. of absolute alcohol + 1 ml. of pyridine.

Solution 4. 15 ml. of absolute (sodium dried) ether + 2 drops of pyridine.

If the wash solutions have been prepared, the determination should be completed within an hour.

**Note.** 1. For practice in this estimation, the student may employ about 0·25 g., accurately weighed, of A.R. zinc sulphate, or about 0·3 g. of pure zinc ammonium sulphate (see Note to determination A).

**E. Determination of zinc as anthranilate.** Procedure. The solution (150 ml.) may contain not more than 0·1 g. of Zn, and should be free from mineral acids and interfering elements. (If acids are present, they may be removed by neutralisation with 3 per cent sodium carbonate solution to methyl red.) Heat the solution to boiling and treat it with 20 ml. of 3 per cent sodium anthranilate solution. Allow to stand for about 15 minutes. Filter on a sintered-glass or porous-porcelain crucible, wash with cold 0·2 per cent sodium anthranilate solution, and finally with alcohol. Dry to constant weight at 105–110° C. Weigh as $\text{Zn(C}_7\text{H}_8\text{O}_2\text{N)}_2$.

**F. Determination of zinc as 8-hydroxyquinaldinate.** Procedure. The solution may contain up to 0·05 g. of Zn in 200 ml. Add dilute ammonium hydroxide solution until a white precipitate of zinc hydroxide just appears. Re-dissolve the zinc hydroxide with a drop of acetic acid. Add a slight excess of the reagent (1) (2 ml. for each 10 mg. of Zn present) and then 2–3 drops of concentrated ammonia solution; the $\text{pH}$ should be at least 5·5. Digest the precipitate at 60–80° C. for 15 minutes, allow to stand for 10–20 minutes, and filter through a sintered-glass or porous-porcelain crucible. Dry to constant weight at 130–140° C. Weigh as $\text{Zn(C}_{10}\text{H}_8\text{ON)}_2$.

If aluminium is present, add 1 g. of ammonium tartrate to the clear, slightly acid solution. Introduce the reagent (2 ml. for each 10 mg. of Zn present), dilute the solution to 200 ml., and heat to 60–80° C. Neutralise the excess of acid by adding dilute ammonia solution (1 : 5) dropwise until the complex salt which forms on the addition of each drop just re-dissolves on stirring. Add, with stirring, 45 ml. of 2N-ammonium acetate solution. The $\text{pH}$ should be at least 5·5. Allow the solution to stand for 10–20 minutes, and complete the determination as above.

**Note.** 1. The reagent is prepared by dissolving 5 g. of 8-hydroxyquinaldine in 12 g. of glacial acetic acid and diluting to 100 ml. with water.
IV, 35. MANGANESE

Discussion. The only method which is at all widely used for the gravimetric estimation of manganese is the precipitation as manganese ammonium phosphate, $\text{MnNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$, in slightly ammoniacal solution containing excess of ammonium salts. The precipitate may be weighed in this form after drying at 100-105°C, or it may be ignited and subsequently weighed as manganese pyrophosphate, $\text{Mn}_2\text{P}_2\text{O}_7$. The latter procedure is by far the better one. The method is, however, of limited application because of the interfering influence of numerous other elements. Volumetric methods are generally preferred (see Chapter III); the potentiometric determination of manganese (see Section VI, 12) may also be recommended.

Determination of manganese as the ammonium phosphate or as the pyrophosphate. Procedure. The solution (200 ml.) should be slightly acid, contain not more than 0.2 g. of Mn in 200 ml., and no other cations except those of the alkali metals (1). Almost neutralise the solution with dilute ammonia solution, add 20 g. of ammonium chloride and a considerable excess of diammonium hydrogen phosphate ($\text{(NH}_4\text{)}_2\text{HPO}_4$) (say, 2 g. of the solid). If a precipitate forms at this point, dissolve it by the addition of a few drops of 1:3 hydrochloric acid. Heat the solution almost to boiling (90-95°C), and add dilute ammonia solution (1:3) dropwise and with constant stirring until a precipitate ($\text{Mn}_2\text{(PO}_4\text{)}_3$) begins to form; immediately suspend the addition of the alkali. Continue the heating and stirring until the precipitate becomes crystalline ($\text{MnNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$). Then add another drop or two of ammonia solution, stir as before, etc., and so continue until no more precipitate is produced and its silky appearance remains unchanged. The precipitate must be maintained at 90-95°C throughout; a large excess of ammonia solution must be avoided. Allow the solution to stand at room temperature (or, better, at 0°C.) for 2 hours. Filter through a quantitative filter-paper or through a weighed porcelain crucible, and wash the precipitate with cold, 1 per cent ammonium nitrate solution until free from chloride. Dry at a gentle heat, ignite at as low a temperature as possible until the carbon is oxidised (2), and then heat at 1000°C. (in an electric crucible furnace or within a larger nickel crucible) to constant weight. Weigh as $\text{Mn}_2\text{P}_2\text{O}_7$. Alternatively, but less desirably, the precipitate in the porous-porcelain crucible may be dried at 100-105°C. to constant weight and weighed as $\text{MnNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ (3); in this case, a Gooch or sintered-glass crucible may also be used.

Notes. 1. A suitable solution for practice may be prepared by one of the following methods:

(a) Dissolve 0.7 g., accurately weighed, of A.R. manganous sulphate $\text{MnSO}_4\cdot\text{4H}_2\text{O}$ in 200 ml. of water.

(b) Dissolve 0.5 g., accurately weighed, of A.R. potassium permanganate in very dilute sulphuric acid, and reduce the solution with sulphur dioxide or with alcohol (see reduction of potassium dichromate, Section IV, 300). Remove the excess of sulphur dioxide or of acetaldehyde (and alcohol) by boiling. Dilute to 200 ml.

2. These remarks apply, of course, when filter-paper is used.

3. The precipitate, collected on a porous-porcelain or sintered-glass crucible, may be weighed more rapidly but less accurately as follows. Wash the
Gravimetric Analysis

manganese ammonium phosphate five or six times with rectified spirit, five times with small volumes of anhydrous ether, and then suck the precipitate dry at the pump for 10 minutes. Wipe the outside of the crucible dry with a clean linen cloth, and leave in a vacuum desiccator for 10 minutes. Weigh as MnNH₄PO₄·H₂O, which contains 29·53 per cent of Mn.

IV, 36. VANADIUM

Discussion. This element, as vanadate, may be determined in one of the following forms:

A. Mercurous vanadate, Hg₂VO₄, and subsequent weighing as vanadium pentoxide, V₂O₅. This method is applicable only in the absence of substances which give precipitates with mercurous nitrate solution (e.g., chromate, arsenate, molybdate, tungstate, and phosphate). Actually the precipitate obtained in the determination consists of a mixture of mercurous ortho- and pyro-vanadates; this is ignited to, and weighed as, vanadium pentoxide. The solution may contain free nitric acid but not ammonium salts.

B. Silver vanadate, Ag₃VO₄. Vanadates are precipitated by excess of silver nitrate solution in the presence of sodium acetate, followed by boiling, as silver orthovanadate. The following reactions occur with a solution of a metavanadate:

\[
2\text{NaVO}_3 + 2\text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Na}_4\text{V}_2\text{O}_7 + 2\text{H}_2\text{C}_2\text{H}_3\text{O}_2
\]

\[
\text{Na}_4\text{V}_2\text{O}_7 + 4\text{AgNO}_3 \rightleftharpoons \text{Ag}_4\text{V}_2\text{O}_7 + 4\text{NaNO}_3
\]

\[
\text{Ag}_4\text{V}_2\text{O}_7 + 2\text{AgNO}_3 + 2\text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{Ag}_3\text{VO}_4 + 2\text{H}_2\text{C}_2\text{H}_3\text{O}_2 + 2\text{NaNO}_3
\]

Volumetric methods (see Chapter III) are, however, more convenient, less influenced by interfering elements, and are generally preferred.

A. Determination of vanadium as mercurous vanadate and ignition to vanadium pentoxide. Procedure. The alkali vanadate solution (100 ml.) should be faintly acid with nitric acid, and contain not more than 0·1 g. of vanadium as vanadate in 100 ml. of solution. Add 5 ml. of 20-volume hydrogen peroxide and then mercurous nitrate solution (1) dropwise until, after the precipitate has settled, a further addition of 2-3 ml. of the reagent causes no precipitation. Boil the covered beaker for 30 minutes to destroy the excess of hydrogen peroxide, and then allow the grey precipitate to settle. Filter the precipitate through a Whatman No. 40 or 540 filter-paper, and wash it with water containing a few drops of mercurous nitrate solution. Dry the filter and precipitate in the steam-oven (or at 100° C.), ash the filter-paper apart from the precipitate (Section II, 36C) in a weighed porcelain, silica, or platinum crucible, ignite gently at first and then strongly with a Méker-type burner to constant weight. Alternatively, the precipitate may be collected in a weighed porous-porcelain crucible; ignition is carried out by placing the latter in a nickel crucible (Fig. II, 31, 4) or in an electric muffle furnace. Weigh as V₂O₅. Owing to the poisonous nature of mercury fumes, the whole of the operation concerned with the ignition must be carried out in a fume cupboard which is provided with a good draught.

Note. 1. For preparation of mercurous nitrate solution, see Note 1 in Section IV, 30B.
B. Determination of vanadium as silver vanadate. Procedure.
Neutralise the solution (200 ml.), containing not more than 0·2 g. of alkali vanadate, if acid, by aqueous sodium hydroxide, or, if alkaline, by the addition of nitric acid to the boiling solution until it becomes yellow, followed by decolorisation with dilute ammonia solution. Add 3 g. of ammonium acetate, 0·5 ml. of concentrated ammonia solution, and then excess of silver nitrate solution, heat to boiling and then keep on a steam-bath for 30 minutes. Test for complete precipitation with more silver nitrate solution; if a turbidity is produced, boil the liquid until it becomes clear. Allow the dense brown precipitate of silver vanadate to settle, and collect it on a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), wash with hot water, dry at 110° C., and ignite gently to constant weight within a larger crucible. Weigh as Ag₃VO₄.

Discussion.
Uranium, as uranyl salts, may be determined in either of the following forms:

A. Ammonium diuranate, (NH₄)₂U₂O₇, and ignition to uranous uranate, U₃O₈. The uranyl solution is precipitated by ammonium hydroxide solution as ammonium diuranate; the latter is ignited to, and weighed as, uranium oxide, U₃O₈. All elements that are precipitable by ammonia solution must be absent. The reagents and solutions must be free from carbonates and organic matter, both of which prevent precipitation of the uranium.

B. Uranyl oxinate, UO₂(C₆H₅ON)₂C₆H₅ON. The formula of the compound is noteworthy, for it differs from all other metallic oxinates (compare Section I, 620). This method may also be employed for the volumetric determination of uranium with standard potassium bromate solution (compare Section III, 138). Here 1 ml. N-KBrO₃ = 0·01985 g. U.

C. Uranous cupferron complex, and ignition to uranous uranate, U₃O₈. Cupferron does not react with hexavalent uranium, but tetravalent uranium is quantitatively precipitated. These facts are utilised in the separation of iron, vanadium, titanium, and zirconium from uranium (VI). After precipitation of these elements in acid solution with cupferron, the uranium in the filtrate is reduced to the tetravalent state by means of a Jones or cadmium reductor and then precipitated with cupferron (thus separating it from aluminium, chromium, manganese, zinc, and phosphate). Ignition of the uranium (IV) cupferron complex affords U₃O₈.

A. Determination of uranium as ammonium diuranate. Procedure.
The uranium should be in the form of uranyl sulphate in dilute sulphuric acid solution; the uranyl sulphate content should not exceed 1 per cent. Add a few drops of methyl-red indicator, heat to boiling, and treat with dilute ammonia solution that is free from carbonate until the indicator just becomes distinctly yellow (the precipitate also is yellow). Add a Whatman accelerator or one-third of an ashless tablet, and warm for 1 or 2 minutes. Filter off on a Whatman No. 41 or 541 filter-paper, and wash the precipitate well with a hot 2 per cent solution of ammonium nitrate. Dry the wet paper and precipitate in a platinum or a Main-Smith crucible at as low a temperature as possible until the carbon is destroyed, and then heat strongly over a Meker (or similar) burner, the crucible being placed in a slanting position so as to maintain good oxidising conditions (with the Main-Smith crucible, the lid should be removed and placed on one side). Cool in a
Gravimetric Analysis

B. Determination of uranium with oxine. Procedure. The uranium should be present as uranyl nitrate or chloride in 1–2 per cent acetic acid solution (1); up to 0·3 g. of U may be present in 200 ml. of solution. Add 5 g. of A.R. ammonium acetate, heat to boiling, and add 4 per cent oxine solution (2) dropwise and with stirring: use 0·5 ml. of the reagent for every 10 mg. of U present and a further 4–5 ml. Now add whilst stirring a volume of N-ammonium hydroxide solution equal to that of the oxine reagent used, and boil for 1–2 minutes. Allow to cool to 40° C. and filter through a sintered-glass or porous-porcelain crucible; wash with 50–150 ml. of hot 0·4 per cent oxine solution. Dry to constant weight at 120–130° C., and weigh as U₂O₅. Alternatively, the precipitate may be ignited to and weighed as U₃O₈.

Notes. 1. If the solution contains mineral acid, almost neutralise with ammonia solution (or add dilute ammonia solution until a faint turbidity persists and render the solution just clear with a few drops of dilute hydrochloric acid), add 5 g. of A.R. ammonium acetate and then sufficient acetic acid to give a 1–2 per cent solution.

2. The oxine reagent may be prepared by dissolving 4 g. of A.R. oxine in 8·5 ml. of warm A.R. glacial acetic acid, pouring into 80 ml. of water, and diluting to 100 ml.

C. Determination of uranium with cupferron. Procedure. If uranium is to be determined in the filtrate from the precipitation of the iron group by cupferron, concentrate the solution to 50 ml., add 20 ml. of concentrated nitric acid and 10 ml. of concentrated sulphuric acid (if not already present) and evaporate until fumes of sulphur trioxide appear. If organic matter still remains (as shown by the appearance of a dark colour upon evaporation), repeat the treatment with nitric acid. Finally, expel the nitric acid by evaporation, after the addition of a little water, to strong fumes. Dilute the solution so that it contains about 6 ml. of concentrated sulphuric acid per 100 ml. Cool to room temperature and pass the solution through a Jones or cadmium reductor; wash the reductor with 5 per cent. sulphuric acid, cool the combined reduced solution and washings to 5–10° C., and add excess of a freshly prepared 6 per cent solution of cupferron. The precipitate does not usually form until about 5 ml. of cupferron solution has been added. Introduce a Whatman “accelerator” or one-quarter of an “ashless tablet,” allow to settle for a few minutes, and filter through a quantitative filter-paper. Wash with cold 4 per cent sulphuric acid containing 1·5 g. of cupferron per litre. Dry the precipitate at 100° C., ignite cautiously in a platinum crucible, first at a low temperature and then at 1000° C., to constant weight. Weigh as U₃O₈.

IV, 38.

THORIUM

Discussion. Thorium may be determined in either of the following forms:

A. Thorium oxalate, Th(C₂O₄)₂, and subsequent ignition to thoria, ThO₂. This method is of rather limited application, since phosphates and all the rare earths must be absent. Thorium oxalate is soluble in ammonium oxalate solution and in strong mineral acids (concentration greater than, for example, 0·4N-hydrochloric acid).
B. Thorium sebacate, \( \text{Th(C}_4\text{H}_8\text{CO}_2\text{)}_2 \), and subsequent ignition to thoria, \( \text{ThO}_2 \).

This procedure permits of the separation by a single precipitation of thorium from relatively large amounts of the rare earths (Ce, La, Pr, Nd, Sa, Gd) and also from quadrivalent cerium.

C. Thorium iodate, \( \text{Th(IO}_3\text{)}_4 \), and subsequent ignition to thoria, \( \text{ThO}_2 \), via the oxalate. Thorium iodate is precipitated quantitatively by potassium iodate from nitric acid solution: a separation from the rare earths, trivalent cerium, iron, aluminium, and phosphoric acid is thus achieved. Titanium, zirconium, and cerium (IV) accompany thorium, and must therefore be absent. The thorium iodate is dissolved in hydrochloric acid, precipitated as the oxalate, and ignited to and weighed as thorium, \( \text{ThO}_2 \).

A. Determination of thorium as oxalate. Procedure. The thorium should be in hydrochloric acid solution (100 ml.) containing not more than 3·5 per cent of hydrochloric acid by volume and not more than 0·1 g. of Th. Heat the solution (100 ml.) to boiling, and add slowly and with constant stirring sufficient of a boiling 10 per cent solution of oxalic acid to combine with all the thorium and leave an excess of 20 ml. Allow the solution to cool and stand overnight. Filter through a quantitative filter-paper, wash with a solution containing 3·5 ml. of concentrated hydrochloric acid and 2·5 g. of oxalic acid per 100 ml., and ignite with the full heat of a Meker (or similar) burner (ca. 1100° C.) in a weighed platinum, porcelain, or silica crucible to constant weight. Weigh as \( \text{ThO}_2 \).

B. Determination of thorium as sebacate. Procedure. The solution (100 ml.) should be neutral or faintly acid, and contain not more than 0·1 g. of Th. Heat the solution to boiling and add slowly and with constant stirring a hot almost saturated solution of pure sebacic acid in slight excess. The precipitate is voluminous, but granular, and therefore easily manipulated. Filter off immediately, wash thoroughly with hot water, dry, ignite, and weigh as \( \text{ThO}_2 \) (see A).

C. Determination of thorium as iodate. Procedure. The solution (100 ml.) should be chloride-free (1) and contain not more than 0·2 g. of Th. Add 50 ml. of concentrated nitric acid and cool in ice water.

Add a cold solution of 16 g. of A.R. potassium iodate in 30 ml. of water and 50 ml. of concentrated nitric acid; stir occasionally during 30 minutes. Allow to settle, filter, and break up any lumps of precipitate with a glass rod flattened at one end, wash with 250 ml. of a cold solution containing 8 g. of potassium iodate and 200 ml. of dilute nitric acid (1:1) per litre, and allow to drain. Transfer the precipitate back into the original beaker with the aid of 100 ml. of the wash solution, stir thoroughly and filter through a quantitative filter-paper. Allow to drain and again transfer the precipitate back into the beaker, but this time with a little hot water. Heat nearly to boiling, and dissolve the precipitate by adding 30 ml. of concentrated nitric acid slowly and with stirring. Dilute to 60–100 ml., and re-precipitate the thorium as iodate by adding a solution of 4 g. of A.R. potassium iodate dissolved in a little hot water acidified with nitric acid: allow to cool. Filter, wash by decantation as before with 100 ml. of the wash solution, and transfer the precipitate to the paper.

To remove any titanium, zirconium, or cerium (IV) which may be present, place the filter and precipitate in the original beaker and dissolve the precipitate by boiling with hot dilute hydrochloric acid and a little sulphurous acid. Dilute, precipitate with ammonia solution,
filter, and wash the precipitate with hot water until free from iodides. Dissolve the precipitate again in hydrochloric acid, and precipitate the thorium as oxalate as detailed in A. Weigh as ThO$_2$.

Note. 1. The solution may contain sulphuric acid, for example, that obtained by dissolving monazite sand in sulphuric acid.

IV, 39. CERIUM

Discussion. Cerium may be determined as ceric iodate, Ce(IO$_3$)$_4$, which is ignited to, and weighed as, ceric oxide, CeO$_2$. Thorium (also titanium and zirconium) must, however, be first removed (see Section IV, 38); the method is then applicable in the presence of relatively large quantities of rare earths. Volumetric methods (see Section III, 32) are generally preferred.

Determination of cerium as ceric iodate and subsequent ignition to ceria. Procedure. The solution should not exceed 50 ml. in volume, all metallic elements should be present as nitrates, and the cerium content should not exceed 0.11 g. Treat the solution with half its volume of concentrated nitric acid, and add 0.5 g. of potassium bromate (to oxidise the cerium). When the latter has dissolved, add ten to fifteen times the theoretical quantity of potassium iodate in nitric acid solution (1) slowly and with constant stirring, and allow the precipitated ceric iodate to settle. When cold, filter the precipitate through a fine filter-paper (e.g., Whatman No. 42 or 542), allow to drain, rinse once, and then wash back into the beaker in which precipitation took place by means of a solution containing 0.8 g. of potassium iodate and 5 ml. of concentrated nitric acid in 100 ml. Mix thoroughly, collect the precipitate on the same paper, drain, wash back into the beaker with hot water, boil, and treat at once with concentrated nitric acid dropwise until the precipitate just dissolves (20–25 ml. of acid are required per 0.1 g. of ceria). Add 0.25 g. of potassium bromate and as much potassium iodate–nitric acid solution as before. When cold, collect the ceric iodate upon the same filter-paper, wash once with the washing solution, return to the beaker, stir with the washing solution, filter again, and wash thrice with the same solution. Place the filter-paper and precipitate in the same beaker, add 5–8 g. of oxalic acid and 50 ml. of water, and heat to boiling. After all the iodine has been expelled, set aside for several hours, filter, wash with cold water, dry, and ignite to constant weight in a platinum crucible. Weigh as CeO$_2$.

Note. 1. This is prepared by dissolving 50 g. of potassium iodate in 167 ml. of concentrated nitric acid, and diluting to 500 ml.

IV, 40. TITANIUM

Discussion. Titanium may be determined in one of the following forms:

A. Titanium oxinate. TiO(C$_4$H$_4$O$_2$N). Full experimental details of this method are given in Section III, 138, Procedure F. Alkaline-earth metals, magnesium, and the alkali metals do not interfere. The precipitate of TiO(C$_4$H$_4$O$_2$N)$_2$2H$_2$O is collected in a weighed sintered-glass or porous-porcelain crucible, dried to constant weight at 110° C., and weighed as TiO(C$_4$H$_4$O$_2$N)$_2$. 

B. Titanium dioxide, TiO₂, after precipitation with tannin and antipyrine. This method affords a separation from iron, aluminium, chromium, manganese, nickel, cobalt, and zinc, and is applicable in the presence of phosphates and silicates. Small quantities of titanium (2–50 mg.) may be readily estimated.

C. Titanium dioxide, TiO₂, after precipitation with selenious acid. This procedure may be applied in the presence of aluminium, beryllium, manganese, nickel, cobalt, the alkaline-earth metals, and magnesium; zinc is not precipitated, but may be occluded if the selenious acid is added too rapidly.

D. Titanium dioxide, TiO₂, after precipitation with para-hydroxyphenylarsonic acid. This procedure will separate titanium from most other commonly occurring ions by a single precipitation. Zirconium, tin, ceric cerium, and hydrogen peroxide must be absent.

E. Titanium dioxide, TiO₂, after precipitation with cupferron. Titanium is precipitated quantitatively from acid solutions (e.g., containing up to 10 per cent sulphuric acid or 10 per cent hydrochloric acid)—compare Section I, 62B. It may thus be separated from aluminium, chromium, uranium (VI), ferrous iron, phosphate, nickel, and the alkaline-earth elements. The only drawback to the method is that many other elements are also precipitated: these include ferrous iron, zirconium, vanadium, molybdenum, tungsten, tin, antimony, and bismuth. The cupferron complex is cautiously heated and subsequently ignited to and weighed as TiO₂ (for experimental details, see Section IV, 31B).

B. Determination of titanium with tannin and antipyrine. Procedure. The Ti content of the solution should not exceed 0·1 g. of TiO₂, and the titanium should be present as the sulphate or chloride. Add dilute ammonia to the solution until the odour persists, then (cautiously) 10 ml. of concentrated sulphuric acid and 40 ml. of 10 per cent tannin solution. Dilute to 400 ml., stir thoroughly, and cool. Introduce a 20 per cent aqueous solution of antipyrine ("phenazone") with constant stirring until an orange-red flocculent precipitate is obtained. Stop the stirring, and continue the addition of the antipyrine solution until a white, cheese-like precipitate (produced by the interaction of tannin and antipyrine) is formed in addition to the red precipitate. Boil the mixture, remove the flame, add 40 g. of ammonium sulphate, and allow to cool with occasional stirring. Filter the bulky precipitate through a Whatman No. 41 or 541 filter-paper, supported on a Whatman filter-cone (hardened, No. 51), with slight suction, and wash with a solution of 100 ml. of water, 3 ml. of concentrated sulphuric acid, 10 g. of ammonium sulphate, and 1 g. of antipyrine. Dry the precipitate at 100° C., transfer to a weighed crucible, heat gently at first, and then ignite to constant weight. Weigh as TiO₂.

Note. If the wet precipitate is heated directly, caking occurs which renders the complete oxidation of the carbonaceous matter very slow. If alkali metals were originally present, the ignited titania must be washed with hot water, filtered, and re-ignited to constant weight.

C. Determination of titanium with selenious acid. Procedure. The titanium should be in solution in dilute acid, preferably hydrochloric acid, in which precipitations and separations are more facile than in dilute sulphuric acid; the solution should contain not more than about 0·1 g. of Ti. Treat the cold acid solution of titanium with dilute ammonia solution until the acid concentration is reduced below 0·2N, and then add with constant stirring 5 per cent aqueous selenious acid
solution until the precipitate coagulates. The precipitate has the composition \( \text{H}_2[\text{TiO}_2\text{SeO}_3]_2\text{H}_2\text{O} \) and becomes anhydrous at 110° C.; it adsorbs traces of selenious acid, however, so that weighing in this form is not permissible. Add a Whatman accelerator (or one-third of an ashless tablet) and allow the precipitate to settle for a few hours. Filter the precipitate through a Whatman No. 41 or 541 filter-paper, supported upon a Whatman filter-cone (hardened, No. 51), with slight suction, and wash with cold water. Transfer the wet precipitate to a weighed porcelain, silica, or Main-Smith crucible, dry over a small flame, heat until all the selenium is expelled, and ignite to constant weight. Weigh as TiO₂.

D. Determination of titanium with para-hydroxy-phenylarsonic acid.

Procedure. Dissolve the sample (1) containing not more than about 0·06 g. of TiO₂ in sulphuric or hydrochloric acid, and dilute to 200 ml. The amount of the acid present should be such that the solution will be approximately, but not more than, 0·6N in hydrochloric acid or 1·8N in sulphuric acid after the reagents have been added and the precipitation is complete. Heat the solution to boiling; if iron is present, add 2–3 g. of A.R. ammonium thiocyanate; add 100 ml. of a 4 per cent aqueous solution of para-hydroxyphenylarsonic acid, \( \text{HO·C}_6\text{H}_4\text{AsO}_3\text{H}_2 \) (2). Boil gently for 15 minutes to coagulate the precipitate. Allow to cool to room temperature, and filter with suction on a Whatman No. 542 or 42 filter-paper supported on a filter-cone (Whatman, No. 51, hardened). Wash the precipitate five or six times with a wash liquid of 0·25N-hydrochloric or sulphuric acid containing about 0·5 g. of the solid reagent per 100 ml. (if iron is present, 1–2 g. of ammonium thiocyanate should be also added to each 100 ml. of wash liquor). Finally, wash the precipitate two or three times with 2 per cent aqueous ammonium nitrate solution. Transfer the filter to a Main-Smith crucible, ignite gently at first until all the carbon is burnt off (this operation must be carried out in a fume chamber provided with an efficient draught) and then with the full blast of a Fisher burner until constant weight is attained. Weigh as TiO₂.

Notes. 1. For practice in this determination the Bureau of Analysed Samples "Iron Ore, No. 175A" may be used. Dissolve 4 g. of this in 100 ml. of dilute hydrochloric acid and filter. Fuse the undissolved residue with sodium carbonate, wash the melt into the main filtrate, remove the silica in the usual manner, add 4 g. of A.R. ammonium thiocyanate, dilute to 200–250 ml., and continue the estimation as above.


IV, 41. ZIRCONIUM

Discussion. Zirconium may be determined in one of the following forms:

A. Secondary zirconium phosphate, \( \text{ZrH}_2(\text{PO}_4)_2 \), and subsequent ignition to the pyrophosphate, \( \text{ZrP}_2\text{O}_7 \). Zirconium is quantitatively precipitated from solutions containing 10 per cent by volume of sulphuric acid by a 50–100-fold excess of diammonium hydrogen phosphate. The precipitate is washed with a moderate amount of 5 per cent ammonium nitrate solution to remove excess of phosphate; prolonged washing results in hydrolysis of the zirconium phosphate and consequent loss of phosphate, thus introducing errors which may be as high as 1 or 2 per cent. If titanium is present, excess of
hydrogen peroxide must be added before the addition of the phosphate precipitant. Cerium should preferably be in the tervalent condition; a double precipitation is required in the presence of thorium. Iron must be in the ferrous state; uranium and tin interfere and must be absent.

B. Basic zirconium selenite and subsequent ignition to the dioxide, \( \text{ZrO}_2 \).
The zirconium is precipitated as the basic selenite with selenious acid in hot dilute hydrochloric acid solution, the precipitate washed with dilute hydrochloric acid, and then ignited to, and weighed as, \( \text{ZrO}_2 \). No other acids should be present, and the hydrochloric acid content should preferably be 5 per cent and not over 7 per cent by volume. This method enables a separation to be effected by a single precipitation from the rare earths (cerium being in the tervalent condition) and from aluminium. Iron, if present up to 10 per cent of the weight of the zirconium, does not interfere if precipitation is made in dilute solution (100–200 ml. of solution containing 0.05 g. \( \text{ZrO}_2 \)) and double the quantity of selenious acid solution is used for precipitation.

In an alternative method the zirconium is converted into the normal selenite, \( \text{Zr(SeO}_3\text{)}_2 \), after digestion at 80–100°C (Section III, 152) and weighed as such after drying at 110–150°C.

C. Zirconium \( \text{n-propylarsonate} \) and subsequent ignition to the dioxide, \( \text{ZrO}_2 \).
Zirconium is quantitatively precipitated in dilute sulphuric acid solution by aqueous \( \text{n-propylarsonic acid} \); tin interferes, but may be removed from the zirconium oxide residue obtained upon ignition by adding powdered ammonium iodide, and re-igniting (see Section IV, 22A). Titanium, aluminium, chromium, cobalt, nickel, copper, uranium, vanadium, thorium, molybdenum, and tungsten do not interfere. Complete precipitation of the zirconium takes place in the presence of large quantities of iron, but a small quantity of iron is adsorbed upon the zirconium precipitate; the iron is completely removed by re-precipitation. The method is therefore of particular value for the analysis of complex steels containing zirconium. Full particulars are given in Section IV, 96L; the method for the determination of zirconium in a simple compound or mixture should be obvious from these details.

D. Zirconium \( \text{para-hydroxy-phenylarsonate} \) and subsequent ignition to the dioxide, \( \text{ZrO}_2 \).
The procedure is similar to that already given for titanium (Section IV, 40D); the hydrochloric acid concentration should not exceed 3N and the sulphuric acid concentration 1.5N. The method permits the separation in a single precipitation from copper, cadmium, vanadium (V), molybdenum (VI), uranium (VI), iron (III), aluminium, chromium, nickel, cobalt, zinc, manganese, bismuth, and the alkaline earths. If ferric iron is present, ammonium thiocyanate (about 2.5 g. for a maximum of 100 mg. of Zr) is added to prevent interference by this element. Phosphates must, of course, be absent; titanium, thorium, cerium, and tin interfere. The determination is concluded by heating in hydrogen in a Rose crucible, followed by ignition in air to the dioxide: the precipitate obtained by direct ignition may contain arsenic, which is otherwise difficult to remove.

E. Zirconium mandelate and subsequent ignition to the dioxide, \( \text{ZrO}_2 \).
Zirconium may be precipitated from a hydrochloric acid solution with mandelic acid (\( \text{C}_6\text{H}_5\text{CO(OH)}\cdot\text{COOH} \)) as zirconium mandelate, \( \text{Zr(C}_6\text{H}_5\text{O}_4)\text{Cl} \), which is ignited to and weighed as the dioxide. Quantitative separation is thus made from titanium, iron, vanadium, aluminium, chromium, thorium, cerium, tin, barium, cadmium, copper, bismuth, antimony, and cadmium. If sulphuric acid is employed, the concentration should not exceed 5 per cent: higher concentrations give low results.

A. Determination of zirconium as pyrophosphate. **Procedure.** The zirconium solution should contain about 10 per cent by volume of sulphuric acid (ca. 3-7N) and not more than 0.1 g. of Zr. Add a few ml. of "100-volume" hydrogen peroxide to oxidise any titanium
Gravimetric Analysis

present and keep it in solution; if titanium is known to be absent, the addition of hydrogen peroxide is unnecessary. Add a freshly prepared 10 per cent aqueous diammonium hydrogen phosphate solution in 50-100-fold excess; use 10 ml. for every 10 mg. of Zr present, but not less than 20 ml. Dilute to 300 ml. and adjust the acidity so that it is about 3-7N in sulphuric acid (or in hydrochloric acid). Boil the solution for a few minutes, allow to digest for 15-30 minutes on a water-bath, and allow to cool to about 60° C. Add a Whatman "accelerator" (or an equivalent quantity of macerated filter-paper) and filter through a quantitative filter-paper. [If small amounts of Zr (<10 mg.) are being determined, allow to stand overnight.] Wash first with 100-150 ml. of 2N-sulphuric acid containing 2·5 g. of diammonium hydrogen phosphate in 150 ml., and finally with cold 5 per cent ammonium nitrate solution until the filtrate is sulphate-free. [If the solution contains only zirconium and alkali metals, washing with the ammonium nitrate solution alone suffices.] Dry the filter and precipitate at 100-110° C., place in a platinum crucible (previously ignited at 1150° C.) and burn off the filter-paper at as low a temperature as possible. After most of the carbon has been burnt off, raise the temperature gradually to a dull red heat and finally to 1100-1150° C., for 1-3 hours, preferably in an electric muffle furnace. Weigh as ZrP2O7.

B. Determination of zirconium with selenious acid. Procedure. The solution (200 ml.) should contain about 5 per cent by volume of hydrochloric acid (sulphuric acid is undesirable) and not more than 0·2 g. of zirconia. Treat with 20 ml. of 12·5 per cent aqueous selenious acid solution, and boil for a few minutes. Allow the precipitate of basic selenite to settle, filter through a quantitative filter-paper, wash with hot 3 per cent hydrochloric acid containing a little selenious acid, dry in a weighed porcelain, platinum, or Main-Smith crucible, and ignite to constant weight. Weigh as ZrO2.

Alternatively, precipitate the zirconium as the normal selenite (Section III, 152), filter through a sintered-glass crucible (porosity No. 4), wash with hot dilute hydrochloric acid, followed by cold water until the washings are free from selenious acid, and dry at 110-150° C. to constant weight. The precipitate contains 26·43 per cent Zr. Some reduction may occur with large quantities of precipitate, leading to slightly high results. For this reason the volumetric method (Section III, 152) is preferable.

E. Determination of zirconium with mandelic acid. Procedure. The solution (20-30 ml.) may contain 0·05-0·2 g. of Zr, and should possess a hydrochloric acid content of about 20 per cent by volume. Add 50 ml. of 16 per cent aqueous mandelic acid solution and dilute to 100 ml. Raise the temperature slowly to 85° C. and maintain this temperature for 20 minutes. Filter off the resulting precipitate through a quantitative filter-paper, wash it with a hot solution containing 2 per cent of hydrochloric acid and 5 per cent of mandelic acid. Ignite the filter and precipitate to the oxide in the usual manner. Weigh as ZrO2.

IV, 42.

THALLIUM

Discussion. Thallium may be determined in either of the following forms:

A. Thallous chromate, Tl2CrO4. The thallium must be present in the thallous state. If present as a thallate salt, reduction must be effected with sulphur dioxide before precipitation; the excess of sulphur dioxide is boiled off.
B. Thallous cobaltinitrite, $\text{Tl}_2[\text{Co(NO}_2)_6]$. It is possible to precipitate a thallous salt quantitatively by means of a special sodium cobaltinitrite reagent at 30-40° C. in the presence of 5 per cent of formic acid.

A. Determination of thallium as chromate. **Procedure.** The solution (100 ml.) should contain about 0.1 g. of Tl, no excessive amounts of ammonium salts, and no substances that form precipitates with ammonia solution, or reduce potassium chromate, or react with potassium or thallous chromate in ammonical solution. Neutralise the thallium solution (100 ml.) with dilute ammonia solution (2 : 1), and add 3 ml. in excess. Heat to about 80° C., and add 2 g. of potassium chromate in the form of a 10 per cent solution slowly and with constant stirring. Allow to stand at the laboratory temperature for at least 12 hours. Filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), wash with 1 per cent potassium chromate solution, then with 50 per cent alcohol, and dry at 120° C. to constant weight. Weigh as Tl$_2$CrO$_4$.

B. Determination of thallium as cobaltinitrite. **Procedure.** The solution (100 ml.) should contain about 5 per cent of free formic acid, and about 0.1-0.2 g. of Tl; potassium and other elements which give precipitates with the sodium cobaltinitrite reagent should be absent. Warm the solution to 30-40° C. and add an excess of the reagent (1) at the same temperature. Allow to stand for 1 hour, collect the scarlet precipitate on a weighed sintered-glass or porous-porcelain crucible, wash with cold water, and dry at 100° C. to constant weight. Weigh as Tl$_4[\text{Co(NO}_2)_6]$.

**Note.** 1. The reagent is prepared by mixing equal volumes of (a) 28.6 g. of cobalt nitrite and 50 ml. of 50 per cent formic acid in 500 ml. of water, and (b) 180 g. of sodium nitrite per 500 ml. of water.

IV, 43. **CALCIUM**

**Discussion.** Calcium may be determined in one of the following forms:

- Calcium oxalate, $\text{CaC}_2\text{O}_4$, $\text{H}_2\text{O}$, calcium carbonate (best method), and calcium oxide, $\text{CaO}$. These methods are fully discussed in Section IV, 10 (see also Section III, 154). A separation from magnesium with a single precipitation may be obtained by precipitation as calcium molybdate, $\text{CaMoO}_4$ (Section IV, 98G; compare Section IV, 18A).

- Calcium may be determined in neutral solution (pH 7-8) as calcium tungstate, $\text{CaWO}_4$, by precipitation with a solution of sodium tungstate. This procedure is applicable in the presence of magnesium; the concentration of magnesium should not, however, exceed that of the calcium.

**Determination of calcium as tungstate.** **Procedure.** The solution (100 ml.) should contain about 0.04 g. of Ca and possess a pH of 7-8 (1). Add either dilute sodium hydroxide solution or dilute acetic acid to attain the correct pH with the aid of cresol-red indicator. Large quantities of ammonium salts hinder precipitation. Heat the solution to about 80° C. and introduce, with stirring, 2.0 ml. of the sodium tungstate reagent (2). Calcium tungstate is precipitated immediately. Cool in ice for 30 minutes, filter through a sintered-glass (porosity No. 3) or porous-porcelain crucible, wash with 20 ml. of warm water, and dry at 110° C. for 1 hour or to constant weight. Weigh as $\text{CaWO}_4$. 
Gravimetric Analysis

Notes. 1. For practice in this determination a solution may be prepared by dissolving 1·0 g. (accurately weighed) of A.R. calcium carbonate in a little dilute hydrochloric acid, and diluting to 250 ml. in a volumetric flask. A 25-ml. portion of this solution, diluted to 100 ml., may be used.

2. The reagent is prepared by dissolving 19·0 g. of A.R. sodium tungstate, $\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O}$, in 100 ml. of water.

IV, 44. STRONTIUM

Discussion. Strontium may be estimated in one of the following forms:

A. Strontium sulphate, $\text{SrSO}_4$. In this determination (the most accurate for strontium) calcium, barium, and lead must be absent, and the solution (preferably of the chloride) should be as neutral as possible. If considerable acid is present, this must be removed by evaporation. Strontium sulphate dissolves appreciably in an acid medium because of the reaction:

$$\text{SrSO}_4 + \text{H}^+ \rightleftharpoons \text{HSO}_4^- + \text{Sr}^{2+}$$

Strontium sulphate has a solubility of about 0·14 g. per litre at the ordinary temperature; the solubility is decreased by the addition of a slight excess of sulphuric acid, and of alcohol (50 per cent).

B. Strontium oxide, $\text{SrO}$. The strontium is precipitated as the oxalate, $\text{SrC}_2\text{O}_4\cdot\text{H}_2\text{O}$, and is ignited to, and weighed as, the oxide, $\text{SrO}$. The experimental details are similar to those given in Section IV, 10, except that some alcohol should be added to reduce the solubility. Calcium, barium, magnesium, and other interfering elements must be absent.

A. Determination of strontium as sulphate. Procedure. The solution (100 ml.) should contain about 0·2 g. of Sr and be very slightly acid with hydrochloric acid (1). Add slowly a ten-fold excess of dilute sulphuric acid, followed by a volume of alcohol equal to that of the solution. Stir well, and allow to stand for at least 12 hours. Transfer the precipitate to a weighed Vitreosil or porous-porcelain filter-crucible, wash with 75 per cent alcohol to which a few drops of sulphuric acid have been added, and finally with pure alcohol (or rectified spirit) until the washings are free from sulphate. Dry and ignite (crucible-ignition dish or in a large nickel crucible) at dull redness to constant weight. Alternatively, a filter-paper may be used: here the paper should be burnt apart from the precipitate (Section II, 360) (to prevent possible reduction of the latter to the sulphide), and the residue then ignited together with the main precipitate in a weighed porcelain, silica, or platinum crucible. Weigh as $\text{SrSO}_4$.

Note. 1. A solution for practice in this determination may be prepared by dissolving 0·3-0·4 g., accurately weighed, of pure strontium carbonate (the A.R. product may be obtained from the Mallinckrodt Chemical Works, U.S.A.) in a little dilute hydrochloric acid (see Section IV, 10), and diluting to 100 ml.

IV, 45. BARIUM

Discussion. Barium may be determined in one of the following forms:

A. Barium sulphate, $\text{BaSO}_4$. This method is most widely employed. The effect of various interfering elements and radicals (e.g., calcium, strontium, lead, nitrate, etc., which contaminate the precipitate) has been fully dealt with in Section IV, 6.

B. Barium chromate, $\text{BaCrO}_4$. This method is of limited application because of the influence of numerous interfering elements. It is useful,
Quantitative Inorganic Analysis

however, in the separation of barium from both calcium and strontium. Barium chromate may be heated to a red heat without decomposition. If green spots of chromic oxide, due to the reduction of the chromate, should appear, continued ignition with free access of air will result in re-conversion into chromate.

Precipitation of barium chromate is usually carried out in a dilute acetic acid solution which is buffered with ammonium acetate; a double precipitation is desirable in the presence of much strontium and/or calcium.

A. Determination of barium as sulphate. Procedure. The solution (100 ml.) should contain not more than 0.15 g. of barium (1), and not more than 1 per cent by volume of concentrated hydrochloric acid. Heat to boiling, add a slight excess of hot N-sulphuric acid slowly and with constant stirring. Digest on the steam-bath until the precipitate has settled, filter, wash with hot water containing a few drops of sulphuric acid, and then with a little water until the acid is removed. Full experimental details of the filtration, washing, and ignition processes are given in Section IV, 6. Weigh as BaSO$_4$.

Note. 1. A suitable solution for practice may be prepared by dissolving about 0.3 g., accurately weighed, of A.R. barium chloride in 100 ml. of water and adding 1 ml. of concentrated hydrochloric acid.

B. Determination of barium as chromate. Procedure 1. The solution (200 ml.) (1) should contain not more than 0.4 g. of Ba, and be neutral in reaction. Add 1.0 ml. of 6N-acetic acid and 10 ml. of neutral 3N-ammonium acetate solution to the solution, heat to boiling, and treat with a slight excess of a hot dilute solution of ammonium chromate (2) which is added dropwise from a burette with constant stirring. Place the beaker on a water-bath until the precipitate settles; test for completeness of precipitation by adding a little more of the reagent. Allow to cool, filter through a weighed porous-porcelain crucible, wash with hot water until 1 ml. of the washings gives scarcely any reddish-brown coloration with neutral silver nitrate solution. Place the crucible upon a crucible-ignition dish inside a larger porcelain or nickel crucible, and heat to a temperature not exceeding dull-red heat until the precipitate has a uniform bright-yellow colour, and is constant in weight. Weigh as BaCrO$_4$.

Notes. 1. A suitable solution for practice in this determination may be prepared by dissolving about 0.4 g., accurately weighed, of A.R. barium chloride in 200 ml. of water.

2. The ammonium chromate solution is prepared by dissolving 10 g. of pure ammonium dichromate (free from sulphate) in 100 ml. of water, and adding dilute ammonia solution until the colour of the solution is clear yellow.

Procedure 2. The solution (100 ml.) should contain not more than 0.30 g. of Ba, and be neutral in reaction. Add 10 ml. of N-acetic acid and 5 g. of pure ammonium chloride, and stir until the solid has dissolved. Heat to boiling, and add 10 ml. of 10 per cent A.R. potassium chromate solution slowly and with constant stirring. Boil gently for 2–3 minutes, and allow to stand overnight. Collect the barium chromate on a weighed filter-crucible (Gooch, porous-porcelain, or sintered-glass), wash with 50 ml. of cold water, and dry to constant weight at 130$^\circ$ C. Weigh as BaCrO$_4$. 
Gravimetric Analysis 481

IV, 46. MAGNESIUM

Discussion. Magnesium may be estimated in one of the following forms:

A. Magnesium ammonium phosphate hexahydrate, \( \text{MgNH}_2\text{PO}_4 \cdot 6\text{H}_2\text{O} \), or as magnesium pyrophosphate, \( \text{Mg}_2\text{P}_2\text{O}_7 \). These determinations are fully discussed in Section IV, 4.

B. Magnesium "oxinate" (8-hydroxyquinolate), \( \text{Mg(C}_{10}\text{H}_6\text{O}_2\text{N})_2 \cdot 2\text{H}_2\text{O} \). The experimental details, applicable if only alkali metals are present with the magnesium, have been described in Section III, 138, Procedure B. Satisfactory results are also obtained utilizing the slightly modified experimental conditions given below.

Heavy metals, other than copper, cadmium, and zinc, are prevented from interfering if the magnesium is precipitated from a solution (originally neutral) to which 10–20 ml. of 2N-sodium hydroxide and 5 g. of sodium tartrate have been added. If copper, cadmium, and/or zinc are present they may be precipitated from acetic acid solution by oxine, and after their separation, magnesium is determined in the filtrate by the usual method. If aluminium is present, it is precipitated in neutral or weakly acid solution by oxine (see Section III, 138, Procedure A). In all other cases where metals other than those of the alkalis occur in solution, re-precipitation is necessary. The first precipitate of magnesium oxinate is dissolved in the minimum volume of dilute hydrochloric acid, 1–2 g. of ammonium acetate and a few drops of the oxine solution added, and the solution made alkaline with dilute ammonia solution (use o-cresolphthalein as indicator). The mixture is boiled for a few minutes to render the precipitate crystalline, and the latter is then collected, dried, and weighed.

C. Magnesium 8-hydroxyquinaldinate ("2-methyloxinate"), \( \text{Mg(C}_{10}\text{H}_6\text{O}_2\text{N})_2 \). Magnesium may be precipitated by 8-hydroxyquinalidine (2-methylquinoline) in ammoniacal solution (pH at least 9.3) as the complex \( \text{Mg(C}_{10}\text{H}_6\text{O}_2\text{N})_2 \), and weighed as such after drying at 130–140°C. Numerous ions interfere (see Section I, 62P).

B. Determination of magnesium as the 8-hydroxyquinolate ("oxinate"). Procedure. For practice in this determination, the student may employ about 0.20 g., accurately weighed, of A.R. magnesium sulphate dissolved in 100 ml. of water. Add 2 g. of ammonium chloride and 0.5 ml. of o-cresolphthalein indicator (0.2 per cent solution in alcohol), neutralise with 6N-ammonium hydroxide solution until a violet colour is obtained (pH about 9.5) and then add 2 ml. of the ammonia solution in excess. Heat to 70–80°C., add very slowly and with constant stirring a 2 per cent solution of oxine in 2N-acetic acid until a small excess is present as shown by the deep-yellow colour of the supernatant liquid. Avoid a large excess of the precipitant, as there is danger that the reagent itself may precipitate. Digest the precipitate on the steam-bath for 10 minutes with frequent stirring, and collect the precipitate on a weighed sintered-glass or porous-porcelain crucible. Wash the precipitate with dilute ammonia solution (1:40), dry to constant weight at 100–110°C. and weigh as \( \text{Mg(C}_{10}\text{H}_6\text{O}_2\text{N})_2 \cdot 2\text{H}_2\text{O} \). Alternatively, the precipitate may be dried at 155–160°C. and weighed as the anhydrous compound \( \text{Mg(C}_{10}\text{H}_6\text{O}_2\text{N})_2 \).

C. Determination of magnesium as the 8-hydroxyquinaldinate ("2-methyloxinate"). Procedure. The solution (150–200 ml.) may contain up to 0.05 g. of Mg. Add 3 ml. of the 8-hydroxyquinalidine (2-methyl-oxine) reagent (1) for each 10 mg. of Mg present, and then add concen-
Quantitative Inorganic Analysis

trated ammonia solution until the pH is at least 9.3 or until no further precipitate forms. Digest the solution at 60–80° C. for 20 minutes and filter through a sintered-glass or porous-porcelain crucible. Wash the precipitate with hot water and dry to constant weight at 130–140° C. Weigh as Mg(C₁₅H₈O₇N₄)₂.

Note. 1. The reagent is prepared by dissolving 5 g. of 8-hydroxyquinoline in 12 g. of glacial acetic acid and diluting to 100 ml. with water.

IV, 47. SODIUM

Discussion. Sodium may be determined in one of the following forms:

A. Sodium sulphate, Na₂SO₄. Any sodium compound of a volatile acid may be converted into sodium sulphate by repeated evaporation with sulphuric acid. Some bisulphate, NaHSO₄, is formed in the process, and this is converted (via the pyrosulphate, Na₂S₃O₇) into the normal salt with some difficulty. The latter change is facilitated by the addition of a little powdered ammonium carbonate; this is because ammonium sulphate, which is completely volatilised on heating, is formed:

\[ \text{Na}_2\text{S}_3\text{O}_7 + \text{(NH}_4\text{)}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{(NH}_4\text{)}_2\text{SO}_4 + \text{CO}_2 \]

B. Sodium zinc uranyl acetate, NaZn(UO₂)₂(C₅H₇O₄)₆·6H₂O. Treatment of a concentrated solution of a sodium salt with a large excess of zinc uranyl acetate reagent results in the precipitation of sodium zinc uranyl acetate. This substance is moderately soluble in water (68.5 g. per litre at 21° C.), so that a special procedure must be adopted in the washing and collecting of the precipitate. Potassium does not interfere, provided not more than 0.05 g. is present per ml. of solution immediately prior to the precipitation. Ammonium, calcium, strontium, barium, magnesium, iron, aluminium, and chromium do not interfere if present in reasonable amounts (say, up to 200 mg. if 100 ml. of the reagent are used), but lithium, which also forms a sparingly soluble triple acetate, must be absent. Oxalates, tartrates, phosphates, and arsenates, which yield precipitates with the uranyl ion, should not be present. Sulphate must be absent when potassium is present, for potassium sulphate is sparingly soluble in the reagent; sulphate may be converted into chloride by treatment with barium chloride.

C. Sodium magnesium uranyl acetate, NaMg(UO₂)₂(C₅H₇O₄)₆·6H₂O. This determination is similar to B except that magnesium uranyl acetate reagent is used. The method is applicable to solutions containing up to 25 mg. of Na, although with care 50 mg. may be estimated; the volume of the solution should be 5 ml. Ammonium and calcium ions are practically without effect; the maximum quantities of potassium permissible with 50 and 100 ml. of the reagent are 0.1 and 0.25 g. respectively. The procedure may be applied to the determination of sodium in felspar (see Section IV, 99F).

The solubility of the triple complex is 32.8 g. per litre of water and 0.25 g. per litre of 100 per cent ethyl alcohol. The solubility is greatly decreased by a large excess of its ions, thus permitting the use of the triple acetate for the quantitative determination of sodium. Both the zinc and magnesium triple acetates tend to form supersaturated solutions, and consequently the solution must be stirred vigorously, preferably mechanically, for at least 30 minutes to ensure complete precipitation. The precipitation must be carried out at a temperature not exceeding 20° C.; the temperature must be controlled within 1° C., since the temperature coefficient of solubility is large.

A. Determination of sodium as sulphate. Procedure. This estimation is most conveniently carried out in a Main–Smith crucible (Section
II. MB). Evaporate the solution (1) to dryness in a weighed Main-Smith crucible on the water-bath. Transfer to a triangle (or to hot-plate, the temperature of which can be controlled), add a few ml. of concentrated sulphuric acid dropwise on to the cover of the crucible, and evaporate gently to dryness in the fume cupboard until fuming ceases. Repeat this operation twice. Allow to cool, add a few small pieces (about the size of a pea) of solid ammonium carbonate to decompose any pyrosulphate present, and heat to dull redness for 15 minutes. Allow to cool in a desiccator for 25 minutes, and weigh immediately at the end of this period. Repeat the ignition until constant weight is attained. Weigh as Na₂SO₄.

Note. 1. A suitable solution for practice may be prepared by weighing out accurately about 0·5 g. of A.R. sodium chloride, and dissolving it in a little water.

B. Determination of sodium as sodium zinc uranyl acetate. Procedure. The final solution may contain up to 0·05 g. of Na per ml., but the method is best applied to solutions containing not more than 0·008 g. of Na per ml. Treat the concentrated sodium solution (say, 1·5 ml.) (1) with 15 ml. of zinc uranyl acetate reagent (2), and stir vigorously, preferably mechanically for at least 30 minutes. Allow to stand for 1 hour, and filter through a weighed sintered-glass crucible (porosity No. 4). Wash the precipitate four times with 2-ml. portions of the precipitating reagent (allow the wash liquid to drain completely before adding the next portion), then five times with 95 per cent alcohol saturated with sodium zinc uranyl acetate (2-ml. portions), and finally with a little dry ether or acetone. Dry for 30 minutes only at 105° C. (3). Weigh as NaZn(UO₂)₃(C₂H₄O₂)₉·6H₂O.

Notes. 1. A suitable solution for practice may be prepared by evaporating 20 ml. of 0·1N-sodium chloride, prepared from the A.R. salt, to 1·5 ml. on a water-bath.
2. The reagent is prepared by mixing equal volumes of solutions A and B and filtering.

Solution A: dissolve 20 g. of crystallised uranyl acetate UO₄(C₂H₄O₂)₂·2H₂O in 4 ml. of glacial acetic acid and 100 ml. of water (warming may be necessary).
Solution B: dissolve 90 g. of crystallised zinc acetate Zn(C₂H₄O₂)₂·3H₂O in 3 ml. of glacial acetic acid and 100 ml. of water.
3. Alternatively, draw air through the crucible for 5 minutes, wipe off any condensed moisture on the outside with a clean linen cloth, allow to stand in the air or in a desiccator for 10–15 minutes, and weigh.

C. Determination of sodium as sodium magnesium uranyl acetate. Procedure. The solution of the sodium salt should be evaporated to 5 ml. if 10 mg. or more of Na are present; if 1 mg. is present, the volume should be reduced to 1–2 ml. Treat the solution (1) with excess of the clear reagent (2)—as a rough guide the number of ml. of the reagent should be 10 times the number of mg. of Na present; excess of the reagent does no harm. Immerse the vessel in a bath maintained at 20° ± 1° C., and stir vigorously (preferably by means of a mechanical stirrer) for 30–45 minutes. Filter the precipitate immediately through a weighed sintered-glass crucible using gentle suction, and after all the solution has run through, wash the precipitate four to five times with successive 5-ml. portions of 95 per cent alcohol.
Quantitative Inorganic Analysis

saturated with sodium magnesium uranyl acetate and kept at a temperature of 20° ± 1° C. Dry for 30 minutes at 105° C., and weigh as NaMg(UO₂)₃(C₂H₃O₂)₁₉·6·5H₂O.

Notes. 1. A suitable solution for practice in the determination may contain 25 mg. of Na in 5 ml.
2. The reagent is prepared as follows:
   Solution A: 21·3 g. of crystallised uranyl acetate, 15 g. of glacial acetic acid, and 230 ml. of water.
   Solution B: 125 g. of crystallised magnesium acetate Mg(C₂H₃O₂)₂·6H₂O, 15 g. of glacial acetic acid, and 250 ml. of water.

Heat solutions A and B separately to 70° C. until all the salts are dissolved, and then mix the solutions at 70° C., and allow to cool to 20° C. Place the vessel containing the mixed reagent in water at 20° ± 1° C., and maintain at this temperature for 1–2 hours until the slight excess of salts has crystallised out. Filter through a dry filter into a dry bottle. The solution is stable for prolonged periods (8 months) if kept away from direct sunlight.

IV, 48. POTASSIUM

Discussion. Potassium may be determined in one of the following forms:

A. Potassium chloroplatinate, K₂[PtCl₆]. This method is applicable only to those potassium compounds which can be completely converted into potassium chloride by evaporation with hydrochloric acid (as by technique of Section IV, 47A), because it is only from a solution containing chloride that potassium can be completely precipitated as K₂[PtCl₆] by chloroplatinic acid solution. Ammonium salts and all metals other than sodium and potassium must be removed, as must also sulphate, phosphate, and similar radicals. Sodium chloroplatinate is soluble in 80 per cent alcohol, hence this method provides a means of separation of sodium from potassium. Indeed, potassium was frequently determined by this method when a separation from sodium was required. This separation has been superseded by the procedure employing the less-expensive perchloric acid (see B below).

The potassium chloroplatinate may be reduced by magnesium to the metal and weighed as such:

$$K₂[PtCl₆] + 4H = Pt + 2KCl + 4HCl$$

If this method is adopted, potassium may be estimated in the presence of phosphates, borates, silicates, sulphates, calcium, magnesium, and many other metals. Ammonium salts must be absent.

B. Potassium perchlorate, KClO₄. This method employs the comparatively inexpensive perchloric acid as the precipitating reagent. All metals and ammonium, other than the alkali metals, should be absent; the metals should be in the form of chlorides. Under these conditions the procedure may be employed for the quantitative separation of potassium, sodium, and lithium. The three metals, as chlorides, are converted into the perchlorates by evaporation with perchloric acid (DANGER, see Section IV, 70). The mixed perchlorates are treated with a mixture of four volumes of anhydrous n-butyl alcohol and one volume of absolute ethyl acetate. The sodium and lithium perchlorates dissolve, leaving the potassium perchlorate, which can be weighed. The ethyl acetate in the washings is removed by evaporation (i.e., until the volume has been reduced by 80 per cent), and the sodium is precipitated as sodium chloride by the addition of a solution of hydrogen chloride in n-butyl alcohol. This is filtered off and weighed. The filtrate from the sodium estimation is evaporated, and the lithium is determined as sulphate.
If potassium alone is to be determined, the mixed perchlorates are treated with anhydrous ethyl acetate. This dissolves the lithium and sodium perchlorates, leaving potassium perchlorate, which can be weighed. [The solubilities, expressed in grams per 100 ml. of solution at 25° C., of LiClO₄, NaClO₄, and KClO₄ are 63.4, 8.4, and 0.0013 respectively.]

The ethyl acetate extraction process may also be applied to the determination of potassium in the presence of the chlorides or nitrates of the alkaline-earth metals and magnesium, the perchlorates of which are very soluble in anhydrous ethyl acetate. Ammonium salts and sulphates must be absent. The former are removed by evaporating to dryness in a porcelain dish and igniting carefully until all ammonium salts are decomposed: the dish is allowed to cool, the sides rinsed down with a little water, evaporated to dryness, and ignited at a dull red heat; the cold residue is dissolved in a little water and transferred quantitatively to a small Pyrex beaker. Sulphates are removed by acidifying with a little hydrochloric acid and adding hot dilute barium chloride solution dropwise until no further precipitation occurs; the precipitate is filtered after 15–20 minutes and washed with hot water.

Pure anhydrous ethyl acetate is available commercially. The A.R. product is rendered completely anhydrous by shaking with a little anhydrous calcium sulphate and filtering.

C. Potassium sulphate, K₂SO₄. The experimental details are similar to those given in Section IV, 47A. The method is applicable to any potassium compound of any volatile acid. All other metals must be absent. The temperature of ignition must not exceed 800° C., owing to the danger of loss by volatilisation above this temperature. The addition of a little ammonium carbonate permits the change to be carried out at a lower temperature, since any potassium pyrosulphate, K₂S₂O₇, formed is thus readily converted into potassium sulphate (see Section IV, 47A).

D. Dipotassium sodium cobaltinitrite, K₂Na[Co(NO₂)₆]·H₂O. By precipitation of potassium solutions with sodium cobaltinitrite reagent under the experimental conditions given below, a quantitative yield of dipotassium sodium cobaltinitrite is obtained. This method, unlike the perchlorate procedure, is applicable in the presence of sulphate.

Formerly precipitation was made in an acetic acid solution with a reagent prepared by mixing a solution of cobalt nitrate or acetate in dilute acetic acid and of sodium nitrite in water. There is some evidence that the composition of the precipitate may, upon occasion, vary slightly from the formula given above. If precipitation is made from a nitric acid solution by a solution of trisodium cobaltinitrite, Na₃[Co(NO₂)₆], the precipitate invariably has the composition K₂Na[Co(NO₂)₆]·H₂O for amounts of potassium up to 10 mg. The precipitate may be weighed as such after drying at 100–110° C. for 2 hours, or it may be converted into potassium perchlorate. A volumetric method may also be employed. The precipitate is treated with excess of standard potassium permanganate solution in the presence of alkali and, after acidifying, titrating the excess with standard sodium oxalate solution:

\[
5K₂Na[Co(NO₂)₆] + 11KMnO₄ + 14H₂SO₄ = 21KNO₃ + 5CoSO₄ + 5NaNO₃ + 2Mn(NO₃)₂ + 9MnSO₄ + 14H₂O
\]

Titration may also be carried out with standard ceric sulphate solution.

E. Potassium periodate, KIO₄. Potassium may be quantitatively precipitated as the periodate by adding periodic acid to a concentrated solution of the nitrate and then adding a large volume of a mixture of equal volumes of anhydrous aldehyde-free ethyl alcohol and anhydrous ethyl acetate; the solution must be maintained at 0° C. and stirred mechanically for 30 minutes. The precipitated potassium periodate may be weighed after drying for
10 minutes at 105°C, or it may be dissolved in a boric acid-borax buffer solution, potassium iodido added, and the liberated iodine titrated with standard sodium arsenite solution:

$$\text{IO}_4^- + 2\text{I}^- = \text{IO}_3^- + \text{I}_2$$

It is essential to carry out the determination at 0° to secure accurate results: experiments at room temperature give results which are up to 0.6 mg. too low when much sodium is present.

The volumetric procedure provides a separation of potassium from moderate amounts of lithium, sodium, magnesium, calcium, aluminium, zinc, nickel, and cobalt, but not from ammonium, iron, manganese, and chromium. The gravimetric procedure is applicable in the presence of lithium, sodium, calcium (in the absence of sulphate), and of magnesium; sulphate must in any case be absent. In both the volumetric and gravimetric methods, chloride must be absent. The procedure may be applied to the determination of potassium in the mixed chlorides obtained by the J. Lawrence Smith technique (Section IV, 99F), provided that they are converted into nitrates by evaporation with nitric acid.

### A. Determination of potassium as chloroplatinate. Procedure.

Weigh out accurately about 0.25 g. of the mixed sodium and potassium chlorides (1) into a small porcelain dish, and dissolve it in 5–10 ml. of water. Treat with sufficient chloroplatinic acid reagent (2) to react completely with both the sodium and potassium. The necessary amount to use is readily calculated by assuming that the mixed chlorides are wholly sodium chloride—1.7 ml. of the reagent will precipitate 0.1 g. of sodium chloride. The dilution of the resultant solution should be such that when heated on the water-bath, any precipitate that may have formed dissolves completely; this is to prevent occlusion of mother liquor in a mass of crystals suddenly formed. Evaporate nearly to dryness on the water-bath, i.e., until the solution is syrupy but solidifies on cooling. (Complete evaporation to dryness will dehydrate the sodium salt and render it less soluble in alcohol.) Add 10–15 ml. of 80 per cent (by volume) ethyl alcohol (3) to the cold dish, and break up the mass of crystals into a fine powder by means of a stirring-rod having a flattened end. Decant the supernatant liquid through a weighed sintered-glass or porous-porcelain crucible (4). Repeat this treatment with 2-ml. portions of 80 per cent alcohol, grinding up the precipitate thoroughly each time, until the alcohol runs through entirely colourless and the residue is golden-yellow in colour; an orange-red colour indicates incomplete removal of the sodium salt. Transfer the residue to the filter-crucible with the aid of a little 80 per cent alcohol, and drain off most of the alcohol. Dry at 135°C. to constant weight: the crucible should be covered to avoid loss by decrepitation. Weigh as K₂[PtCl₆].

#### Notes.
1. For practice in this procedure, the student may employ either A.R. potassium chloride or an artificial mixture of, say, equal weights of A.R. sodium and potassium chlorides.
2. The chloroplatinic acid reagent is prepared by dissolving 1 g. of chloroplatinic acid in 10 ml. of water.
3. This may be prepared by mixing 5 volumes of 95 per cent alcohol with 1 volume of water.
4. All washings must be kept, and the platinum contained in them subsequently recovered.
Weighing of potassium chloroplatinate as metallic platinum. As a check on the result obtained by the above method (and indeed to obtain a more trustworthy result since the precipitate does not always possess the exact theoretical composition), the amount of platinum contained in the precipitate may be determined. Dissolve the precipitate by pouring hot water over it, and transfer the filtrate and washings quantitatively to a small beaker. Add 2 ml. of concentrated hydrochloric acid, followed by approximately 0.5 g. of magnesium ribbon (previously washed with water). Stir the solution, and hold the ribbon at the bottom of the beaker by means of a glass rod with a flattened end. When the magnesium has nearly disappeared, add a few ml. of dilute hydrochloric acid, and allow the platinum to settle. If the reduction is complete, the liquid is clear and colourless. To make sure add a little more magnesium, and note whether the solution darkens. Add dilute hydrochloric acid, boil to dissolve any basic salts which may be present, collect the platinum on a small filter-paper, wash with water until free from chlorides, and ignite in a weighed porcelain or, preferably, platinum crucible to constant weight. Weigh the platinum, and calculate the potassium equivalent by the proportion Pt = 2K.

B. Determination of potassium as perchlorate. Procedure. Weigh out accurately about 0.3 g. of the mixed chlorides (I) into a small Pyrex beaker and treat with at least two or three times the equivalent quantity of A.R. 60-70 per cent perchloric acid (say, 6-8 ml.) and evaporate to dense fumes of perchloric acid. Evaporate barely to dryness (residue just moist) on a hot-plate at a temperature not exceeding 350° C. Allow to cool, wash down the sides of the beaker with 3-5 ml. of water, and again evaporate barely to dryness on a hot-plate. Cool the residue by immersing the beaker in cold water. Add 20-30 ml. of pure anhydrous ethyl acetate and stir until the soluble sodium perchlorate has dissolved and the potassium perchlorate remains. Cool in cold water and filter through a fine quantitative filter-paper: transfer most of the precipitate with the aid of anhydrous ethyl acetate contained in a small wash bottle. Wash three or four times with 2-ml. portions of ethyl acetate and discard the washings. Dissolve the potassium perchlorate remaining in the beaker with hot water, pour it through the filter, and collect the filtrate in a 150- or 250-ml. Pyrex beaker. Wash with hot water until all the precipitate has dissolved (2), and then at least ten times more with small volumes. Add 1 drop of 20 per cent perchloric acid to the combined filtrate and washings and evaporate gently to dryness. Cool and add 15 ml. of anhydrous ethyl acetate; warm to about 30-40° C. and stir to extract any soluble perchlorate remaining. Cool, transfer to a weighed sintered-glass (preferably of Vitreosil) or porous-porcelain crucible, and wash with five to six portions of dry ethyl acetate of 1 ml. each. Dry at 110° C. for 30 minutes, and then heat the covered crucible in an electric muffle or oven at 310° C. (3) for 20 minutes. Cool and weigh. Re-heat the crucible until constant weight is attained. Weigh as KClO₄.

Notes. 1. For practice in this determination, use about 0.3 g., accurately weighed, of equal weights of dry A.R. potassium chloride and dry A.R. sodium chloride.

2. Potassium perchlorate, owing to a peculiar characteristic of its crystal structure, occludes mother liquor and therefore contains water, some perchloric acid, sodium perchlorate, and any metal perchlorate present.
residue from the extraction with ethyl acetate is therefore dissolved in water and again evaporated to dryness. It is not necessary to add more acid, so that only water is occluded during the second evaporation to dryness. This occluded water, which may amount to as much as 0.3 per cent of the weight of the salt after drying at 150° C., can be removed only by heating to 300–350° C., a temperature sufficiently high for the pressure of water vapour to burst the crystals.

3. The crystals usually burst during the heating at 310° C. and leave a fine powder.

**B'. Note on the determination of potassium and sodium.** If the mixture supplied consists of the sodium and potassium salts of volatile acids, it may be converted into the chlorides by several evaporations with hydrochloric acid in a Main–Smith crucible (compare Section IV, 47A). This will give the total chloride. The potassium is determined as the perchlorate as above, and therefrom the equivalent amount of potassium chloride is computed. The sodium chloride is obtained by difference.

**D. Determination of potassium as dipotassium sodium cobaltinitrite.**

**Procedure A.** (Potassium in potassium sulphate.) Weigh out accurately 0.1 g. of, say, A.R. potassium sulphate, dissolve it in 10–15 ml. of water, add 2 drops of glacial acetic acid, then excess (15–20 ml.) of the sodium cobaltinitrite reagent (1). Evaporate to dryness on the water-bath. Wash the residue by decantation with 5 per cent acetic acid, then transfer it to a weighed sintered-glass or porcelain crucible, and wash it with cold water until free from acid. Dry at 100° C. to constant weight. Weigh as K₂Na[Co(NO₂)₆]·H₂O. Calculate the percentage of potassium in potassium sulphate.

**Note.** 1. The sodium cobaltinitrite reagent is prepared as follows. Dissolve 22 g. of sodium nitrite in 50 ml. of water and add to it a solution containing 13 g. of cobalt acetate tetrahydrate (or 13 g. of the non-deliquesced nitrate) dissolved in 10 ml. of glacial acetic acid made up to 50 ml. with water. When the reaction is over, gently warm the mixture, remove nitrous fumes by evaporation at the pump or by passage of a rapid current of filtered air. After standing for 24 hours, filter off the small amount of yellow precipitate (due to the presence of potassium as impurity). Keep in a dark place.

**Procedure B.** The reagent described above may be replaced with advantage by a solution prepared freshly from A.R. sodium cobaltinitrite, Na₃[Co(NO₂)₆]. The precipitate of K₂Na[Co(NO₂)₆]·H₂O in nitric acid solution is heavy and crystalline, and constant in composition; the determination can be completed either gravimetrically or volumetrically by titration with potassium permanganate in acid solution.

Weigh out accurately 0.03–0.04 g. of A.R. potassium sulphate and dissolve it in 10 ml. of water. Add 1 ml. of conc. N-nitric acid and a solution of 1 g. of A.R. sodium cobaltinitrite in 5 ml. of water, mix, and allow to stand for 2 hours. Filter through a weighed sintered-glass or porcelain filter-crucible and transfer the precipitate completely with the aid of 0.01N-nitric acid. Wash ten times with 2-ml. portions of 0.01N-nitric acid and five times with 2-ml. portions of 95 per cent ethyl alcohol. Suck the precipitate as dry as possible on the pump, dry for 1 hour at 110° C., cool in a desiccator, and weigh as K₂Na[Co(NO₂)₆]·H₂O.
For the volumetric determination, follow the gravimetric procedure to the point of washing with dilute nitric acid. Wash the precipitate into a 250-ml beaker, place the crucible in the beaker, and dilute to 100 ml with water. Add 20 ml of ca. 0.05 N-sodium hydroxide solution and boil for 3 minutes. Place a slight excess of standard 0.05 N-potassium permanganate solution into another beaker, dilute to 50 ml with water, and add 5 ml of concentrated sulphuric acid. Pour the hot potassium cobaltinitrite solution into the cold potassium permanganate solution, transfer the crucible also, and wash the beaker with a small amount of water. Add an excess of standard 0.05 N-sodium oxalate solution and complete the titration with the standard potassium permanganate solution. The reaction is:

\[ 5K_2Na[Co(NO_3)_6] + 11KMnO_4 + 14H_2SO_4 \]
\[ = 5CoSO_4 + 9MnSO_4 + 2Mn(NO_3)_2 + 5NaNO_3 + 21KNO_3 + 14H_2O \]

from which it follows that:

\[ \text{ml. of KMnO}_4 \times \text{normality of KMnO}_4 \times 7.1084 = \text{mg. of K} \]

E. Determination of potassium as periodate. Procedure. Weigh out accurately about 0.1 g of the solid (1), dissolve it in about 5 ml of water, add a solution of 1 g of periodic acid (2) in 3 ml of water, stir, and allow 3–4 minutes for the potassium periodate to precipitate. Then add 90 ml of the ethyl alcohol–ethyl acetate mixture (3), and allow the solution to stand in a bath of finely crushed ice for 30 minutes with continuous mechanical stirring. Collect the precipitate in a weighed sintered-glass or porous-porcelain crucible, wash it with a little anhydrous ethyl acetate which has been cooled to 0°C., and dry at 105°C. for 10 minutes. Weigh as KIO₄.

If the determination is to be carried out volumetrically, place the crucible and the precipitate in a 250-ml beaker and add a solution of 5 g of A.R. boric acid and 5 g of A.R. borax in 125 ml of water (pH ca. 7.5); the potassium periodate dissolves readily. Add 3 g of A.R. potassium iodide, and titrate the liberated iodine with 0.1 N-sodium arsenite solution.

Notes. 1. For practice in this determination, the student may employ 0.1 g accurately weighed, of A.R. potassium nitrate, previously dried at 105–110°C. for several hours. If A.R. potassium chloride is used, it must be evaporated to dryness with 10 ml of concentrated nitric acid; otherwise the chloride will cause reduction of the periodic acid.

2. Periodic acid may be obtained, inter alia, from British Drug Houses, Ltd., Poole, Dorset, or from the G. Frederick Smith Chemical Co., Columbus, Ohio. It may also be prepared as described in Inorganic Syntheses, Volume I, p. 172 (McGraw-Hill, 1939).

3. This is prepared by mixing equal volumes of aldehyde-free ethyl alcohol with anhydrous ethyl acetate. The former is obtained by refluxing 1 litre of 95 per cent ethyl alcohol for 2–3 hours with 2.5 g of silver nitrate and 0.5 g of sodium hydroxide, and then distilling.

4. The 0.1 N-sodium arsenite solution may be prepared by dissolving 4.945 g of A.R. arsenious oxide in a warm (80°C) solution of 10 g of A.R. sodium bicarbonate in 50 ml of water. The solution is then saturated with carbon dioxide and diluted to 1 litre. It is best to standardise this arsenite solution by titration against pure potassium or sodium periodate.
LITHIUM

Discussion. Lithium, if present as a salt of a volatile acid, may be determined as lithium sulphate, \( \text{Li}_2\text{SO}_4 \), by repeated evaporation with sulphuric acid (see Section IV, 47A). No other elements may be present. Here the change from the acid sulphate to the normal sulphate takes place comparatively easily, so that the addition of ammonium carbonate is not essential. When present with sodium and potassium as chlorides, the lithium may be determined:

(a) By the n-butyl alcohol–ethyl acetate method (Section IV, 48B).
(b) By extraction of the lithium chloride with dry isoamyl alcohol or dioxan (diethylene dioxide) or anhydrous acetone, sodium and potassium chlorides being sparingly soluble in these solvents. The best results are obtained with 2-ethylhexanol, although those with n-hexyl alcohol are usually quite satisfactory. The solubilities of the chlorides in anhydrous isoamyl, n-hexyl alcohols, and in 2-ethylhexanol (iso-octyl alcohol), expressed in grams dissolved by 100 ml. of the anhydrous solvent at 25° C., are:

<table>
<thead>
<tr>
<th></th>
<th>isoAmyl Alcohol.</th>
<th>n-Hexanol.</th>
<th>2-Ethylhexanol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>7·3</td>
<td>5·8</td>
<td>3·0</td>
</tr>
<tr>
<td>NaCl</td>
<td>0·0016</td>
<td>0·0008</td>
<td>0·0001</td>
</tr>
<tr>
<td>KCl</td>
<td>0·0006</td>
<td>0·0004</td>
<td>&lt;0·00001</td>
</tr>
</tbody>
</table>

The methods utilising dioxan and 2-ethylhexanol, illustrating two different techniques, will be described.

Determination of lithium in the presence of sodium and potassium. Procedure A. Dioxan method. Heat the mixed alkali chlorides at 120° C. in a sintered-glass crucible for 2 hours, and weigh after cooling in a desiccator. Suspend the crucible by means of platinum wires about 1 cm. above 20–30 ml. of pure dry dioxan contained in a wide-mouthed 250-ml. flask, which is attached to a reflux condenser having a calcium chloride guard tube at the top. Reflux for at least 4 hours, remove the crucible, heat at 120° C. for 1 hour, cool, and weigh. Repeat the process until the weight is constant. The loss in weight is due to the lithium chloride.

Procedure B. 2-Ethylhexanol method. Treat a concentrated solution of 0·3–0·4 g. or less of the mixed chlorides with a suitable volume of 2-ethylhexanol, introduce a little platinum foil or a few fragments of porous porcelain to prevent bumping, and distil until the water has passed over and the boiling point becomes constant (175–180° C.) for some time. Sodium and potassium chlorides are deposited, and lithium chloride is dehydrated and held in solution. Allow to cool, filter through a sintered-glass crucible, and wash thoroughly with successive small volumes of the anhydrous alcohol. Dry the crucible at 200–210° C. to volatilise the residual solvent, and weigh. The loss in weight is due to the lithium chloride.

If the weight of the lithium chloride exceeds 20 mg., a second extraction is necessary in order to remove the small quantity of lithium hydroxide (formed by hydrolysis at the boiling point of the 2-ethylhexanol) present in the residual solid: the latter must be dissolved in a little water containing a few drops of hydrochloric acid.
IV, 50.

**AMMONIUM**

Discussion. For the determination of ammonium by a gravimetric procedure, it must be present as the chloride; all other cations must be absent. A little hydrochloric acid is added, followed by excess of chloroplatinic acid reagent (see Section IV, 48A). The mixture is evaporated almost to dryness on the water-bath; the residue is triturated with absolute alcohol to remove excess of chloroplatinic acid, and then transferred to a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain). The crucible is dried at 130°C, and the residual ammonium chloroplatinate, \((\text{NH}_4)_2\text{PtCl}_6\), weighed. (For details of experimental procedure, see Section IV, 48A.)

If the ammonium salt is present with other cations and anions, a volumetric procedure (see Chapter III) is usually employed.

IV, 51.

**TUNGSTEN**

Discussion. Tungsten, as tungstate, may be determined in one of the following forms:

A. Tungsten trioxide, \(\text{WO}_3\), after precipitation with benzidine. Benzidine forms a white, sparingly soluble tungstate with solutions of tungstates. The precipitate is, however, filtered with difficulty, and may tend to peptise during the washing process. If a little sulphuric acid is present, the slightly soluble and crystalline benzidine sulphate is also formed. This renders filtration facile. Upon igniting the mixture of benzidine tungstate and sulphate, only tungstic oxide remains.

B. Tungsten trioxide, \(\text{WO}_3\), after precipitation with tannin and antipyrine. Tungstic acid is incompletely precipitated from solutions of tungstates by tannin. If, however, antipyrine is added to the cold solution after treatment with excess of tannin, precipitation is quantitative. This process effects a separation from aluminium, and also from iron, chromium, manganese, zinc, cobalt, and nickel if a double precipitation is used.

For the use of cinchonine in the determination of tungsten, see Section VI, 96 I.

C. Tungsten oxinate, \(\text{WO}_2\left(\text{C}_9\text{H}_8\text{O}_2\text{N}\right)_2\). This method is applicable only when all other elements precipitable by oxine in acetic acid solution are absent.

D. Barium tungstate, \(\text{BaWO}_4\). A dilute neutral solution of a tungstate (pH about 7.7) is precipitated by barium chloride solution as barium tungstate. It is important that the solution be dilute: in concentrated solutions high results are obtained, due to co-precipitation of barium chloride. In extremely dilute solutions and at low temperatures, a fine precipitate is slowly formed, which tends to pass through the filter and adhere to the walls of the beaker. The solubility of barium tungstate is 4 mg. per litre at 22°C, and 0.02 mg. per litre in the presence of a 50 per cent excess of barium chloride; it increases rapidly with decreasing pH.

A. Determination of tungsten as the trioxide (benzidine method).

Procedure. The solution of the tungstate (200 ml.) should contain about 0.3 g. of \(\text{WO}_3\), and be almost neutral (1). Add 10 ml. of 0.1N-sulphuric acid, and boil the solution. Introduce immediately 30 ml. of the benzidine reagent (2), and allow to cool to room temperature. Filter through a weighed silica, Gooch, or porous-porcelain crucible, and wash with a solution prepared by diluting 10 ml. of the reagent to 300 ml. Dry the precipitate, and ignite. Weigh as \(\text{WO}_3\).
Notes. 1. For practice in this estimation, a solution prepared from A.R. sodium tungstate may be employed.

2. The reagent is prepared by dissolving 2 g. of A.R. benzidine in 100 ml. of 1 per cent hydrochloric acid.

B. Determination of tungsten as the trioxide (tannin–antipyrine method). Procedure. The solution of tungstate (200–250 ml.) should contain not more than 0·15 g. of WO₃, and be faintly ammoniacal. Add 6–7 ml. of concentrated sulphuric acid and 7–8 g. of ammonium sulphate, and heat to boiling. Treat with 6 ml. of 10 per cent tannin solution, keep the mixture on the water-bath for a few minutes, and allow to cool to room temperature. A flocculent dark-brown precipitate separates. When cold, stir in 10 ml. of a 10 per cent solution of antipyrine ("phenazine"). Filter the precipitate through a weighed silica, Gooch, or porous-porcelain crucible (1), wash with the special wash liquid (2), and ignite to constant weight. Weigh as WO₃.

Notes. 1. The filtrate must be colourless. If it is yellow, insufficient antipyrine has been added.

2. The special wash liquid contains 1 ml. of concentrated sulphuric acid, 10 g. of ammonium sulphate, and 0·4 g. of antipyrine in 200 ml. of water.

C. Determination of tungsten with oxine. Procedure. The solution of tungstate (200 ml.) should contain about 0·05 g. of W, and be slightly alkaline or neutral in reaction; if acid, precipitation is subsequently effected with ammonium acetate. Heat to boiling, add a 4 per cent alcoholic solution of oxine slowly and with constant stirring until present in slight excess, and acidify with dilute acetic acid. Filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain). Wash with hot water, and dry at 120° C. to constant weight. Weigh as WO₂(C₅H₆ON)₂.

D. Determination of tungsten as barium tungstate. Procedure. The solution of tungstate (250 ml.) may contain about 0·15 g. of W (1) and be almost neutral (pH 7–8). Adjust the pH of the solution, if necessary, by the addition of dilute acetic acid or of dilute sodium hydroxide solution. Heat to boiling and add a solution of crystallised barium chloride in 10 ml. of water dropwise and with constant stirring. Allow the suspension to stand to acquire the laboratory temperature, filter through a porous-porcelain crucible, wash with cold water until the washings are free from chloride, dry at about 750° C. (Fig. II, 31, 4, or in an electric crucible furnace) to constant weight. Weigh as BaWO₄.

Note. 1. The student may employ a solution prepared from about 0·25 g. of A.R. sodium tungstate, Na₂WO₄.2H₂O (accurately weighed), for practice in this determination.

IV. 52.

CHLORIDE

Discussion. This anion is determined as silver chloride, AgCl; full details are given in Section IV, 5. Anions which give silver salts which are insoluble in dilute nitric acid must be absent; these include bromide, iodide, thiocyanate, sulphide, thiosulphate, ferrocyanide, and ferricyanide. Heavy metals interfere, and must be removed by precipitation.

If the chloride is insoluble, it is necessary to boil it with a large excess of saturated sodium carbonate solution or, better, to fuse it with sodium carbonate and extract the melt with water. In either case the chloride passes into solution, and is estimated in the usual way after acidification with nitric acid.
IV, 53. **BROMIDE**

**Discussion.** This anion is determined as silver bromide, AgBr, by precipitation with silver nitrate solution in the presence of dilute nitric acid. Silver bromide is less soluble in water than is the chloride. The solubility of the former is 0·11 mg. per litre at 21° C. as compared with 1·54 mg. per litre for the latter, hence the procedure for the determination of bromide is practically the same as that for chloride. Protection from light is even more essential with the bromide than with the chloride because of its greater sensitiveness.

IV, 54. **IODIDE**

**Discussion.** This anion is usually determined by precipitation as silver iodide, AgI. Silver iodide is the least soluble of the silver halides; 1 litre of water dissolves 0·0035 mg. per litre at 21° C. Co-precipitation and similar errors are more likely to occur with iodide than with the other halides. Precipitation is therefore made by adding a very dilute solution, say 0·05N, of silver nitrate slowly and with constant stirring to a dilute ammoniacal solution of the iodide until precipitation is complete, and then adding nitric acid in 1 per cent by volume excess. The precipitate is collected in the usual manner, washed with 1 per cent nitric acid, and finally with a little water to remove nitric acid. Peptisation tends to occur with excess of water. Other details of the estimation will be found in Section IV, 5.

Iodide may also be determined by precipitation as palladous iodide, PdI₂. Substances, such as alcohol, which cause reduction to metallic palladium must be absent; bromides and chlorides are not precipitated and therefore do not interfere. The precipitate is insoluble in water and in dilute hydrochloric acid (1 : 99). The reagent, palladous chloride, is expensive, and the method is therefore rarely employed except for gravimetric separations from other halides.

**Determination of iodide as palladous iodide. Procedure.** The iodide solution should contain 1 per cent by volume of hydrochloric acid, and not more than 0·1 g. of iodide. Warm to 70° C., and add palladous chloride solution, dropwise and with stirring, until no more precipitate is formed. Allow the solution to stand for 24–48 hours at 23–30° C., filter the brownish-black precipitate of palladous iodide on a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), and wash four times with warm water. Dry at 100° C., for 1 hour, and weigh as PdI₂.

IV, 55. **THIOCYANATE**

This anion may be determined in one of the following forms:

A. **Silver thiocyanate, AgCNS.** This method is applicable only in the absence of halides and cyanides. The dilute solution of alkali thiocyanate is acidified with dilute nitric acid and treated in the cold with a slight excess of 0·1N-silver nitrate. After stirring well, the precipitate is collected on a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), washed with water followed by a little alcohol, and dried to constant weight at 130° C. The precipitate is weighed as AgCNS.

B. **Cuprous thiocyanate, Cu₂(CNS)₂.** The solution (100 ml.) should be neutral or slightly acid (hydrochloric or sulphuric acid), and contain not more than 0·1 g. CNS. It is saturated with sulphur dioxide in the cold (or 50 ml. of freshly prepared saturated sulphurous acid solution added), and
Quantitative Inorganic Analysis

then treated dropwise and with constant stirring with about 60 ml. of 0.1N-copper sulphate solution. The mixture is again saturated with sulphur dioxide (or 10 ml. of saturated sulphurous acid solution added), allowed to stand for a few hours, collected on a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), washed several times with cold water containing sulphurous acid until the copper is removed (potassium ferrocyanide test), and finally once with alcohol. The precipitate is dried at 110–120° C. to constant weight, and weighed as Cu₅(CNS)₆.

C. Barium sulphate, BaSO₄. The thiocyanate is oxidised with bromine water to sulphate, and the latter is determined by precipitation as barium sulphate. All other compounds containing sulphur must be absent. The alkali thiocyanate solution is treated with excess of bromine water, heated for 1 hour on the water-bath, the solution acidified with hydrochloric acid, and the sulphuric acid precipitated and weighed as BaSO₄ (see Section IV, 6).

IV, 56.

CYANIDE

Discussion. This anion is determined as silver cyanide, AgCN; the experimental details are similar to those given for Chloride, except that, owing to the volatility of hydrocyanic acid, the solution must not be heated. The cold solution of alkali cyanide is treated with an excess of silver nitrate solution, faintly acidified with nitric acid, the precipitate allowed to settle, collected on a weighed filter-crucible, and weighed as AgCN after drying at 110° C.

IV, 57.

FLUORIDE

Discussion. This anion may be determined in one of the following forms:

A. Lead chlorofluoride, PbClF. The details of this procedure are given in Section III, 39. The precipitate is, however, filtered through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), and weighed as PbClF after drying at 130–140° C.

B. Calcium fluoride, CaF₂. Fluorides, in the absence of phosphates, silicates, and other radicals that give insoluble calcium salts, may be determined as calcium fluoride by precipitation with calcium chloride solution. The precipitate produced in acid or neutral solution is gelatinous and difficult to filter. For this reason a little sodium carbonate solution is often added before precipitation; the precipitate of calcium fluoride and calcium carbonate is more readily filtered. The calcium carbonate is subsequently removed by extraction with dilute acetic acid. A simpler procedure is to carry out the precipitation in ammoniacal solution; the resultant calcium fluoride is much denser, and comparatively easily filtered and washed.

C. Triphenyltin fluoride, (C₆H₅)₃SnF. Triphenyltin chloride reagent precipitates fluorides quantitatively as the corresponding fluoride. The precipitate is crystalline, easily filtered, and quickly washed, and is quite stable. Owing to the insolubility of the reagent in water, precipitation is carried out in 60–70 per cent alcoholic solution, and washing is effected with an alcoholic solution of the reagent saturated with triphenyltin fluoride.

The conversion factor is particularly small (0.05149), so that the method is well adapted for the estimation of small quantities of fluorides. The maximum amount that can be conveniently handled is 0.04 g. of F. The solution should have a pH of 5–7; if acid some fluorine will be lost on heating to boiling, and if basic, triphenyltin hydroxide will be precipitated along with the fluoride. Metals other than those of the alkalis should preferably be absent; the alkali metals may be removed by washing the precipitate several times with the alcohol wash solution, followed by cold water. Small quanti-
ties of nitrates, chlorides, bromides, iodides, and sulphates do not interfere, but silicates (with ammoniacal zinc hydroxide), phosphates (with silver nitrate), and carbonates must be removed before precipitation. Carbonate is best removed by neutralising with dilute nitric acid (to phenolphthalein), and boiling off the carbon dioxide. A disadvantage of the method is that the reagent is expensive.

B. Determination of fluoride as calcium fluoride. Procedure. The alkali fluoride solution should have a volume of 75–100 ml., and contain up to 0·3 g. of F. Add 7 ml. of concentrated ammonia solution and 20 ml. of 0·5M-calcium chloride in the cold, slowly and with stirring. Boil the solution for 1–2 minutes, allow the precipitate to settle, and decant the mother liquor through a quantitative filter-paper. Add 20 ml. of water, and 1 ml. of concentrated ammonia solution, boil, and decant as before; repeat the process. Transfer the precipitate to the filter, and wash three to four times with hot water. Place the filter and precipitate in a weighed Main-Smith crucible, burn off the filter-paper, and ignite at 500–600° C. (dull red heat) to constant weight. Weigh as CaF₂. As an additional check, convert the calcium fluoride into calcium sulphate by two or three evaporations with concentrated sulphuric acid, ignite at about 500° C. and weigh as CaSO₄; if this check determination is to be made, the initial ignition must be carried out in a platinum crucible.

C. Determination of fluoride as triphenyltin fluoride. Procedure. The solution (say, 25 ml.) should contain not more than 0·04 g. of F, and be almost neutral (1). Add 95 per cent ethyl alcohol to the aqueous solution of the fluoride so that it comprises about 60–70 per cent of the final volume. Heat to boiling and treat with twice the calculated quantity of the reagent (2) diluted with an equal volume of 95 per cent alcohol and also heated to boiling. The latter is run slowly into the hot fluoride solution with vigorous stirring, and the whole again heated to the boiling point. Remove the source of heat, and continue the stirring until the solution has cooled somewhat (3). Allow to stand overnight, and cool for 1 hour in ice (4). Filter through a weighed, sintered-glass or porous-porcelain crucible, wash with 95 per cent ethyl alcohol which has been saturated with triphenyltin fluoride (about 50 ml.). Dry for 39 minutes at 110° C., cool in a desiccator, and weigh as \( (C_6H_5)_3SnF \).

Notes. 1. For practice in this estimation, A.R. sodium fluoride (obtainable, inter alia, from the Mallinckrodt Chemical Works, U.S.A.) may be used. If desired, a sample of pure sodium fluoride may be prepared as follows. Treat A.R. anhydrous sodium carbonate with an excess of A.R. hydrofluoric acid in a platinum dish, and allow to stand for a few hours. Remove the excess of acid by heating (fume cupboard), allow to cool, and add more acid. Mix thoroughly with a platinum spatula, heat the dish gently at first, and then strongly until the sodium fluoride is entirely fused. Pulverise in an agate mortar, dry the powder in platinum at 110° C., and store in a desiccator over calcium chloride.

2. The reagent is prepared by shaking vigorously 4·0 g. of triphenyltin chloride (obtainable from the Eastman Kodak Co.) with 200 ml. of 95 per cent ethyl alcohol; filter from the small undissolved residue. This is practically a saturated solution.

About 55 ml. of this reagent are required for 0·04 g. F.

3. If the quantity of fluoride is large, precipitation commences in about
Quantitative Inorganic Analysis

a minute after the addition of the reagent as white crystals, but with small quantities it does not take place until the solution has cooled to room temperature.

4. This is unnecessary if the amount of fluoride is large and the total volume of the solution small.

IV, 58. CHLORATE

Discussion. The chlorate is reduced to chloride, and the latter is determined as silver chloride, \( \text{AgCl} \). The reduction may be performed with ferrous sulphate solution, sulphur dioxide, or zinc. Alkali chlorates may be quantitatively converted into chlorides by three evaporations with concentrated hydrochloric acid, or by evaporation with three times the weight of ammonium chloride; the operations are conveniently carried out in a Main-Smith crucible (Section II, 36B).

Determination of chlorate as silver chloride. Procedure. The chlorate solution should have a volume of about 100 ml., and contain about 0.2 g. of \( \text{ClO}_3^- \). Add 50 ml. of a 10 per cent solution of A.R. crystallised ferrous sulphate, heat with constant stirring to the boiling point, and maintain the boiling for 15 minutes. Allow to cool, add nitric acid until the precipitated basic ferric salt is dissolved, precipitate the chloride by means of silver nitrate solution, and collect and weigh as \( \text{AgCl} \) after the usual treatment (Section IV, 5).

Alternatively, treat the chlorate solution with excess of sulphur dioxide, boil the solution to remove the excess of the gas, render slightly acid with nitric acid, and precipitate the silver chloride as above.

For the reduction with zinc, render the chlorate solution strongly acid with acetic acid, add excess of zinc, and boil the mixture for 1 hour. Dissolve the excess of unused zinc with nitric acid, filter, and react the filtrate with silver nitrate in the usual manner.

Note. Hypochlorites and chlorites may be reduced to chlorides with sulphur dioxide, and determined in the same way.

IV, 59. PERCHLORATE

Discussion. Perchlorates are not reduced by ferrous sulphate solution, sulphurous acid, or by repeated evaporation with concentrated hydrochloric acid; reduction occurs, however, with titanous sulphate solution. Ignition of perchlorates with ammonium chloride in a platinum crucible or in a porcelain crucible in the presence of a little platinum powder results in reduction to the chlorides (the platinum acts as a catalyst), which may be determined in the usual manner. Losses occur when perchlorates are ignited alone.

Perchlorates may also be determined as potassium perchlorate, \( \text{KClO}_4 \). Sodium perchlorate is estimated directly by precipitation with concentrated potassium acetate solution. The sparingly soluble perchlorates of the heavy metals are first precipitated with excess of sodium carbonate solution, filtered, and the filtrate (containing sodium perchlorate), evaporated to dryness on the water-bath. The cold residue is extracted six times with 5-ml. portions of anhydrous ethyl acetate (compare Section IV, 48B), and the filtrate carefully evaporated on the water-bath. The residue is dissolved in 20 ml. of water, and precipitated as \( \text{KClO}_4 \) with potassium acetate solution.

A. Determination of perchlorate as silver chloride. Procedure. The perchlorate, if in the form of a solution, is evaporated to dryness on
the water-bath; otherwise the solid perchlorate is used directly. Intimately mix about 0.4 g. of the perchlorate (1) with 1.5 g. of A.R. ammonium chloride in a platinum crucible covered with a watch-glass or lid, ignite gently until fuming ceases and continue the heating for 1 hour. Do not fuse the resultant chloride, as the crucible may be attacked. Repeat the ignition with another 1.5 g. of ammonium chloride. Dissolve the residue in a little water, filter through a small quantitative filter-paper to remove any platinum powder which may be present, and estimate the chloride in the filtrate as silver chloride (Section IV, 5).

Note. 1. For practice in this estimation, the student may employ A.R. potassium perchlorate.

B. Determination of perchlorate as potassium perchlorate. Procedure. The perchlorate solution should be in the form of the sodium salt (see Discussion above), have a volume of about 25 ml., and contain about 0.4 g. of ClO₄⁻. Warm the solution to 80-90°C., and treat with a slight excess of a cold, saturated solution of potassium acetate. Allow the solution to cool, and after 1 hour collect the precipitate on a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain). Wash twice with 0.05M-potassium acetate, then four times with anhydrous ethyl acetate, and draw air through the precipitate until it appears dry. Dry at 110°C. to constant weight, and weigh as KClO₄.

IV, 60. IODATE

Discussion. Iodates are readily reduced by sulphurous acid to iodides; the latter are determined by precipitation with silver nitrate solution as silver iodide, AgI. Iodates cannot be converted quantitatively into iodides by ignition, for the decomposition takes place at a temperature at which the iodide is appreciably volatile.

Periodates are also reduced by sulphurous acid, and may therefore be similarly determined. Similar remarks apply to bromates; these are ultimately weighed as silver bromide, AgBr.

Determination of iodate as silver iodide. Procedure. Acidify the iodate solution (100 ml. containing ca. 0.3 g. of IO₃⁻ (1) with sulphuric acid, and pass in sulphur dioxide (or add a freshly prepared saturated solution of sulphurous acid) until the solution which at first becomes yellow, on account of the separation of iodine, is again colourless. Boil off the excess of sulphur dioxide, and precipitate the iodide with dilute silver nitrate solution as described in Section IV, 54. Weigh as AgI.

Note. 1. For practice in this determination, the student may employ A.R. potassium iodate.

IV, 61. SULPHATE

Discussion. Full details for the determination of soluble sulphates as barium sulphate, BaSO₄ are given in Section IV, 6. For sulphates which are insoluble in water and acids, it is best to mix the finely powdered solid with six to twelve times its bulk of anhydrous sodium carbonate in a platinum crucible set in an asbestos shield (Section II, 38), heat the covered crucible slowly to fusion, and maintain in the fused state for 15 minutes. The melt
Quantitative Inorganic Analysis

is extracted with water, the solution filtered, the residue washed with hot 1 per cent sodium carbonate solution, and the cold filtrate carefully acidified with hydrochloric acid (to methyl orange). The sulphate is determined as in Section IV, 6. If silica is present, the acid filtrate is evaporated to dryness on the water-bath to dehydrate the silica; a little concentrated hydrochloric acid is added, followed by hot water. The silica is filtered off, and the sulphate determined in the filtrate.

A comparatively rapid method for the determination of sulphate, which is particularly suitable for routine estimations, is based upon the precipitation as \( \text{BaSO}_4 \) in the presence of picric acid (compare use of agar-agar, Section IV, 6). Prolonged digestion is unnecessary, and the solution may be filtered after about 10 minutes. The detailed procedure is as follows. The slightly acidified sulphate solution is treated with 1–5 ml. of saturated picric acid solution according to the sulphate content (1), a slight excess of barium chloride solution is added rapidly (2), and the solution gently boiled for 5–10 minutes. The precipitate may then be filtered off, thoroughly washed, and weighed as in Section IV, 6.

Notes. 1. If large amounts of sodium salts are present, 10–25 ml. of the saturated picric acid solution are necessary.
   2. In this method there is no advantage in adding the barium chloride solution slowly.

IV, 62. SULPHIDE

Discussion. The determination of sulphur in insoluble sulphides by wet and dry processes and subsequent weighing as barium sulphate, \( \text{BaSO}_4 \), is fully dealt with in Section IV, 7. Other methods, which are particularly applicable to soluble sulphides, include oxidation in alkaline solution with sodium hypochlorite or hydrogen peroxide,* followed by the estimation of sulphate as barium sulphate.

IV, 63. SULPHITE

Discussion. Sulphites may be readily converted into sulphates by boiling with excess of bromine water, sodium hypochlorite, sodium hypobromite, or ammoniacal hydrogen peroxide (equal volumes of 20-volume hydrogen peroxide and 1:1 ammonia solution). The excess of the reagent is decomposed by boiling, the solution acidified with hydrochloric acid, precipitated with barium chloride solution, and the barium sulphate collected and weighed in the usual manner (Section IV, 6).

IV, 64. THIOSULPHATE

Discussion. Thiosulphates are oxidised to sulphates by methods similar to those described for sulphites (Section IV, 63), e.g., by heating on a water-bath with an ammoniacal solution of hydrogen peroxide, followed by boiling to expel the excess of the reagent. The sulphate is then determined as barium sulphate, \( \text{BaSO}_4 \). One molecule of thiosulphate corresponds to two molecules of barium sulphate.

* Ammoniacal hydrogen peroxide is usually employed. The hydrogen peroxide must be free from sulphate.
IV, 65.

PHOSPHATE

Discussion. Orthophosphates may be precipitated as magnesium ammonium phosphate, MgNH₄PO₄·6H₂O, by magnesium chloride and ammonium chloride in ammoniacal solution ("magnesia" reagent). Most elements, other than those of the alkalis, interfere, however, by giving precipitates with "magnesia mixture." It is therefore necessary in the majority of cases to separate the phosphate first from interfering substances. This may be readily effected by precipitation as ammonium phosphomolybdate with excess of ammonium molybdate in warm nitric acid solution: arsenic, vanadium, titanium, zirconium, silica, and excessive amounts of ammonium salts interfere. When first precipitated, the yellow precipitate is generally supposed to contain water and nitric acid of crystallisation; upon drying at 120–160°C, the water and nitric acid of crystallisation are driven off and the precipitate has the composition (NH₄)₆[PMo₁₂O₄₀] (2). The precipitate thus obtained is dissolved in dilute ammonia solution, and the phosphate is then precipitated as magnesium ammonium phosphate. A double precipitation of the latter is necessary in order to obtain a precipitate entirely free from molybdate.

If interfering elements are absent, the original yellow precipitate may be weighed either as ammonium phosphomolybdate, (NH₄)₆[PMo₁₂O₄₀], after drying at 120–160°C, or as phosphomolybdic anhydride, P₂O₅·24MoO₃, after heating at 400–450°C for 30 minutes. For practice in this estimation, the student may determine the percentage of phosphate in anhydrous A.R. disodium hydrogen phosphate, Na₂HPO₄, or in any other phosphate supplied by the instructor. (Most of the experimental details are given in Section III, 146.) The precipitate of ammonium phosphomolybdate should, however, be filtered through a weighed porous-porcelain filter-crucible, and washed with the special wash liquid (1) until only a faint brown colour is given when 5 ml. of the washings are tested with potassium ferrocyanide solution. The precipitate is dried at 120–160°C to constant weight (1–2 hours) and weighed as (NH₄)₆[PMo₁₂O₄₀]. The precipitate may now be heated in an electric oven at 400–450°C (or at a dull red heat upon a crucible-ignition dish) and weighed as P₂O₅·24MoO₃. Both solids are appreciably hygroscopic and should be weighed rapidly.

Notes. 1. Prepared by dissolving 10 g. of ammonium nitrate in water, adding 8 ml. of concentrated nitric acid, and diluting to 200 ml.

2. The proportion of P found, depending upon the method and the conditions of precipitation, is 1·63–1·64 per cent; the theoretical value is 1·65 per cent. A factor of 1·64 per cent is often used.

A. Determination of phosphate as magnesium ammonium phosphate hexahydrate or as magnesium pyrophosphate. Procedure. To a neutral or weakly acid solution (50–100 ml.) of the phosphate, containing not more than 0·1 g. of P₂O₅ and free from interfering elements (1), add 3 ml. of concentrated hydrochloric acid and a few drops of methyl-red indicator. Introduce 25 ml. of magnesia mixture (Section IV, 20B, Note 2), followed by pure concentrated ammonia solution slowly whilst stirring the solution vigorously until the indicator turns yellow. The procedure from this stage is the same as described for the determination of magnesium in Section IV, 11, except that when carrying out the re-precipitation from the hydrochloric acid solution 2 ml. of the magnesia mixture are added instead of the 1 ml. of ammonium phosphate solution. Weigh as MgNH₄PO₄·6H₂O or as Mg₅₂P₂O₇.

Note. 1. A suitable solution for practice may be prepared by dissolving about 0·4 g., accurately weighed, of A.R. anhydrous Na₂HPO₄ in 100 ml. of water.
B. Determination of phosphate as magnesium ammonium phosphate hexahydrate or as magnesium pyrophosphate after a preliminary separation as ammonium phosphomolybdate.

Procedure. For practice in this estimation, it is recommended that basic slag (1) be employed. Weigh out accurately about 2·5 g. of the finely powdered basic slag into a 10-cm. porcelain or Pyrex basin. Add 20 ml. of concentrated sulphuric acid, and mix to a smooth paste. Heat the mixture on a sand-bath (or hot-plate) in the fume cupboard until white fumes begin to appear, and then keep it in this condition for 45 minutes with stirring at intervals. Avoid strong fuming of the sulphuric acid. Allow to cool, dilute carefully with water, and, when cold, filter into a 250-ml. volumetric flask, wash the residue thoroughly with cold water, and make up to the mark. Measure out 50 ml. of the solution (do not allow the solution to stand too long, as calcium sulphate is liable to crystallise out) into a 400-ml. beaker, add 10 ml. of concentrated nitric acid, followed by 1 : 1 ammonia solution until a faint permanent precipitate appears. Re-dissolve the precipitate by the addition of a few drops of concentrated nitric acid, heat to 40–45° C. (use thermometer), and treat with 100 ml. of the ammonium molybdate reagent (Section III, 148) previously heated to the same temperature, slowly and with stirring; continue the stirring for about 10 minutes. Allow the precipitate to stand for a few hours, but preferably overnight. Filter through a Whatman No. 40 or 540 filter-paper, leaving as much as possible of the precipitate in the beaker, and wash the precipitate moderately with 5 per cent ammonium nitrate solution. Pour down the sides of the beaker containing the main part of the ammonium phosphomolybdate precipitate a solution prepared by dissolving 0·5 g. of citric acid in 15 ml. of water and 7 ml. of concentrated ammonia solution. (The citric acid serves to keep any iron in solution.) When the precipitate has dissolved, pour this solution slowly into the filter-paper containing the remainder of the precipitate; collect the filtrate and washings in a 400-ml. beaker. Wash the original beaker and filter-paper successively twice each with small volumes of dilute ammonia solution (1 : 20), hot water, hot dilute hydrochloric acid (1 : 20), hot water, and finally with dilute ammonia solution (1 : 20) and hot water. The filtrate and washings should not exceed 200 ml. in volume at this stage. (The above treatment is necessary for the complete removal of the last traces of phosphate from the paper.) Render the ammoniacal solution slightly acid (methyl red) with dilute hydrochloric acid, and introduce 25 ml. of magnesia mixture (Section IV, 20B, Note 2) dropwise and stirring continuously. Next add 10–15 ml. of 1 : 1 ammonia solution slowly and with stirring. Allow the solution to stand for at least 4 hours, but preferably overnight. Filter without attempting to transfer the precipitate, wash the vessel, residue, and paper a few times with 1 : 20 ammonia solution. Dissolve the precipitate on the filter in 25 ml. of warm 1 : 4 hydrochloric acid, and collect the solution in the original beaker containing the bulk of the precipitate. Wash the filter-paper thoroughly with warm 1 : 20 hydrochloric acid. Add to the filtrate and washings, diluted to 100 ml., 2 ml. of magnesia mixture; then re-precipitate the phosphate by the addition of 1 : 1 ammonia solution drop by drop and with thorough stirring, and finally add 10 ml. of the 1 : 1 ammonia solution in excess. Allow to stand for 12 hours. Collect the precipitate on a filter-paper or in a weighed silica, Gooch, or porous-
porcelain crucible, and wash with cold 1 : 20 ammonia solution until free from chloride. Complete the determination as described in Section IV, 11, and weigh as $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$ or as $\text{Mg}_2\text{P}_2\text{O}_7$.

Note. 1. Ridgway’s “Basic Slag (Thomas Phosphate), No. 31” (one of the Analysed Samples for Students) or the Bureau of Analysed Samples “Basic Slag No. 174A” (one of the British Chemical Standards) is suitable.

IV, 66. PHOSPHITE

Discussion. This anion may be determined in either of the following forms:

A. Mercurous chloride, $\text{Hg}_2\text{Cl}_2$. The acid solution of phosphite reduces mercuric chloride solution to calomel, which is weighed. The reaction is:

$$2\text{HgCl}_2 + \text{H}_3\text{PO}_3 + \text{H}_2\text{O} = \text{Hg}_2\text{Cl}_2 + \text{H}_3\text{PO}_4 + 2\text{HCl}$$

whence $\text{Hg}_2\text{Cl}_2 = \text{H}_3\text{PO}_3$

B. Magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$, or as the pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$. The phosphite is oxidised by nitric acid to phosphate, and the latter is determined as magnesium ammonium phosphate hexahydrate or as the pyrophosphate.

A. Determination of phosphite as mercurious chloride. Procedure. The phosphite solution (30 ml.) should contain about 0.1 g. of $\text{HPO}_2^-$.
Place 50 ml. of 3 per cent mercuric chloride solution, 20 ml. of 10 per cent sodium acetate, and 5 ml. of glacial acetic acid in a 250-ml. beaker, and add the phosphite solution dropwise, and with stirring, in the cold. Allow to stand on a water-bath at 30–45° C. for 2 hours. When cold, filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain), wash two or three times with 1 per cent hydrochloric acid, and then four times with warm water. Dry at 105–150° C., and weigh as $\text{Hg}_2\text{Cl}_2$.

B. Determination of phosphite as magnesium ammonium phosphate hexahydrate or as the pyrophosphate. Procedure. Treat the aqueous solution of the phosphite (100 ml.) with 5 ml. of concentrated nitric acid, evaporate to a small volume on the water-bath, add 1 ml. of fuming nitric acid, and heat again. Dilute the solution, and precipitate the phosphoric acid by magnesia mixture and ammonia solution, and weigh as $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$ or as $\text{Mg}_2\text{P}_2\text{O}_7$ (Section IV, 65A).

IV, 67. HYPOPHOSPHITE

Discussion. This anion is determined similarly to phosphite either as mercurous chloride, $\text{Hg}_2\text{Cl}_2$, or as ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$, or as magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$. In this case the reaction with mercurious chloride solution is:

$$4\text{HgCl}_2 + \text{H}_3\text{PO}_2 + 2\text{H}_2\text{O} = 2\text{Hg}_2\text{Cl}_2 + \text{H}_4\text{PO}_4 + 4\text{HCl}$$

so that $2\text{Hg}_2\text{Cl}_2 = \text{H}_4\text{PO}_4$

IV, 68. OXALATE

Discussion. The neutral solution of alkali oxalate is acidified with acetic acid, heated to boiling, and precipitated with boiling calcium chloride solution. After standing for 12 hours, the precipitate is filtered off, washed
Quantitative Inorganic Analysis

with hot water, and weighed either as calcium carbonate, CaCO₃, or as calcium oxide, CaO (for details, see Section IV, 10).

The following rapid method yields results of moderate accuracy. Precipitation of the oxalate is effected in boiling solution containing a little ammonium chloride by a hot solution of calcium chloride. The solution is allowed to cool, treated with one-third of its volume of rectified spirit, and allowed to stand for 30 minutes. The precipitate is washed by decantation through a weighed porous-porcelain or sintered-glass crucible with warm water (50-60° C.) until the chloride reaction is negative. The calcium oxalate is then transferred to the filter-crucible, washed once with cold water, 5 times with rectified spirit, and several times with small volumes of anhydrous ether. The precipitate is sucked dry at the pump for 10 minutes, the outside of the crucible wiped dry with a clean linen cloth, and then left in a vacuum desiccator for 10 minutes. It is weighed as CaC₂O₄·H₂O.

IV, 69. BORATE

Discussion. The most trustworthy methods for the determination of borate are based upon its volatilisation as methyl borate, B(OCH₃)₃; this is achieved by acidifying the alkali or alkaline-earth borates and heating with absolute methyl alcohol (methanol). The methyl borate is saponified by bringing it in contact with a weighed amount of lime in the presence of water:

\[
B(OCH₃)₃ + 3HOH = (BOH)₃ + 3CH₃OH
\]

The boric acid is set free and combines with the lime to form calcium borate. If the paste is then evaporated to dryness and ignited, the increase in weight represents the amount of B₂O₃. Alternatively, the boric acid is titrated after the addition of mannitol as described in Section III, 17. For complete details, the reader is referred to other treatises (1).


IV, 70. SILICATE

Discussion. Silicates may be divided into two classes: (a) those (" soluble" silicates) which are decomposed by acids, such as hydrochloric acid, to form silicic acid and the salts (e.g., chlorides) of the metals present, and (b) those (" insoluble" silicates) which are not decomposed by any acid, except hydrofluoric acid. There are also many silicates which are partially decomposed by acids; for our purpose these will be included in class (b). Insoluble silicates are generally fused with sodium carbonate, and the melt, which contains the silicate in acid-decomposable form, is then treated with hydrochloric acid. The acid solution of the decomposed silicate is evaporated to dryness on the water-bath to separate the gelatinous silicic acid SiO₂·xH₂O as insoluble silica SiO₂·yH₂O; the residue is heated at 110-120° C. to partially dehydrate the silica and render it as insoluble as possible. The residue is extracted with hot dilute hydrochloric acid to remove salts of iron, aluminium, and other metals which may be present. The greater portion of the silica remains undissolved, and is filtered off. The filtrate is evaporated to dryness, and the residue heated at 110-120° C. as before in
order to render insoluble the small amount of silicic acid that has escaped dehydration. The residue is treated with dilute hydrochloric acid as before, and the second portion of silica is filtered off on a fresh filter. The two washed precipitates are combined, and ignited in a platinum crucible at about 1050°C to silicon dioxide, SiO₂, and the latter is weighed. The ignited residue is not usually pure silicon dioxide; it will generally contain small amounts of the oxides of iron, aluminium, titanium, etc. The amount of impurity may be determined, if desired, by treating the weighed residue in the platinum crucible with an excess of hydrofluoric acid and a little concentrated sulphuric acid. The silica is expelled as the volatile silicon tetrafluoride; the impurities (e.g., Al₂O₃ and Fe₂O₃) are first converted into the fluorides, which pass into the sulphates in contact with the less-volatile sulphuric acid, whilst the subsequent ignition (at 1050-1100°C) converts the sulphates back into oxides. Thus, for example:

\[
\begin{align*}
\text{SiO}_2 + 6\text{HF} & \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \\
\text{H}_2\text{SiF}_6 & \rightarrow \text{SiF}_4 + 2\text{HF} \\
\text{Al}_2\text{O}_3 + 6\text{HF} & \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O} \\
2\text{AlF}_3 + 3\text{H}_2\text{SO}_4 & \rightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{HF} \\
\text{Al}_2(\text{SO}_4)_3 & \rightarrow \text{Al}_2\text{O}_3 + 3\text{SO}_3
\end{align*}
\]

The loss in weight therefore represents the amount of pure silicon dioxide present.

Seventy per cent perchloric acid is frequently used for the dehydration of silicic acid (see, e.g., Section IV, 960). The solution, containing hydrochloric and nitric acid, is evaporated to strong fuming with excess of perchloric acid, and heated for a further 15-20 minutes; water is then added and the silica filtered off. A second evaporation is necessary for the filtrate to separate the small amount of dissolved silicic acid. The perchlorates of the metals, except that of potassium, are readily soluble, so that the method possesses certain advantages. Organic compounds must, however, be absent, as dangerous explosions may result.

EXPLOSIVE DANGERS OF PERCHLORIC ACID.—It must be emphasised that aqueous and anhydrous perchloric acids are powerful oxidising agents. In the presence of carbon and easily oxidisable organic compounds, a dangerous explosion may result on heating with the aqueous acid; in some cases explosion may result even in the cold with the aqueous acid. Evaporations with perchloric acid should be carried out in a fume cupboard which is kept clean and free from combustible materials. The acid should be kept in a fire-proof store, and reasonable care should be taken in handling it.

A. Determination of silica in a “soluble” silicate. Procedure. Weigh out accurately about 0.4 g. of the finely powdered silicate (1) into a platinum or porcelain dish, add 10-15 ml. of water, and stir until the silicate is thoroughly wet. Place the dish, covered with a clock-glass or a Fisher “speedyvap” beaker-cover, on the water-bath, and add gradually 25 ml. of 1:1 hydrochloric acid. The contents of the dish must be continuously stirred with a glass rod; when no gritty particles remain, the powder will have been completely decomposed. Evaporate the liquid to dryness: stir the residue continuously and break up any lumps with the glass rod. When the powder appears to be dry, place the basin in an air-oven at 110-120°C for 1 hour in order to dehydrate the silica. Moisten the residue with 5 ml. of concentrated hydrochloric acid, and bring the acid into contact with the solid with the aid of a stirring-rod. Add 75 ml. of water, rinse down the sides of the dish, and heat on a steam-bath for 10-20 minutes to assist in the
solution of the soluble salts. Filter off the separated silica on a Whatman No. 41 or 541 filter-paper. Wash the precipitate first with warm 1:20 hydrochloric acid, and then with hot water until free from chlorides. Pour the filtrate and washings into the original dish, evaporate to dryness on the steam-bath, and heat in an air-oven at 110–120°C for 1 hour. Moisten the residue with 5 ml. of concentrated hydrochloric acid, add 75 ml. of water, warm to extract soluble salts, and filter through a fresh, but smaller, filter-paper. Wash with warm 1:100 hydrochloric acid, and finally with a little hot water. Fold up the moist filters, and place them in a weighed platinum crucible. Dry the paper with a small flame, char the paper, and burn off the carbon over a low flame (Section II, 36); take care that none of the fine powder is blown away. When all the carbon has been oxidised, cover the crucible, and heat for an hour at the full temperature on a Méker type of burner in order to complete the dehydration. Allow to cool in a desiccator, and weigh. Repeat the ignition, etc., until the weight is constant.

To determine the exact SiO₂ content of the residue, moisten it with 1 ml. of water, add 2 or 3 drops of concentrated sulphuric acid and about 5 ml. of the purest available (A.R.) hydrofluoric acid. Place the crucible in a radiator or air-bath (Section II, 13F) and evaporate the hydrofluoric acid in a fume cupboard with a small flame until the acid is completely expelled; the liquid should not be boiled. (The crucible may also be directly heated with a small non-luminous flame.) Then increase the heat to volatilise the sulphuric acid, and finally heat with a Méker-type burner for 15 minutes. Allow to cool in a desiccator and weigh. Re-heat to constant weight. The loss in weight represents the weight of the silica (2).

Notes. 1. For practice in this estimation, powdered, fused sodium silicate may be used.
2. It is advisable to carry out a blank determination with the hydrofluoric acid, and to allow for any non-volatile substances, if necessary.

B. Determination of silica in an "insoluble" silicate. Procedure. Weigh out accurately into a platinum crucible about 1 g. of the finely powdered dry silicate (1), add six times the weight of anhydrous A.R. sodium carbonate (or, better, of A.R. fusion mixture), and mix the solids thoroughly by stirring with a thin, rounded glass rod. Cover the mixture with a little more of the carbonate, and then cover the crucible. Heat the mixture gradually until after about 20 minutes a tranquil melt is obtained; the cover of the crucible is lifted occasionally to examine the contents. Maintain the temperature of a quiet liquid fusion for about 30 minutes. Allow to cool. Place the crucible and lid in a covered deep porcelain or platinum basin (or in a large casserole), cover it with water, and leave overnight, or warm on the water-bath until the contents are well disintegrated. Introduce very slowly by means of a pipette or a bent funnel about 20 ml. of concentrated hydrochloric acid in the covered vessel. Warm on the steam-bath until the evolution of carbon dioxide has ceased. Remove and rinse the cover-glass, crucible, and lid, and evaporate the contents of the dish to complete dryness on the steam-bath, crushing all lumps with a glass rod. Heat the residue for an hour at 110–120°C to dehydrate the silica. Complete the estimation as described in A.
Gravimetric Analysis

Note. 1. Ridsdale's "Felspar (Potash), No. 29b" (one of the Analysed Samples for Students) is suitable.

IV, 71. FLUOSILICATE

Discussion. The determination of this anion is of little practical importance. The methods available for its estimation will, however, be outlined. Alkali fluosilicates are decomposed by heating with sodium carbonate solution into a fluoride and silicic acid:

$$\text{Na}_2[\text{SiF}_6] + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 6\text{NaF} + \text{H}_2\text{SiO}_3 + 2\text{CO}_2$$

Insoluble fluosilicates are brought into solution by fusion with four times the bulk of fusion mixture, and extracting the melt with water. In either case, the solution is treated with a considerable excess of ammonium carbonate, warmed to 40° C, and, after standing for 12 hours, the precipitated silicic acid is filtered off, and washed with 2 per cent ammonium carbonate solution. The filtrate contains a little silicic acid, which may be removed by shaking with a little freshly precipitated cadmium oxide. The fluoride in the filtrate is determined as described in Section IV, 57.

If an acid solution of a fluosilicate is rendered faintly alkaline with aqueous sodium hydroxide and then shaken with freshly precipitated cadmium oxide, all the silicic acid is adsorbed by the suspension. The alkali fluoride is then estimated in the filtrate.

IV, 72. FERROCYANIDE

No satisfactory gravimetric procedure is available. Volumetric methods are described in Chapter III.

IV, 73. FERRICYANIDE

No satisfactory gravimetric method is available. For volumetric methods, see Chapter III.

IV, 74. NITRITE

No satisfactory gravimetric procedure is available. Volumetric methods are described in Chapter III.

IV, 75. NITRATE

Discussion. The mono-acid base nitron, $\text{C}_{10}\text{H}_{16}\text{N}_4\text{OH}$, forms a fairly insoluble crystalline nitrate, $\text{C}_{26}\text{H}_{16}\text{N}_4\text{HNO}_3$ (solubility is 0.009 g. per litre at about 20° C.), which can be used for the quantitative estimation of nitrates (see Section 1, 62, 1). The sulphate and acetate are soluble so that precipitation may be made in sulphuric or acetic acid solution. Perchlorates (0.08 g.), iodides (0.17 g.), thiocyanates (0.4 g.), chromates (0.6 g.), chlorates (1.2 g.), nitrates (1.9 g.), bromides (0.1 g.), ferrocyanides, ferricyanides, oxalates, and considerable quantities of chlorides interfere, and should be absent. The figures in parentheses are the approximate solubilities of the nitron salts in grams per litre at about 20° C.

Determination of nitrate as nitron nitrate. Procedure. The solution (75–100 ml.) should be neutral and contain about 0.1 g. of $\text{NO}_3^-$. Add 1 ml. of glacial acetic acid or 0.5 ml. of 2N-sulphuric acid, and heat the
solution nearly to the boiling point. Then introduce 10–12 ml. of the nitron reagent (1), stir, and cool in ice-water for 2 hours. Filter through a weighed filter-crucible (Gooch, sintered-glass, or porous-porcelain). Wash with 20–40 ml. of a cold saturated solution of nitron nitrate, added in several portions, and drain the precipitate well after each washing. Finally, wash twice with 3-ml. portions of ice-cold water. Dry at 105° C. (1 hour is usually required), and weigh as C20H18N4,HNO3.

Note. 1. Prepare the reagent by dissolving 5 g. of nitron in 50 ml. of 5 per cent acetic acid.

IV, 76. CARBONATE

Discussion. The carbonate is decomposed by dilute acid, and either the loss in weight due to the escape of carbon dioxide determined (indirect method) or the carbon dioxide evolved is absorbed in a suitable medium and the increase in weight of the absorbent determined (direct method). The direct method gives more satisfactory results, and will therefore be described. The indirect method is often employed, however, for samples containing relatively large amounts of carbonate.

The decomposition of the carbonate may be effected with dilute hydrochloric acid, dilute perchloric acid, or syrupy phosphoric acid. The last-named acid is perhaps the most convenient because of its comparative non-volatility and the fact that the reaction can be more easily controlled than with the other acids. If dilute hydrochloric acid is employed, a short, water-cooled condensed should be inserted between the decomposition flask and the absorption train (see below).

Two absorbents are required, one for water vapour and the other for carbon dioxide. The absorbents for water vapour which are generally employed are: (a) anhydrous calcium chloride (14–20 mesh), (b) magnesium perchlorate trihydrate ("dehydrite"), and (c) anhydrous magnesium perchlorate ("anhydrone"). Both (b) and (c) are preferable to (a); the former absorbs about 35 per cent and the latter about 50 per cent of its weight of water. They are, however, expensive, and anhydrous calcium chloride is generally employed for ordinary work. The latter usually contains a little free lime, which will absorb carbon dioxide also; it is essential to saturate the U-tube containing the calcium chloride with dry carbon dioxide for several hours and then to displace the carbon dioxide by a current of pure air. Anhydrous calcium sulphate ("drierite") or anhydrous barium perchlorate ("dessichlor") may also be used.

The absorbents for carbon dioxide in general use are: (d) soda lime (this is available also in the form of self-indicating granules, "sofnoJite", or as "carbosorb" soda lime, which indicate when the absorbent is exhausted), (e) soda lime–asbestos (the "carbosorb" variety gives a marked colour change and therefore indicates the degree of exhaustion), and sodium hydroxide–asbestos ("ascarite"). In all cases the carbon dioxide is absorbed in accordance with the following equation:

$$2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

Water is formed in the reaction, hence it is essential to fill one-quarter or one-third of the tube with any of the desiccants referred to above (Fig. IV, 76, 1).
Determination of carbon dioxide in a carbonate. Procedure. Fit up
the apparatus shown in Fig. IV, 76, 2. A is a flask of about 100 ml.
capacity, B is a dropping funnel containing 20–25 ml. of A.R. syrupy
phosphoric acid, C is a soda-lime guard tube, D is a bubbler containing
syrupy phosphoric acid, E is a U-tube containing calcium chloride
which has been saturated with carbon dioxide and the residual carbon
dioxide displaced by air (this may be replaced by "dehydrite" or
"anhydrone," if available), F and G are soda-lime or "sofno-lite"
tubes (these may be replaced by "carbosorb" or "ascarite"), and H
is a guard U-tube containing the same desiccant as in E. The U-tubes
may be suspended by silver wires attached to hooks on the glass or
metal rod I, or by some other means. All joints are made with short
lengths of stout-walled rubber tubing, and the two ends of the glass

rubber tubing should be in contact. Rubber bungs are employed in A, B,
and C. Before proceeding with the actual estimation, make sure that
the apparatus is gas-tight.

Weigh out accurately 0.5–0.6 g. of the carbonate (1) into the flask A,
which should be clean and dry. Remove the two soda-lime or "sofnolite" tubes F and G, wipe them with a clean linen handkerchief or
cloth, and leave them in the balance-case for 45 minutes. Open the
taps of the U-tubes momentarily to the air in the balance-case, and
weigh them separately. Replace them on the drying train; place 25
ml. of A.R. syrupy phosphoric acid in B, and see that the apparatus
is connected up as in Fig. IV, 76, 2. Open the taps of the U-tubes. Run
in sufficient phosphoric acid from the tap funnel to cover the solid in the
flask (the 25 ml. will more than suffice). Close the tap of the funnel and
heat the flask carefully; regulate the temperature so that not more
than 2 bubbles of gas per second pass through the bubbler D. After
about 30–40 minutes, the contents of the flask should be boiling;
boil for 2–3 minutes. Remove the flame, and immediately attach a
filter-pump and a large bubbler (similar to D, and containing syrupy
phosphoric acid) to the end of the apparatus. Open the tap funnel,
and draw air through the apparatus at the rate of about 2 bubbles per
second for 20 minutes. Remove the tubes F and G, close the taps,
treat them as before, and weigh them. From the increase in weight,
calculate the percentage of CO₂ in the sample (2).
Notes. 1. For practice in this estimation, the student may employ A.R. calcium carbonate, or Ridsdale’s “Limestone, No. 15b or 16d” (Analysed Samples for Students).

2. For the most accurate work, and particularly when the amount of carbon dioxide is small, a “blank” experiment must be run with the reagents alone before the determination proper is carried out.
**ELECTROLYTIC DETERMINATIONS**

**IV, 77. Apparatus.—** A. Electrolysis unit. The actual set-up employed will vary from one laboratory to another according to the financial resources and the equipment otherwise available. A simple circuit, employing the D.C. mains (200–240 volts or 110 volts), is shown in Fig. IV, 77, 1. \( M \) is the D.C. mains, \( R_1 \) is a large variable resistance (which may consist of a bank of lamps), \( R_2 \) is a small variable resistance, \( A \) is an ammeter reading up to 10 amps., \( V \) is a voltmeter reading up to 10–15 volts, \( E \) is an electrolysis vessel, and \( S \) is a switch. Alternatively, the source of D.C. may be a large-capacity 6-volt or 12-volt car battery, or a number of accumulators connected in series. If a D.C. supply is not at hand, some form of rectifier must be employed for the A.C. mains; a convenient circuit, supplying low-tension D.C. current from the A.C. mains, is shown in Fig. IV, 88, 2.

If the polarities of the terminals are not known, they may be determined by touching the two wires from the terminals on to paper moistened with potassium iodide solution: a brown stain of iodine will form at the positive pole.

Many types of commercial apparatus for electrolytic analysis are available,* but only two will be described here. Fig. IV, 77, 2, depicts the B.T.L. "unity" apparatus. This unit operates from an external low-tension D.C. supply (up to 7 amps. at 12 volts). A large rotary rheostat controls the D.C. supply; provision is made for rotating the electrode at various speeds, and the electrolysis vessel may be heated by means of a hot-plate. The apparatus shown is the "master unit"; up to five "slave" units may be coupled with the "master unit," thus converting the single unit into a "multi-test" outfit. A similar form of apparatus for use with stationary electrodes but arranged for independent stirring of the electrolyte is also made by the same firm.

The Fisher "electro analyser" is shown in Fig. IV, 77, 3. This instrument operates directly from the 110-volt 50–60-cycle mains,

incorporates a rectifier, etc., and the output can be varied from zero to 6 volts. Two like determinations can be made simultaneously. The apparatus is equipped with two stirring motors, two sets of control switches, and one control knob for regulating the voltage at both sets of electrodes; the two sets of electrodes are connected in parallel so that the voltage at each is identical but not independently variable. Two monel-metal chucks are provided for each stirring-motor, one chuck holds \( \frac{1}{2} \) in. glass stirrers, and the other holds platinum stirring-electrodes. There is a swivelled beaker support below each motor.

**B. Electrodes.** These are generally made of platinum (or platinum-iridium), although cathodes of tantalum are occasionally employed for the deposition of certain metals. Silver electrodes (Fig. IV, 77, 7, a) are useful as cathodes for copper and zinc determinations. Numerous types of electrodes have been employed. The present tendency is to use gauze electrodes, particularly for the cathode, because they are considered to be the most satisfactory. It is probable that the interstices in the gauze bring about a much better circulation of the electrolyte so far as conditions at the surface of the electrode are concerned, the improved circulation serving to reduce any local depletion of the electrolyte.
Gravimetric Analysis

alyte that might tend to occur. These gauze electrodes may not be in the possession of every laboratory, so that other, in some cases less-expensive, electrodes will be described also.

The simplest apparatus to employ is a platinum dish as cathode and a circular platinum plate as anode (Fig. IV, 77, 4, a): a circular platinum gauze electrode (Fig. IV, 77, 5, e) may also be used. The filter-flask (Fig. IV, 77, 4, b) is for the removal of the electrolyte after the electrolysis. L. Classen (1927) gives the following details: diameter of dish 9 cm.; depth in the centre 4·2 cm.; capacity about 250 ml.; weight 35–40 g.; the inside surface should be matted (e.g., by sand blasting) so that the deposit adheres more easily; surface area for 150 ml. is ca. 100 sq. cm., and for 180 ml. of liquid ca. 130 sq. cm.; diameter of anode 4·5 cm.; the electrodes should be used exclusively for electrolytic determinations. For a dish 6·5 cm. in diameter, the diameter of the anode should be 3·5 cm.

Two other designs of cathode are shown in Fig. IV, 77, 5, a and b; these are made of platinum sheet and wire. The anodes c, d, and e may be used with a, and the anode f with b. These are chiefly employed for stationary or slow electrolysis. The cylinders may be provided with thin slits to facilitate the circulation of the electrolyte. The “flag” type of electrodes are shown in Fig. IV, 77, 6, a and b.

For routine work in rapid electrolysis a platinum-gauze cylinder (Fig. IV, 77, 7, a) and the associated gauze cylinder (Fig. IV, 77, 7, b) or spiral (Fig. IV, 77, 5, f) are generally employed.

Sand’s original type (1907) of electrodes for rapid electrolysis are shown diagrammatically in Fig. IV, 77, 8, a and b; a glass sleeve passes through b in order to insulate the electrodes from one another. These are particularly well adapted for very rapid electrolysis. The electrodes shown in Figs. IV, 77, 8 and IV, 77, 5–8 are drawn to approximately one-third the actual size.**

* These are reproduced by the courtesy of Messrs. Johnson, Matthey and Co., Ltd., of Hatton Garden, London, E.C.I., England. They can, of course, be modified to suit any particular purpose. Apparatus of smaller dimensions down to “micro” size can be obtained from this firm.
Sand's original electrodes, although very convenient in use, suffer from the disadvantage that they are expensive. A modification, also due to Sand, which possesses most of the advantages of the original design but requires comparatively little platinum is shown in Fig. IV, 77, 9, together with the details of construction. The inner electrode is made of Pyrex glass, and the platinum gauze and the four connecting wires are lightly fused on to the surface of the glass; a platinum wire is wound round the glass to prevent "sticking" during rotation. The outer electrode (a in Fig. IV, 77, 9) is of platinum gauze and weighs 9–12 g.; it is supported by means of a Pyrex-glass tripod, and a terminal is provided. In use, the stem of the inner electrode is slipped through the guide tube of the tripod and fitted into the holder or clutch (see, for example, Fig. IV, 77, 16); the outer electrode is pushed inside the tripod, and both it and the tripod are held by the cathode clamp.

The advent of comparatively inexpensive commercial electrolytic analysis apparatus has tended to limit the types of electrodes employed in electrochemical analysis. The electrodes depicted in Figs. IV, 77, 7–9 are widely employed when the anode is rotated: stirring of the electrolyte is very efficient with these electrodes. The rotating anode usually weighs 25–40 g. A considerable economy in platinum may be effected by the use of the paddle-shaped electrode (Fig. IV, 77, 10)
Gravimetric Analysis

designed by J. C. Chaston and H. W. Webb in 1942; * this is usually 30 mm. square, weighs about 13 g., and is used in conjunction with a cylindrical gauze cathode, Fig. IV, 77, 7, or Fig. IV, 77, 11. Attention is directed to the split cylindrical gauze cathode (Fig. IV, 77, 11), originally designed by C. Winckler in 1899: this form has some advantage over the closed cylinder in that it can easily be bent into shape after minor mishaps.

Some simplification, possibly at the cost of a slight reduction in the efficiency of stirring, may be achieved by the use of an independent glass stirrer; the stationary anode may then be less robust; furthermore, the electrical connexions through the chuck (supporting the anode) are now no longer necessary. The electrodes most widely used with an independent stirrer are shown in Fig. IV, 77, 12, and are a slight modification of those described by A. Fischer in 1907; the cathode, which may also be of the split-cylinder pattern, is provided with two rings to house a glass tube which fits over the anode stem, thereby giving excellent insulation and assisting to locate the stems when employing

a commercial electrolytic apparatus. Two patterns are manufactured to this design in different weights.

In unstirred electrolytes, any of the electrodes described above may be used. It is usual to employ gauze electrodes. When anodic deposits are not required or if the deposits are small (e.g., if the percentage of lead does not exceed 0.2), a small spiral electrode (Fig. IV, 77, 5, f) will suffice as the anode.

A mercury cathode is sometimes employed for special operations. The most important of these is the separation of aluminium from such metals as iron, manganese, chromium, nickel, cobalt, zinc, molybdenum, cadmium, copper, tin, bismuth, and lead, which can, under suitable conditions, be deposited on the mercury. The method is therefore of particular value for the determination of aluminium in steels and alloys.

Four types of mercury cell are shown in Fig. IV, 77, 13. In (a) the platinum wire is sealed into the side of a lipped Pyrex beaker (250 ml.), whilst in (b) the platinum wire is sealed into the side tube, thus permitting the almost complete separation of the aqueous and mercury layers. The platinum terminal is, of course, covered with mercury. Apparatus (c) (A. D. Melaven, 1930) is perhaps the most useful form; the diagram is almost self-explanatory. The electrolysis vessel contains the platinum anode (preferably of the rotating type) immersed in the electrolyte. Electrical contact to the mercury in the levelling-bulb is made through a platinum wire sealed into its side (alternatively, a piece of amalgamated copper wire dipping into mercury contained in a glass tube, into the lower end of which a short platinum wire is sealed, may be used for electrical contact); the mercury acts as cathode. The solution is best stirred mechanically by a stirrer which agitates both the mercury and the solution. When electrolysis is complete,
the levelling-bulb is lowered until the mercury reaches the upper end of the stopcock bore, keeping the circuit closed at all times; the stopcock is then turned through 180° and the electrolyte is collected in a suitable vessel. Apparatus (d) (J. R. Cain, 1911) utilises a slightly modified separatory funnel which permits the facile removal of the electrolyte and washings. Mercury is placed in the cell to within 1 mm. of the top of a small inwardly projecting tube of capillary bore sealed to the stopcock entrance. Electrical contact is made by a platinum wire sealed into the bottom of the funnel. It must be pointed out that in addition to aluminium the following elements are also not removed in a mercury cathode cell: titanium, uranium, tungsten, silicon, phosphorus, the alkaline earths, and the rare earths; the electrolyte is generally sulphuric acid of about 0.1 N concentration, but higher concentrations (up to N) have been used for particular separations.

It is frequently necessary to calculate the current density. For a smooth platinum surface, the estimation of the surface area presents no particular difficulty. As a rough approximation the usual gauze electrode may be regarded as having an effective area twice that of a plain foil electrode of the same dimensions: this applies only if the surface of the foil cathode next to the anode is effective in the deposition. For a closer approximation of the effective area of a gauze electrode, it is probably best to compute the surface area of the wire used in making the gauze. The total length of wire can be calculated from the number of meshes and the dimensions of the electrode. The effective area will then be the total length of the wire multiplied by \( \pi d \), where \( d \) is the diameter of the wire.

C. Electrode vessel. Tall-form beakers, without lip, are generally employed to hold the solution to be electrolysed. These should be of such size that there is the smallest practicable volume of liquid between the cathode and the glass. The apparatus should be so arranged that the beaker can be easily removed without touching any other part of the apparatus, and also so that the electrolyte can be warmed, if necessary. To prevent loss by spraying, split clock-glasses with a central hole (Fig. IV, 77, 14) are used for covering the electrolytic vessel.
A form of electrode vessel, which has been employed for rapid electrolysis is shown in Fig. IV, 77, 15. At the end of the electrolysis the solution may be easily drawn off (and used in other determinations, if desired) and the electrodes washed without interrupting the circuit. The disadvantages are: (i) the vessel cannot be heated easily, and (ii) the liquid just above the tap does not readily mix with the bulk of the solution.

D. Stirring. It has already been pointed out (Section I, 70) that stirring of the electrolytes during electrolysis reduces considerably the time required for deposition. The method commonly employed is to rotate the inner electrode; this is usually made the anode except in lead determinations (as PbO₂), when it is the cathode. Speeds up to 500–1000 r.p.m. are permissible; those usually employed are 300–600 r.p.m. The rotation is generally obtained by drive from an electric motor; a device is always incorporated for varying the speed, for example, an electrical resistance with a D.C. motor, pulleys, gears, etc. Sometimes an independent stirrer is employed, but this is not generally quite so satisfactory as rotating one of the electrodes. Magnetic stirring is occasionally employed (see Fig. IV, 87, 2).

Many of the commercial apparatuses (see footnote in A) have the stirring arrangement incorporated in the main stand. A simple apparatus, utilising Sand's electrodes, is shown in Fig. IV, 77, 16. The inner electrode is attached through a silver or silver-plated chuck and rubber tubing to a pulley shaft so that it can be rotated; electrical connexion is made through mercury contained in the rubber tube. The cathode is separated from the anode by a glass tube surrounding the stem of the latter, and the electrical circuit is completed through the silver-plated clamp holding the stem of the cathode.

E. Use and care of electrodes. Electrodes must be free from grease, otherwise an adherent deposit may not be obtained. For this reason an electrode should never be touched on the deposition surface with the fingers; it should always be handled by the platinum rod or wire attached to the main body of the electrode. Platinum electrodes are easily rendered grease free by heating them to redness in a flame.

Before use electrodes must be carefully cleaned to remove any previous deposits. Deposits of copper, silver, cadmium, mercury, and
many other metals can be removed by immersion in dilute nitric acid (1 : 1), rinsing with water, then boiling with fresh 1 : 1 nitric acid for 5–10 minutes, followed by a final washing with water. Copper may also be removed by means of a solution composed of 20 g. of trichloroacetic acid, 100 ml. of concentrated ammonia solution, and 100 ml. of water. Deposits of lead dioxide are best removed by means of 1 : 1 nitric acid containing a little hydrogen peroxide to reduce the lead to the bivalent form; alcohol or oxalic acid may replace the hydrogen peroxide. In all cases it is recommended that the electrodes be heated to bright redness over the colourless flame of a Bunsen- or Meker-type burner before use.

When the electrolysis is complete, the electrode with its deposit is washed by a stream of water (ca. 100 ml.) from a wash bottle or other supply while in place and with the current still on; this is necessary, since otherwise the electrolyte in contact with the electrode may dissolve some of the deposit. The electrode is then disconnected and rinsed with alcohol * or, better, with pure (e.g., A.R.) acetone (15–20 ml.), and then dried at 100–110°C for 5–10 minutes. In some instances the electrode may be dried by suspending it from a hook clamped to the electrolysis apparatus, and waving a flame below it. The drying should not be prolonged, as there may be some danger of oxidising the metal deposit (e.g., with copper). The electrode with its deposit is weighed after cooling to the laboratory temperature. In a few cases there is evidence that a small transfer of platinum takes place. If this is suspected, the electrode plus deposit should be weighed, the deposit dissolved, the electrode weighed again, and the difference taken. The occurrence of anode corrosion is most simply detected by weighing the anode before and after electrolysis.

The method adopted for the removal of the electrolyte after the electrolysis is complete will naturally depend upon the type of cell that is employed. With a platinum dish or beaker, the electrolyte may be separated by means of the siphon arrangement shown in Fig. IV, 77, 4, b, or by some equivalent device. If the electrolysed solution is not to be preserved for a subsequent determination, a very satisfactory method of washing consists in siphoning the solution out of the electrolysis vessel while maintaining the liquid level in the vessel by adding distilled water; the removal of the electrolyte is shown by the ammeter needle dropping back towards zero. If the beaker rests on a block of wood, the latter may be displaced and the beaker lowered. In the commercial types of apparatus referred to in A, a simple device (e.g., a swivelled support) for lowering the beaker is usually incorporated. If the vessel is of the type shown in Fig. IV, 77, 15, the liquid is simply run out by opening the tap, and the electrode washed.

Electrolysis may be carried out in chloride solutions provided a sufficient amount (1–5 g.) of either a hydrazine or a hydroxylamine salt (usually the hydrochloride) is added as an anodic depolariser. If no depolariser is added to an acidic chloride solution, corrosion of the anode occurs and the dissolved platinum is deposited on the cathode,

* The use of ether after the alcohol washing is not recommended, since ether frequently contains peroxides which may oxidise the metal. If suitable precautions are taken to remove and to prevent the accumulation of peroxides, e.g., by first shaking the ether with potassium permanganate solution or with a weakly acid solution of ferric sulphate followed by a little water, and then storing in a dark place and including a copper spiral below the cork, ether may be employed.
leading to erroneous results and to destruction of the anode. A num-
ber of metals (for example, zinc and bismuth) should not be deposited
on a platinum surface. These metals, particularly zinc, appear to
react with the platinum in some way, for when they are dissolved off
with nitric acid the platinum surface is dulled or blackened. Injury
to the platinum can be prevented in this case by first plating it with
copper, and then depositing the metal on this surface; alternatively, a
silver-gauze electrode (as Fig. IV, 77, 7, a) may be used.

IV, 78. COPPER

Discussion. The general principles of electro-analysis have been discussed
in Sections I, 64-70; these should be mastered before any determinations
are made. Copper may be deposited from either sulphuric or nitric acid
solution, but, usually, a mixture of the two acids is employed. If such a
solution is electrolysed with an e.m.f. of 2-3 volts, the following reactions
occur:

\[
\begin{align*}
\text{Cathode:} & \quad Cu^{++} + 2e^- \rightleftharpoons Cu \\
& \quad 2H^+ + 2e^- \rightleftharpoons H_2 \\
\text{Anode:} & \quad 2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^- 
\end{align*}
\]

The acid concentration of the solution must not be too great, otherwise
the deposition of the copper may be incomplete or the deposit will not adhere
satisfactorily to the cathode. The addition of a drop of 0.1N-hydrochloric
acid helps to produce a bright deposit. The beneficial effect of the nitrate
ion is due to its depolarising action at the cathode:

\[
NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O
\]

The reduction potential of the nitrate ion is lower than the discharge potential
of the hydrogen, and therefore hydrogen is not liberated in the free state.
The nitric acid must be free from nitrous acid, as the nitrite ion hinders
complete deposition and introduces other complications. The nitrous acid
may be removed by boiling the nitric acid before adding it, or by the addition
of urea to the solution:

\[
2HNO_2 + CO(NH_2)_2 = 2N_2 + CO_2 + 3H_2O
\]

Nitrous acid is most efficiently removed by the addition of a little
sulphamic acid:

\[
H_2SO_3 \cdot NH_2 + HNO_2 = N_2 + H_2SO_4 + H_2O
\]

the action is rapid, and the acidity of the electrolyte is unaffected. The
error due to nitrous acid is increased by the presence of a large amount of
iron; iron is reduced by the current to the ferrous state, whereupon the
nitric acid is reduced. This error may be minimised by the proper regula-
tion of the pH and by the addition of ammonium nitrate instead of nitric
acid, or, best, by the removal of the iron prior to the electrolysis.
The solution should be free from the following, which either interfere or
lead to an unsatisfactory deposit: silver, mercury, bismuth, selenium,
tellurium, arsenic, antimony, tin, molybdenum, gold and the platinum
metals, thiocyanate, chloride, oxidising agents such as oxides of nitrogen,
or excessive amounts of ferric nitrate or nitric acid. The electrolytic deposit
should be salmon-pink in colour, silky in texture, and adherent. If it is
dark, the presence of foreign elements and/or oxidation is indicated. Spongy
or coarsely crystalline deposits are likely to yield high results; they arise
from the use of too high current densities or improper acidity and absence
of nitrate ion.
Gravimetric Analysis

Procedure. The solution (100 ml.) may contain 0.2-0.3 g. of Cu (1). Add cautiously 2 ml. of concentrated sulphuric acid, 1 ml. of concentrated nitric acid (free from nitrous acid by boiling or by the addition of a little urea or, better, 0.5 g. of sulphamic acid), 1 drop of 0.1N-hydrochloric acid and transfer to, unless already present in, the electrolysis vessel. For simplicity of description, it will be assumed that the cathode is of the gauze form (Fig. IV, 77, 7, a or Fig. IV, 77, 11) and the anode is either a thick platinum wire spiral (Fig. IV, 77, 5, f) or a gauze cylinder (Fig. IV, 77, 7, b, compare Fig. IV, 77, 12); the student should be able to adapt the procedure easily to other types of electrode if he reads Section IV, 77, carefully. Clean the platinum-gauze cathode by heating it in 1:1 nitric acid, and washing it thoroughly with distilled water. Dry the electrode at 100-110° C., cool in a desiccator, and weigh. Handle the electrode by the stem and not by the gauze, since a trace of grease may cause a non-adherent deposit of copper. Arrange the circuit as shown in Fig. IV, 77, 1, or suitably adapted according to the source of current (if accumulators or storage batteries supplying not more than 12 volts are employed, one large resistance will suffice), but do not connect the source of current (2). Be sure that the cathode is connected to the negative terminal and the anode to the positive terminal. If a rotating anode is to be used subsequently, make certain that it can rotate without coming into contact with the cathode at any point. Place the electrolysis vessel in position (e.g., a beaker resting on a wooden block or upon a stand), and adjust the height so that the electrodes extend nearly to the bottom of the beaker and the cathode is 80-90 per cent immersed in the solution. Cover the electrolysis vessel (beaker) with a split clock-glass (Fig. IV, 77, 14), and with all the resistance in the circuit, so that only a small current will flow, close the circuit, and proceed as A or B, depending upon whether or not stirring is employed.

A. Slow electrolysis, without stirring. With an applied potential of 2-2.5 volts, adjust the resistance until a current of approximately 0.3 amp. flows, as indicated by the ammeter in the circuit; electrolyse, preferably overnight (3). Rinse off the split clock-glasses and test for complete deposition after the blue colour of the solution has disappeared. This is best done by adding more water to raise the level of the electrolyte (say, by 0.5 cm.) and continuing the electrolysis for 30 minutes. If at the end of this time no copper deposit has appeared on the freshly immersed surface of the cathode, it may be assumed that the deposition is complete. If a deposit does form, continue the passage of the current as long as may be judged necessary, and again test as before. If the solution is not to be used for a further estimation, a drop or two may be removed and tested with sodium acetate and hydrogen sulphide water or with potassium ferrocyanide solution.

B. Rapid electrolysis, with stirring. Start the motor driving the anode (or, less satisfactorily, the glass propeller) and adjust its speed (300-800 r.p.m.) so that the solution is vigorously stirred without there being any danger of mechanical loss of liquid. Use a voltage across the terminals of the cell of 3-4 volts, and adjust the resistance so that the current is 2-4 amps. Continue the electrolysis until the blue colour of the solution has entirely disappeared (usually somewhat less than 1 hour), reduce the current to 0.5-1 amp., and test for completeness of deposition by rinsing the split clock-glasses, raising the level of the liquid
by about 0·5 cm. by the addition of distilled water, and continuing the electrolysis for 15–20 minutes. If no copper plates out on the fresh surface of the cathode, electrolysis may be regarded as complete.

When electrolysis has been shown to be complete, the subsequent procedure is the same whether slow or rapid electrolysis has been employed. Two methods may be employed: (i) is used only when the residual electrolyte is not required for further determination, and (ii) is of universal application.

(i) Siphon off the liquid (for example, with a glass siphon provided with a stopcock). Whilst siphoning the heavier liquid from the bottom of the beaker, add water from the top to keep the level of the liquid in the electrolysis vessel nearly constant. Continue this process until the ammeter needle drops practically to zero. Then rinse the cathode with a little pure alcohol or with A.R. acetone (4), and dry it for 5–10 minutes at 100–110° C. Weigh when cold.

(ii) Lower the beaker very slowly, or raise the electrodes, and at the same time direct a continuous stream of distilled water from a wash bottle or supply bottle against the upper edge of the cathode. This washing must be done immediately the cathode is removed out of the solution, and the circuit must not be broken during the process. When the cathode has been thoroughly washed, break the circuit, dip the cathode into a beaker of distilled water, and then rinse it with alcohol or A.R. acetone (4). Dry at 100–110° C. for 5–10 minutes, and weigh when cold.

From the increase in weight of the cathode, calculate the copper content of the solution. After the cathode has been weighed, it should be cleaned with nitric acid as described in Section IV, 77, and re-weighed; the loss in weight will serve as a check.

Notes. 1. Larger quantities of copper may be present, particularly if rapid electrolysis is employed; the quantity given is, however, convenient for instructional purposes. For practice in the determination, the student may prepare the solution either by weighing out accurately about 1 g. of A.R. copper sulphate pentahydrate or by dissolving about 0·25 g., accurately weighed, of A.R. copper in 1 : 1 nitric acid, boiling to remove nitrous fumes, just neutralising with ammonia solution, and then just acidifying with dilute sulphuric acid and diluting to 100 ml.

2. This is, of course, unnecessary if a commercial "electro-analyser" or electrolysis unit is employed (compare Figs. IV, 77, 2–3).

3. If conditions do not allow this practice, use a current of 1·5–3·0 amps.: deposition is usually complete in 2–4 hours. This procedure is, however, less satisfactory if stirring is not employed.

4. This is best effected by completely immersing the cathode in a beaker containing pure alcohol or acetone.

IV, 79.

LEAD

Discussion. Lead is deposited quantitatively as the dioxide at the anode in the presence of a high concentration of nitric acid (10–15 ml. of concentrated acid per 100 ml. of the electrolyte). The addition of 3–4 drops of concentrated sulphuric acid is said to make the deposit more adherent. With a gauze anode of the usual size (Fig. IV, 77, 7, a) about 0·1 g. of lead is the maximum that can be firmly deposited. Sand's electrodes (Fig. IV, 77, 9) permit the deposition of about 0·3 g. With a platinum dish (matted or sand-blasted internal surface) as anode, quantities up to 2 g. may be
readily deposited; this method is therefore frequently employed when large quantities of lead are to be determined in one operation.

It is difficult to remove all the water from the electrode by drying at low temperatures. For a temperature of 120° C., the conversion factor 0.8640, instead of the theoretical conversion factor of 0.8662, is employed. However, by drying at 220° C. for about an hour, the theoretical factor may be employed for quantities up to 0.1 g. For quantities of 0.1-0.3 g., the factor 0.8650 has been recommended, whilst for larger weights 0.8635 has been suggested (L. Classen, 1927). A useful method is to dissolve the dioxide, without drying, in standard oxalic acid solution, and to titrate the excess acid with standard potassium permanganate solution.

The following interfere in this determination: mercury, arsenic, antimony, tin, selenium, tellurium, phosphorus, chromium, chloride, iodide, silver, bismuth, and manganese (the last three metals tend to form peroxides at the anode).

Procedure. For a platinum-gauze electrode (Fig. IV, 77, 7, a), the solution (100 ml.) should contain not more than 0.1 g. of Pb as lead nitrate, 15 ml. of concentrated nitric acid (free from nitrous acid), and none of the interfering elements mentioned above. Somewhat greater quantities may be deposited with the aid of Sand’s electrodes (Figs. IV, 77, 8, and IV, 77, 9). Larger quantities of lead may be determined, as already pointed out, with a platinum (Classen) dish. The present details apply, however, chiefly to the gauze electrode, but can be readily adapted to the use of a platinum dish.

Heat the anode to 120° C. in an electric oven for 1 hour, allow to cool in a desiccator, and weigh. Connect the positive terminal of the source of current to the gauze anode or platinum dish, and the negative terminal to the wire or gauze cathode (1). Adjust the current to 0.05-0.1 amp. at 2 volts with the aid of the rheostat, and allow the electrolysis to proceed overnight. Test for completeness of deposition by adding about 20 ml. of distilled water and continuing the electrolysis for 15 minutes; if no darkening of the freshly covered anode surface occurs, deposition is complete. When the electrolysis is complete, either lower the beaker from the electrodes or slowly raise the electrodes out of the solution without interrupting the current, and at the same time rinse the electrodes very thoroughly with a jet of water from a wash-bottle. Then disconnect the source of current, wash the anode with alcohol or acetone, and dry at 120° C.; cool in a desiccator and weigh.

The determination may be carried out more rapidly by one of the following methods. In these the outer electrode is the anode.

(i) With a current of 1.5-2.0 amps. at 2 volts at the ordinary temperature. Electrolysis is complete in about 1-5 hours.

(ii) With 2 volts and an initial current of 0.5 amp., which is subsequently raised to 5 amps. 0.1 Gram of lead dioxide may be deposited in 6-8 minutes at room temperature; this time is still further reduced by working at about 60° C.

(iii) By the use of Sand’s electrodes (Fig. IV, 77, 9) 0.3 g. of lead may be deposited in about 10 minutes from a solution (total volume 85-100 ml.) containing 10 ml. of concentrated nitric acid by electrolysis at 90-95° C., with a current of 5 amps. Under these conditions electric endosmosis expels most of the water from the deposit, and it may be dried by dipping into alcohol or acetone in the ordinary way.
The deposited dioxide is removed from the electrode, after weighing as above, by immersion in warm 1:1 nitric acid to which a little pure hydrogen peroxide has been added. As an additional check the solution may be evaporated with sulphuric acid, and the lead determined as sulphate (Section IV, 14A).

Note. 1. Full experimental details of the general technique are given under Copper (Section IV, 78), and will therefore not be repeated in the description of this and the succeeding determinations.

IV, 80. CADMIUM

Discussion. Cadmium is best determined from a faintly alkaline solution containing only enough potassium cyanide to keep the cadmium in solution, i.e., containing the complex $K_2[\text{Cd(CN)}_4]$ (Procedure A). Less accurate results, but sufficiently precise for most routine analyses, may be obtained in very dilute sulphuric acid solution (Procedure B). Deposition may also be made from a hydrochloric acid solution in the presence of hydroxylamine hydrochloride, which acts as an anodic depolariser (Procedure C).

Procedure A. The solution should contain about 0.4 g. of Cd as the sulphate, acetate, or, less desirably, the nitrate. Add a drop of phenolphthalein, followed by ca. 0.1N-sodium or potassium hydroxide until a permanent pink colour is just obtained. Then add a solution of pure (e.g., A.R.) potassium or sodium cyanide dropwise and with constant stirring until the precipitated cadmium hydroxide just dissolves. A large excess of alkali cyanide should be avoided. Dilute to 100–150 ml., and electrolyse the cold solution, preferably with a platinum-gauze cathode, and a current of 0.5–0.7 amp. at 4.8–5.0 volts (1). At the end of 6 hours, increase the current to 1.0–1.2 amp., and continue the electrolysis for another hour. Wash the split clock-glass and the sides of the beaker with about 20 ml. of water, and continue the electrolysis for 15 minutes. If the newly exposed surface of the cathode remains bright, thus indicating that the deposition of the cadmium is complete (2), remove the electrolyte from the electrodes, rinse immediately with water, stop the current, and rinse the cathode with alcohol or A.R. acetone. Dry at 100°C, cool, and weigh. Test the residual electrolyte for cadmium by any of the recognised tests.

The determination may be carried out more rapidly by using a rotating cathode (600–800 r.p.m.) with a current of 1.5–2.0 amps. at 2.7–3.0 volts. 0.2 Gram of Cd may thus be deposited in 30 minutes.

Procedure B. The cadmium should be present in the solution (100 ml.) as sulphate; nitrates and chlorides must be absent. The maximum concentration of free sulphuric acid is 0.5N, and 5 g. of potassium hydrogen sulphate is added. Electrolyse at room temperature with 0.1–0.2 amp. at 2.4–2.8 volts; after 3 hours increase to 0.5 amp. until electrolysis is complete. 0.3 Gram of Cd is thus deposited in 3–4 hours. Alternatively, use a rotating electrode with 1.5–1.7 amps. at 2.7 volts. 0.2 Gram of Cd may thus be deposited in 20 minutes.

Procedure C. The cadmium (up to 0.3 g.) should be present in the solution (200 ml.) as chloride. Add 2 g. of hydroxylamine hydrochloride, acidify slightly with hydrochloric acid, and electrolyse at the laboratory temperature, using a current of about 1 amp.
Notes. 1. If left overnight, use a current of 0.2–0.3 amp. at 2.8–3.2 volts.
   2. It is sometimes difficult to detect the deposition of the bright cadmium on the platinum surface. This difficulty is readily overcome by heavily plating the platinum electrode with copper or silver first and then proceeding with the electrolysis in the usual manner. An added advantage is that the removal of the cadmium after the electrolysis is rendered more facile; also, if the temperature of drying should accidentally exceed 100° C., there is little danger of harming the platinum electrode.

IV, 81.  

Nickel  

Discussion. The most satisfactory method for the determination of nickel by electrolysis is from strongly ammoniacal solution containing ammonium sulphate. The nickel is present largely as the complex ion:

\[
[Ni(NH_3)_6]^{2+} \rightleftharpoons Ni^{2+} + 6NH_3
\]

and is deposited as a dense, adherent layer, bright silver-grey in colour, upon the cathode. The nickel should be present preferably as the sulphate, but the chloride may also be employed; the nitrate introduces difficulties, and should be absent. The metals of the hydrogen sulphide group, zinc, vanadium, tungsten, molybdenum, chromates, and ferrous salts should be absent; cobalt is deposited with the nickel. Small amounts of the precipitated hydroxides, such as that of iron, are not occluded by the deposit to any appreciable extent; as a general rule, however, they are best removed first. The electrolysis should not be unduly prolonged, because there is a slight tendency towards solution of the anode, with subsequent deposition of platinum upon the cathode.

Procedure. The solution should contain not more than about 0.2 g. of Ni as sulphate or chloride. Add 5–10 g. of ammonium sulphate, 30–40 ml. of concentrated ammonia solution, and dilute to 150 ml. Electrolyse, using 1 amp. at 3–4 volts; about 0.15 g. of Ni is deposited in 2 hours (1). Test for completeness of precipitation in the usual way by adding about 20 ml. of water, and continuing the electrolysis for 15–20 minutes; no nickel should be deposited on the freshly immersed surface (2). Alternatively, the dimethylglyoxime test, suitably modified, may be applied. Wash, dry, and weigh the cathode as in the estimation of Copper (Section IV, 78).

The determination may be carried out more rapidly by using a rotating electrode with 4 amps. at 3–4 volts; 0.1 gram of nickel is thus deposited in about 10 minutes.

The nickel is best removed from the electrode by means of dilute nitric or sulphuric acid; concentrated nitric acid should not be employed because of the danger of inducing passivity. If difficulty is experienced in stripping the nickel from the platinum cathode, anodic solution of the metal in warm dilute nitric acid may be employed.

Notes. 1. With a current of 0.2–0.3 amp., the deposition is generally complete in 12–15 hours. This current is used if the electrolysis can be allowed to proceed overnight.
   2. This test is not always satisfactory, for deposits of nickel are sometimes obtained which can hardly be distinguished from the platinum of the electrode (compare Cadmium, Section IV, 80, Note 2).
IV, 82. COBALT

Discussion. The determination of cobalt follows along the same lines as given under Nickel (Section IV, 81). The addition of a little hydrazine sulphate improves the character of the cathode plate by reducing the tendency to form an oxide deposit at the anode.

IV, 83. SILVER

Discussion. Silver may be determined by electrolysis in nitrate, ammoniacal, or cyanide solutions. In cyanide solution the silver is present largely as the complex ion:

\[ [\text{Ag(CN)}_2]^\text{-} \rightleftharpoons \text{Ag}^+ + 2\text{CN}^- \]

an excellent plate is obtained, and separation from other elements (e.g., copper and lead) may be effected. The cyanide method will be described.

The disadvantage of the electrolytic method is that so many other elements are also deposited, either wholly or in part, that a number of preliminary separations are usually required before it can be applied. For this reason, it is not widely employed.

Procedure. The silver (ca. 0·2 g.) should be present in solution as the nitrate. Add pure (e.g., A.R.) potassium cyanide until the precipitate of silver cyanide is dissolved, and then add an excess such that about 2 g. of potassium cyanide is present in the solution. Dilute to 100–120 ml. Electrolyse with 0·2–0·5 amp. at 3·7–4·8 volts at 20–30° C.; about 0·1 g. of Ag is deposited in 3 hours. Alternatively, electrolyse with a rotating electrode with 0·5–1·0 amp. at 2·5–3·2 volts; 0·2 g. of Ag is deposited in 20–25 minutes. Completeness of deposition is tested for by transferring a few drops of the electrolyte to a test-tube, acidifying with a little nitric acid, boiling off the hydrocyanic acid (caution: poisonous), rendering ammoniacal, and adding a few drops of ammonium sulphide solution; no brown precipitate should be obtained. The determination is completed as under Copper (Section IV, 78).

Note. If insoluble silver salts are to be analysed, e.g., chloride, bromide, iodide, and oxalate, these may be dissolved directly in the potassium cyanide solution.

IV, 84. ZINC

Discussion. Zinc is quantitatively deposited from an alkaline zincate solution containing excess of alkali. The proportion of alkali is not of great importance, provided that it exceeds a minimum of 10 molecules of alkali hydroxide to 1 molecule of zinc salt: it is unnecessary to employ a larger excess of alkali than is required to keep the solution clear during the whole of the electrolysis. Ammonium salts, if present, must be decomposed by the addition of excess of caustic alkali and boiling. Chlorides and nitrates interfere; they must be removed, if present, by evaporation to fuming with sulphuric acid.

Zinc should not be directly deposited on a platinum surface, as it is difficult to remove it completely (it tends to leave black stains), and upon heating may alloy with the noble metal. The platinum electrode should be plated
with copper or, preferably, with silver. Alternatively, a silver-gauze cathode (as Fig. IV, 77, 7, e) may be used. Cathodes of nickel have also been used, and are quite satisfactory.

A useful application of the electrolytic method is in the analysis of alloys containing aluminium and zinc.

**Procedure.** For practice in this method, weigh out accurately about 0.3 g. of A.R. zinc oxide, dissolve it in the minimum volume of dilute sulphuric acid, add a concentrated solution of 7 g. of A.R. sodium hydroxide in water, stir until the solution is clear, dilute to 125 ml., and electrolyse, using a copper- or silver-plated platinum cathode or a silver cathode. For slow electrolysis, use a current of 0.4–0.8 amp. at 3.8–4.2 volts. For rapid electrolysis (rotating electrode), the current may be increased up to 5 amps. The metal is more rapidly deposited at about 60° C. When electrolysis is complete, remove the solution without interrupting the current, wash thoroughly with water, then with alcohol or acetone, dry at 60–70° C., and weigh. Calculate the percentage of Zn in the sample.

**IV, 85. BISMUTH**

**Discussion.** The most satisfactory results are obtained by the use of controlled potential at the cathode (see Sections IV, 87–88). In chloride solution, oxalic acid is added as a solvent for the oxychloride and basic salts, and hydrazine hydrochloride is introduced as a depolariser and also to prevent the formation of bismuth pentoxide at the anode. The deposition from sulphate solution takes place in the presence of a high concentration of sulphuric acid, a hydrazine salt, and at elevated temperatures.

**Procedure. From Chloride Solution.** For practice in this determination, use a solution prepared by dissolving 0.2–0.25 g. of pure bismuth in 10 ml. of concentrated hydrochloric acid containing a small amount of nitric acid. Add 5 g. of oxalic acid, 0.5 g. of hydrazine hydrochloride, and dilute to 100 ml. Use Sand’s electrodes (Figs. IV, 77, 8–9) and carry out the determination at 80–85° C. Regulate the current to give a cathode-saturated calomel electrode potential of −0.15 to −0.17 volt. When the current has fallen to a very small value, adjust the cathode potential in steps of 0.02 volt to −0.25 to −0.30 volt. The determination is complete in 15–20 minutes.

**From Sulphate Solution.** A solution for practice in the determination may be prepared by dissolving the metal (0.15–0.25 g.) in concentrated sulphuric acid, if necessary by the addition of one-tenth of the volume of concentrated nitric acid. Cool the solution and dilute with water so that the resulting test solution, volume about 100 ml., contains 20–25 ml. of concentrated sulphuric acid. Add 1 g. of hydrazine sulphate as depolariser. Heat the solution to 100° C. and electrolyse, using an initial cathode potential to the saturated calomel electrode of −0.055 volt. When the current has fallen to a small value, adjust the cathode potential in three steps to −0.15 volt. Discontinue the electrolysis when the current has fallen to almost zero at −0.15 volt. The determination is complete in 10–30 minutes.

It has been stated that electro-deposited bismuth tends to alloy with platinum; it is therefore advisable to protect the cathode by plating it with silver from a cyanide solution.
IV, 86. Electrolytic separation and determination of copper and nickel.—

Discussion. This determination has been included at this stage in order to indicate the use of the electrolytic method in the separation and determination of metals in simple alloys. More complex alloys require the application of methods utilising controlled potential at the cathode; examples of such separations will be found in Section IV, 89. The theory of simple separations is discussed in Section I, 69. There are a number of alloys, which include Monel metal, certain coinage alloys (e.g., American), and “cupro-nickel,” which are composed principally of copper and nickel, together with small amounts of iron and manganese and not more than traces of other elements. These are suitable for practice in electrolytic separation.

The copper is determined in strongly acid solution at a potential not exceeding 4 volts (above this potential nickel may plate out). The solution is evaporated to fuming in order to remove excess of nitric acid, the iron present is precipitated with ammonia solution, and the nickel deposited from the filtrate after the addition of a large excess of ammonia solution.

The separation of lead and copper by electrolysis is described in Section IV, 91 (analysis of brass).

Silver and copper in silver-copper alloys (silver solder, sterling silver, and certain coinage alloys) may be separated and determined electrolytically by dissolving the sample in 1:1 or 1:2 nitric acid, removing the excess of nitric acid by evaporation, and then estimating the silver after the addition of excess of pure potassium cyanide at a voltage not exceeding 1.5 (Section IV, 83). The residual solution is acidified with nitric acid, the hydrocyanic acid boiled off, and the copper deposited as detailed in Section IV, 78. Alternatively, the silver may be deposited from ammoniacal solution (5 ml. of free concentrated ammonia solution per 100 ml. of solution). Most of the silver is deposited with a current of 0.4 amp., a little hydrogen peroxide is added to oxidise cuprous salts and to re-dissolve any particles of silver not plated on the electrodes, and the deposition completed at 0.2 amp. It is essential that the solution be vigorously stirred during the whole of the estimation. The copper is determined in the residual electrolyte after acidifying with nitric acid and diluting.

Procedure (analysis of a copper-nickel alloy). Weigh out accurately about 0.5 g. of the clean alloy (1) into a 150-ml. beaker, which should be suitable as an electrolytic vessel. Add a mixture of 10 ml. of water, 1 ml. of concentrated sulphuric acid, and 2 ml. of concentrated nitric acid to dissolve the alloy. When solution is complete, boil off the oxides of nitrogen, and dilute to 100 ml. The solution is now ready for the deposition of copper.

Copper. Proceed as directed in Section IV, 78, and employ either the slow or rapid method of electrolysis. Wash the copper deposit thoroughly with water, and keep the solution for the estimation of iron and nickel.

Iron. Evaporate the solution and washings from which the copper has been removed on a low-temperature hot-plate as far as possible, and then heat at a higher temperature until fumes of sulphur trioxide appear. Cool the residue, and carefully add water until the volume is about 25 ml. Precipitate the small quantity of iron that is now present in the ferric state by adding to the warm solution about 10 ml. of 1:1 ammonia solution in excess. Filter through a small quantitative filter-paper, and collect the filtrate in a 150-ml. electrolytic beaker (A). Wash the precipitate three times with water. Place the original
beaker under the filter; dissolve the precipitate in a little hot 1:5 sulphuric acid and wash the paper with water. Precipitate the iron again with the same large excess of 1:1 ammonia solution, and filter through the same paper. Wash the precipitate, and collect the filtrate and washings in beaker (A) containing the filtrate and washings from the first precipitation. Ignite the ferric hydroxide to ferric oxide, and weigh it (Section IV, 8).

Alternatively (since the weight of ferric hydroxide is small), the washed precipitate may be dissolved in dilute hydrochloric acid and the iron determined colorimetrically (Section V, 13).

Nickel. Add 15 ml. of concentrated ammonia solution to the ammoniacal nickel solution, and dilute to 100-120 ml. Carry out the determination as detailed in Section IV, 81.

Calculate the percentage of copper, iron, and nickel in the alloy.

Note. 1. Either Ridsdale's "Cupro-Nickel, No. 19" (one of the Analysed Samples for Students) or the Bureau of Analysed Samples "Cupro-Nickel No. 180A" (one of the British Chemical standards) is suitable for this estimation.

DEPOSITIONS WITH CONTROLLED POTENTIAL AT THE CATHODE

IV, 87. General considerations.—The theory of electro-analysis employing controlled potential at the cathode is given in Section I, 71.

![Diagram](image_url)

Fig. IV, 87, 1.

A simple manual apparatus is also shown diagrammatically in Fig. I, 71, 1. In practice, the source of current may be a car (or other large-
capacity) battery or a D.C. output unit (Fig. IV, 88, 2); $V$ is preferably a valve voltmeter (Fig. IV, 88, 6), although a potentiometer or a high-resistance voltmeter may be used; $A$ is a multi-range ammeter (0-0.1, 0-1.0, and 0-10 amps.); $P$ is a voltmeter (0-10 volts); and $R$ is an adjustable resistance capable of carrying up to 15 amps. The saturated calomel (or other reference) electrode, also termed the auxiliary electrode, may conveniently be of the form shown in Fig. IV, 87, 1 (Lindsey and Sand, 1934), and is supported in the special stand $S$. The electrode vessel is sealed to a glass stem 15-18 cm. in length, into the bottom of which the connecting terminal is cemented. The reservoir funnel $R$, which is placed on the top of a side tube of about 6 mm. diameter sealed about one third-way up the body of the electrode vessel, is attached to an arm of 4 mm. bore, which has bends at $B$ and $C$ of the shape indicated. The purpose of these bends is to prevent the test solution from mixing with that in the auxiliary electrode, the double bend $B$ being kept mainly outside the test solution, whereas the single bend $C$ is inside it. The stand $S$ enables the electrode to be held securely, but is also adjustable to any position in the electrolysis vessel.

The sliding resistance $R$ (Fig. I, 71, 1) may be replaced by a manually controlled Variac; by its aid the cathode potential may be maintained at any desired value as read on the valve voltmeter. Full experimental details are given in the following section. In principle, the Variac is employed to control the input potential of a step-down transformer, which in turn provides the input potential to a selenium rectifier.

The electrolysis cell may incorporate platinum-gauze electrodes (see Fig. I, 71, 1, and Section IV, 77B) and the auxiliary electrode may be of the type shown in Fig. IV, 87, 1; the tip of the reference electrode should be adjusted outside the cathode, as close to it as possible and near its middle. Alternatively, the electrodes may be stationary (compare Fig. IV, 77, 12), and provision is made for efficient stirring either by a motor-driven stirrer or by a magnetic stirrer as in Fig. IV, 87, 2. The magnetic stirrer includes a soft-iron bar sealed in a tube, which is caused to rotate at high speed by a rotating magnet placed beneath the beaker.

It will assist the student in obtaining a further insight into the underlying principles of controlled potential electro-analysis if the reversible cathode potential at an electrode in contact with a solution of one of its ions at 25°C be considered:

$$E_{\text{cathode}} = E^\circ + \frac{0.0591}{n} \log [M^{n+}]$$  (Sections I, 48, and I, 66.)

where $E^\circ$ is the standard reduction potential of the metal $M$. For copper, $E^\circ = +0.345$ volt. If a copper electrode is immersed in solu-

Gravimetric Analysis

529

tions of copper ions of concentrations 1 M, 0.01 M, 0.001 M, and 0.0001 M respectively, the corresponding electrode potentials (on the hydrogen scale) are:

\[ E_{Cu} = +0.345 + \frac{0.0591}{2} \log 1 = +0.345 \text{ volt} \]
\[ E_{Cu} = +0.345 + \frac{0.0591}{2} \log 10^{-2} = +0.286 \text{ volt} \]
\[ E_{Cu} = +0.345 + \frac{0.0591}{2} \log 10^{-3} = +0.256 \text{ volt} \]
\[ E_{Cu} = +0.345 + \frac{0.0591}{2} \log 10^{-4} = +0.227 \text{ volt} \]

When referred to the saturated calomel electrode \( (E^0 = +0.246 \text{ volt}) \), the values are +0.099, +0.040, +0.010, and -0.019 volt respectively. It is clear that for every ten-fold decrease in the concentration of a univalent metal ion, the cathode potential becomes +0.0591/1 volt more negative; similarly, for a bivalent ion 0.0591/2 = 0.0295 volt more negative, and for a trivalent ion 0.0591/3 = 0.0197 volt more negative. Neglecting for the moment the overvoltage at the cathode, we have here a means of following the change in the concentration of the metal ion during the electrolysis and, by controlling the potential, of separating one metal from another lying somewhat higher in the electromotive series. In order to prevent the cathode potential from exceeding a predetermined value it is simply necessary to decrease the potential applied to the cathode and anode by suitable means. If an accuracy of 0.1 per cent (1 part in 10^3) suffices for the analysis, the applied potential must be decreased by 3 \times 0.039 = 0.177, 3 \times 0.0295 = 0.088, and 3 \times 0.0197 = 0.059 volt for univalent, bivalent, and trivalent ions respectively during the analysis.

The optimum potential for a particular electrolysis cannot be calculated with any precision from theoretical principles because of the variable nature of the overvoltage at the cathode; this value is usually small, but it must be pointed out that the overvoltage depends upon the rate of stirring, the current, and the nature of the metal surface. If the electrode reaction is reversible or nearly so, the potential may be computed approximately from the Nernst equation; the overvoltage must be added to this figure. The limiting potential is usually determined more or less empirically. The most trustworthy procedure is to determine experimentally the current–cathode potential curve under exactly the same conditions as will prevail in the proposed estimation. The optimum conditions for controlled potential with the mercury cathode can be deduced from polarograms obtained with the dropping-mercury cathode; the optimum potential range corresponds to the diffusion-current plateau in the polarogram (compare Chapter VIII). In order to separate or separately determine two elements by the controlled-potential technique, their reduction potentials must differ by at least 0.15–0.20 volt, and a somewhat larger difference may be necessary in unfavourable instances.

When the potential of the cathode is controlled during electrolytic depositions, the auxiliary electrode is usually connected to the positive and the cathode to the negative terminal of the valve voltmeter or high-resistance voltmeter. After the stirring motor has been switched
on, the current is adjusted to a suitable value and the cathode-S.C.E. (or auxiliary electrode) potential is read on the voltmeter. The voltage is prevented from exceeding this value by adjusting the slider on the large (current) rheostat (Fig. I, 71, 1) or by manipulating the Variac. When the current has fallen to about 0·2 amp., Sand (1940), utilising a relatively simple apparatus, recommends that the current be increased until the voltmeter registers an increase of 0·05 volt; the voltmeter reading at this value is again maintained constant by adjustment of the current until the latter has fallen to the previous lowest value. Two more increases of 0·05 volt are usually made, the last voltage being maintained for 3–5 minutes.

Alternatively, using a stirring speed of 600–800 r.p.m., the current is turned on and the variable resistance or Variac is adjusted until a current of 2–4 amps. is obtained. When the cathode-saturated calomel-cell voltage attains the limiting value as indicated by the valve voltmeter, the external resistance is increased or the Variac setting is decreased sufficiently to maintain the limiting cathode potential. Meanwhile the appropriate range of the multi-range ammeter is brought into circuit. The electrolysis is discontinued when the current has been reduced to 20–30 mA. Under these experimental conditions a copper determination, for example, may be completed in 10–15 minutes.

For the separation by controlled potential of metals, such as silver, which are more noble than, say, bismuth, it would be necessary to reverse the connexions to the valve voltmeter, and as the metal is removed, the readings would clearly decrease instead of increasing; a reversing switch is therefore desirable in the voltmeter circuit.

Finally, attention is directed to the fact that washing and disconnection, when working with controlled potential, are carried out as already detailed for simple depositions (Section IV, 77E). The motor should not be stopped before the electrodes are outside the electrolyte, and the current should not be turned off until the cathode has been removed.

IV, 88. Controlled potential electro-analysis. Apparatus for automatic control of cathode potential.—The apparatus enables one to maintain a constant potential at the cathode at a definite predetermined value during electro-analysis. The range of D.C. potential available is 0–1·8 volts when a 2-volt accumulator is employed with the potentiometer, but it may be extended, if desired, to 3·6 volts by using two 2-volt accumulators in series. The potentiometer is standardised against the standard Weston cell with the aid of the built-in valve voltmeter. The current used in the electrolytic cell may vary from a few milliamperes to 10 amps; under normal working conditions the maximum current will not generally exceed 2–4 amperes. The potential difference between the cathode and a reference electrode (usually a saturated calomel half-cell) may be set to about a millivolt and maintained at this value automatically. This sensitivity is somewhat higher than is usually necessary for most applications of controlled-potential electro-analysis: a variation of ± 0·01 volt is generally permissible.

A diagrammatic representation of the set-up of the whole apparatus is shown in Fig. IV, 88, 1. The operation of the instrument depends on *This apparatus was designed and built by J. F. Palmer with the assistance of C. Wadsworth under the general direction of the author.
upon the detection of a D.C. "error voltage" between a fixed cell (potentiometer, Fig. IV, 88, 7) and the controlled cell (cathode of the electro-deposition cell and saturated calomel reference electrode). This "error voltage" is impressed between the vibrating "reed" of a polarised relay (Fig. IV, 88, 5) and the centre tap of a mu-metal step-up transformer, the two fixed contacts of the relay being connected to each end of the primary winding of the transformer. The secondary winding is connected to the input of a three-stage, resistance-capacity-coupled voltage amplifier. The output of this amplifier is fed to the paralleled grids of two 6SN7 valves, the plates (anodes) of which are connected directly to the secondary of the centre-tapped mains power transformer (Fig. IV, 88, 5). The valves therefore act as phase-discriminating power amplifiers: the phase relationship between the amplified pulse and the voltage of the secondary winding produces a rectified impulse in the motor winding $L_2$ (Fig. IV, 88, 3). The phase relationship between this amplified pulse and its counterpart through

the secondary winding $L_2$ determines the direction of rotation of the motor.

The geared-down reversible induction motor (Fig. IV, 88, 3) is coupled to the 6-amp.-capacity Variac controlling the A.C. input to the electrolysis unit. When a D.C. "error voltage" is present, the motor (which controls the variable arm of the Variac) will slowly rotate and thus alter the potential difference between the anode and cathode until the "error input" is reduced to zero, at which point the motor will cease to rotate. Thus by varying the potential difference between the anode and cathode, the potential of the cathode relative to the saturated calomel reference electrode is maintained at a constant value.

The apparatus, excluding the electro-deposition cell and associated electrodes, is composed of seven units.

1. A D.C. output unit, working from the A.C. mains, to supply the necessary current at low voltage to the electro-deposition cell.
2. A motor-driven Variac to control the A.C. input to the D.C. output unit.
3. A valve-amplifier unit, operating on a minimum stimulus of 1 mV. D.C. to the polarised relay, which is connected to the reversible motor controlling the Variac.
4. A valve voltmeter for calibrating the potentiometer and for measuring the cathode-reference cell potential.

Fig. IV, 88, 1.
5. A potentiometer, which may be set to the algebraic sum of the desired potential drop between the cathode and the potential of the reference electrode, or it may be set to any other predetermined value. This unit incorporates the Weston cell required for the standardisation of the valve voltmeter, which is in turn employed in the calibration of the potentiometer.

6. A high-tension power pack for the amplifier (3).

7. A high-tension power pack for the valve voltmeter (4). [In practice, the instrument has been so designed that 6 and 7 are identical.]

1. D.C. output unit. The direct current required for the electrolysis is obtained from the A.C. mains by the use of a step-down transformer $T_1$ (10 amps., 15 volts), a selenium bridge rectifier $SE$, and a smoothing filter circuit. Voltages of 3, 6, 9, 12, and 15 volts may be drawn from the transformer secondary by setting the switch $S_1$. The bridge rectifier can handle up to 20 volts, and the switch $S_1$ ensures that there is an adequate margin with due regard to the maximum possible input from the Variac.

The rectifier $SE$ (Fig. IV, 88, 2) is followed by an inductance capacity smoothing filter, consisting of a 3,000-$\mu$fd., 24-volt, paper condenser $C_1$, a 40-milli-henry choke $L_1$, and a 9,000-$\mu$fd., 24-volt, condenser $C_2$ (the latter was obtained by wiring three 3000-$\mu$fd. condensers in parallel). $M_2$ is a triple-range ammeter (0–0.1, 0–1.0, and 0–10 amps.), and $M_1$ is a triple-range voltmeter (0–1.0, 0–5.0, and 0–20.0 volts); these indicate the electro-deposition current and voltage respectively. [The low-tension unit is fed from the socket $P_2$ on the Variac unit.]

2. Variac unit. The mains input to the low-voltage unit (Fig. IV, 88, 2) is controlled by a Variac, the variable arm of which is attached to a geared-down, reversible, two-phase, four-pole induction motor $L_2$ and $L_3$ (Fig. IV, 88, 3). The motor (5 ft.lb. torque per 1 r.p.m.) is geared down to rotate at 1 r.p.m. Provision is made in this unit for control of the motor either manually or by the amplifier (3). With the double-pole change-over switch $S_6$ in the position shown in the figure and the six-pin plug from the amplifier connected, the motor $M$ will be controlled by the amplifier. With switch $S_6$ in the alternative position and the two-way manual motor direction control unit (Fig. IV, 88, 4) plugged in at $P_1$ in lieu of the six-pin plug from the amplifier, the Variac may be set manually. The safety switches $S_6$ and $S_7$ are fitted to the Variac unit in order to prevent the moving contact arm of the Variac rotating too far and thus damaging the carbon brush. If
the automatic control, for some reason or another, does not operate correctly and, in consequence, either of the safety switches $S_6$ or $S_7$ are brought into action, the motor will cease to function. To bring the moving arm of the Variac back to its normal working range, it will then be necessary to connect temporarily the manual unit (Fig. IV, 88, 4).

With correct working of the instrument, the over-running of the moving arm of the Variac should not occur.

The possibilities should be borne in mind that if the anode becomes disconnected during an experiment or if the switch $S_1$ on the transformer (Fig. IV, 88, 2) be set at too low a value initially, either of the safety switches may come into operation. Switch $S_6$ (Fig. IV, 88, 3) disconnects the windings when the motor is idle between determinations, and thus prevents overheating of its windings.

The A.C. output of the Variac is brought out to a socket $P_2$; the

latter is connected to the A.C. input of the low-tension unit (Fig. IV, 88, 2). The rotation of the motor in either direction will be indicated by the movement of the needle of the voltmeter $M_5$.

3. Valve-amplifier unit. The amplifier (Fig. IV, 88, 5) is fed from a polarised relay, vibrating at 50 cycles per second, through a mu-metal transformer $T_2$. The energising current for the relay is derived from a 20-volt winding on the transformer $T_3$, and is controlled by the variable resistance $V_1$, which is set at the minimum required for regular satisfactory operation. The D.C. "error voltage" between the fixed cell (potentiometer, Fig. IV, 88, 7) and the controlled cell (cathode of electrolysis cell and reference electrode) is impressed between the vibrating reed of the polarised relay and the centre tap of a mu-metal step-up transformer $T_2$. 

---

**Gravimetric Analysis** 533

---

![Figure IV, 88, 3.]

![Figure IV, 88, 4.]

![Figure IV, 88, 5.]
The amplifier itself incorporates two stages of resistance-capacity-coupled amplification wired in cascade employing a 6SL7, followed by another r.c.c. stage using a 6SL7 strapped as a single valve. A potentiometer $V_2$ is connected in the grid circuit of the final 6SL7, and this serves as a sensitivity control for the amplifier and can be used to eliminate "hunting" caused by over-sensitivity. At the maximum setting of this control, rotation of the motor will occur with a D.C. "error input" (or "error voltage") of less than one-half of a millivolt.*

The output of the voltage amplifier is fed to the paralleled grids of the two 6SN7 valves acting as phase-discriminating amplifiers (since their plates are connected directly to the secondary of the centre-tapped transformer) and thus control the direction of rotation of the motor through $L_2$ (Fig. IV, 88, 3). The condenser $C_5$ is connected in parallel with condenser $C_4$ (Fig. IV, 88, 3) when the amplifier unit is plugged into the Variac unit: this condenser increases the torque of the motor to a satisfactory value when it is under automatic control.

4. Valve voltmeter. The circuit (Fig. IV, 88, 6) is of the Wheatstone-bridge type: two arms consist of two equal resistances $R_{13}$ and $R_{14}$ of 20,000 ohms each, whilst the other two arms are formed by the internal resistances of two EF39 valves, which should possess similar characteristics. The control grid of one of the valves is earthed. The voltage to be measured is applied to the control grid of the other valve: this causes an unbalance in the circuit which is indicated on the meter $M_5$, the deflection being linear to well within 1 per cent. If greater accuracy is required, a calibration curve must be prepared. The initial balancing of the bridge circuit (i.e., bringing the meter deflection to zero) is

* This sensitivity refers to an input resistance of 100 ohms (i.e., that of the auxiliary, e.g., saturated calomel, electrode); it will be somewhat less for a higher input resistance, but can easily be restored (if required) to a value of at least one millivolt by the insertion of another stage of amplification in the circuit of Fig. IV, 88, 5.
Gravimetric Analysis

controlled by the 2,300 ohms potentiometer $V_3$. If it is found that the potentiometer cannot reduce the deflection to zero (due to differences in the two EF39 valves), a small fixed resistance of about 100 ohms, placed in one of the cathode leads, will enable the zeroing to be carried out. Alternatively, one or both of the EF39 valves should be replaced. The smooth action of the control will be adversely affected if the resistance of $V_3$ is increased.

The sensitivity of the valve voltmeter is controlled by a two-gang potentiometer $(V_4 + V_6)$, each section being of approximately 7,000 ohms resistance. Fine adjustment is provided by the potentiometer $V_6$ (22,000 ohms). The fixed resistance $R_{15}$ and the condenser $C_{12}$ serve to filter out any alternating current in the input voltage.

The selector switch $S_{12}$ permits the use of any of the four ranges (0–0.5, 0–1.0, 0–2.5, and 0–5.0 volts), the upper three ranges being pre-set by the potentiometers $V_{A}$, $V_{B}$, and $V_{C}$; the lowest range is controlled by the sensitivity controls $V_4 + V_5$ (coarse) and $V_6$ (fine). A chain of high stability resistors $R_{16}$, $R_{17}$, $R_{18}$, and $R_{19}$ is connected across the input to the valve voltmeter, giving a total input resistance of 10 megohms. A reversing switch $S_{13}$ is incorporated in the circuit to provide for change in the polarity of the cathode relative to the reference electrode.

The high tension (150 volts) is supplied from a stabilised power pack, whilst the low tension (6.3 volts) is fed directly from the appropriate winding on the power pack transformer (Fig. IV, 88, 8).

Prior to installation in the cabinet, the initial calibration of the valve voltmeter is carried out as follows. The instrument is allowed to warm up for 10–15 minutes, and a voltage of 0.500 volt (e.g., from a Tinsley low resistance potentiometer) is applied to the external input with the selector switch $S_{15}$ (Fig. IV, 88, 7) set at $E_{BXR}$. The sensitivity

![Diagram](image-url)
controls \((V_4 + V_5)\) and \(V_6\) are adjusted to give a reading of 0.500 volt with the range selector switch \(S_{12}\) (Fig. \(IV, 88, 6\)) set at the 0–0.5 volt range. The zero is then checked by disconnecting the external voltage, short-circuiting the external input terminals of the valve voltmeter, and adjusting the sensitivity control \(V_6\) (fine) if necessary. The range selector switch \(S_{12}\) is now turned to the 0–1.0 volt range and the potentiometer \(V_A\) is adjusted to give a reading of 0.500 volt. The zero should again be checked as before. Once these two proportional ranges have been adjusted, the two higher ranges may be set with the aid of the Weston cell. The external voltage is disconnected, the meter \(M_5\) adjusted to read zero, switch \(S_{12}\) is retained at the 0–1.0 volt range, the selector switch \(S_{15}\) isturned to \(E\) INPUT and switch \(S_{16}\) to STD. CELL; \(V_6\) is adjusted so that a reading of 1.018 volts is obtained on the meter. The range selector switch \(S_{12}\) is then set at 0–2.5 volts and the potentiometer \(V_2\) adjusted to give a reading of 1.018 volts; the zero is again checked by turning the switch \(S_{16}\) to D.C. INPUT. The range selector switch is finally rotated to the 0–5.0 volts range and the potentiometer \(V_0\) adjusted to give a reading of 1.018 volts; the zero is again checked as in the previous calibration. Once the adjustments of the potentiometers \(V_A\), \(V_B\), and \(V_0\) have been made and the ranges checked against the Weston cell, the valve voltmeter may be assembled in the cabinet.

The valve voltmeter is calibrated as follows prior to use. The range selector switch \(S_{12}\) is set at the 0–1.0 volt range, the instrument is allowed to warm up for 10–15 minutes, and \(V_3\) is adjusted so that the meter \(M_5\) reads zero. Switch \(S_{16}\) (Fig. \(IV, 88, 7\)) is set at STD. CELL and the valve voltmeter input selector switch \(S_{15}\) at \(E\) INPUT. The meter should read 1.018 volts. If this is not the case (due to accidental movement of the calibration controls, variation in the voltage of the mains, etc.), the zero should again be checked by turning \(S_{16}\) to D.C. INPUT and \(V_6\) re-adjusted to give a reading of 1.018 volts. It is important that the leads from the deposition cell to the D.C. INPUT socket should not be inserted whilst the zero of the meter is being adjusted; if this connection be made, an unbalance of the voltmeter may result and a false zero will be obtained.

5. Potentiometer. The potentiometer circuit is depicted in Fig. \(IV, 88, 7\). Seventeen fixed and equal resistances \((R_{20}–R_{36})^*\) give steps of 0.1 volt, whilst a variable resistance \(V_7\) provides fine adjustment over a range of 0.1 volt. The various steps are selected by the eighteen-way single-pole switch \(S_{14}\). The current is supplied by a 2-volt accumulator \(B\) through terminals brought out on to the panel of the instrument. The potentiometer is adjusted so that it reads the values on the dials (0.0–1.7 volts in steps of 0.1 volt) with the aid of the variable resistances \(V_8\) (coarse) and \(V_9\) (fine) in conjunction with the valve voltmeter (Fig. \(IV, 88, 6\)).

The valve voltmeter input selector switch \(S_{15}\) is set at \(E\) INPUT and a high-resistance precision voltmeter (20,000 ohms per volt) is connected temporarily across the potentiometer, i.e., across the same leads as pass to the valve voltmeter.† The potentiometer is set at 0.9 volt (the

* The values of the seventeen resistances were made exactly equal to the resistance of \(V_4\). The resistance of \(V_7\) was rated as 100 ohms by the manufacturers, but upon measurement its value was found to be 98.0 ohms.

† This independent check of the valve voltmeter was carried out before the instrument was finally assembled in order to determine the error introduced by measuring potentials.
setting of maximum resistance), and the calibration controls are adjusted so that the high-resistance voltmeter reads 0.900 volt precisely; the high-resistance voltmeter is then disconnected. The zero position of the valve voltmeter is again checked, and the reading (y volts) corresponding to the potentiometer setting of 0.9 volt is noted accurately (the actual reading with the author's instrument was 0.895 volts). Henceforth when calibrating the potentiometer, the calibration controls are adjusted so that a reading of y volts on the

valve voltmeter is obtained with the potentiometer set at 0.9 volt. The potentiometer is then ready for use.

It must be pointed out that the vibrator must be switched off when $E_{\text{INPUT}}$ or $E_{\text{FOT}}$ is measured; a reduced reading of the valve voltmeter will be recorded if the vibrator is left in circuit. A two-pole on/off switch, $S_{18}$, was inserted in the lead to the vibrator winding from the 20-volt winding of the transformer $T_5$.

If two volt accumulators are employed for $B$, the potentiometer may be calibrated to give steps of 0.2 volt.

6 and 7. High-tension power pack for the amplifier and the valve voltmeter. The power packs supplying the high tension required for the amplifier and the valve voltmeter were identical. One is shown in Fig. IV, 88, 8. It consists of a mains transformer $T_4$ operating in conjunction with a full-wave valve rectifier $U_{50}$. The heating coil of the thermal-delay switch $S_{17}$ is connected across the heater winding of

at low resistance since the valve voltmeter was calibrated against a high resistance Weston cell. The error proved to be 5 millivolts; this may be neglected for most routine electro-depositions at controlled cathode potential.
which supplies the rectifier valve. This delays the switching of the high-tension supply to the valve anodes until the valves have warmed up, thus avoiding the voltage surge which would be harmful to the smoothing condensers $C_{12}$ and $C_{13}$. The thermal-delay switch $S_{17}$ is followed by an inductance capacity filter consisting of two 10 µfd. paper condensers $C_{12}$ and $C_{13}$ (minimum working voltage 300 volts), and a 30-henry, 40-mA. choke $L_4$. Finally, a voltage regulator $VR$ 150/30 is connected as shown in the figure. The resistance $V_{10}$ is adjusted until the amplifier and the regulator, or the valve voltmeter and the regulator, are drawing 30 mA. The resistance $R_{37}$ (fixed) + $V_{10}$ (variable) should be arranged so that:

$$R_{37} + V_{10} = \frac{1000 (V_s - V_p)}{\text{Maximum current (mA.) drawn by regulator}}$$

where $V_s$ is voltage across $R_{38}$ and $V_p$ is voltage taken from regulator.

A photograph of the complete assembly is reproduced in Fig. IV, 88, 9. The cabinet (1) on the extreme left houses the motor and Variac unit, the adjacent cabinet (2) contains the amplifier, potentiometer,
Gravimetric Analysis

valve voltmeter, and the two high-tension power packs (one for the amplifier and the other for the valve voltmeter). The low-tension D.C. unit is immediately behind the cabinet (2), and the electrolytic cell is on the extreme right of the photograph. The Variac unit (1) is connected by cable to the low tension D.C. unit (3), and the former supplies alternating current for the latter. A 6-wire cable connects (1) and (2). The cabinet (2) and the cell unit (4) are connected to two wires from the D.C. INPUT terminals (one to the cathode and the other to the reference cell); the anode and cathode are also connected by two wires to two terminals on the low tension D.C. unit (3). Provision is also made for supplying power to the motor operating the stirrer in the electro-deposition cell. The above description should be read in conjunction with Fig. IV, 88, 1.

Operation of the complete instrument for controlled potential electro-analysis

The apparatus is first earthed by attaching the terminal marked GROUND (which is connected to all ∇ signs in the circuit diagrams) to a water-pipe or other suitable earthing conductor; the earthing connexion should preferably be soldered.

The electro-deposition cell is then connected to the apparatus. Two wires (15-amp. single covered cable) are run from the D.C. OUTPUT terminals on the low-tension unit (Fig. IV, 88, 2) to the anode and cathode respectively. Two further wires (screened) are run from the D.C. INPUT terminals on the potentiometer unit (Fig. IV, 88, 7) to the cathode and reference electrode respectively, the negative terminal being connected to the cathode and the positive terminal to the reference electrode. It is important to use four wires for connecting the cell to the apparatus in the manner described. If the negative output terminal of the D.C. low-tension unit were joined to the negative D.C. INPUT terminal of the potentiometer unit and a common wire were run to the cathode, it would be found that the valve voltmeter would indicate, and the amplifier respond to, the voltage drop through the common lead superimposed upon the cathode/reference cell potential.

The main "on/off" switch $S_9$ (Fig. IV, 88, 5) is turned on, the "stand-by" switch $S_9$ is retained in the "off" position, the voltage selector switch $S_4$ (Fig. IV, 88, 2) is set at zero, and the following turned on: valve voltmeter ($S_{11}$, Fig. IV, 88, 5), amplifier ($S_{10}$, Fig. IV, 88, 5), and low-tension D.C. power unit ($S_4$, Fig. IV, 88, 2).

The accumulator is then connected to the appropriate terminals on the potentiometer panel. After 10–15 minutes the valve voltmeter is calibrated against the Weston cell. The latter is brought into circuit by setting switch $S_{16}$ (Fig. IV, 88, 7) at STD. CELL and switch $S_{15}$ at E INPUT. The mode of adjustment of the valve voltmeter has been described under 4. Valve Voltmeter.

The potentiometer may now be calibrated by setting the valve voltmeter input selector switch $S_{15}$ (Fig. IV, 88, 7) at $E_{DCST}$, $S_{14}$ at 0:9 volt, and $V_0$ at zero; the valve voltmeter is turned to the 0–1:0 volt range. $V_8$ (coarse) and $V_9$ (fine) are then adjusted so that the valve voltmeter reads exactly 0:900 volt (full-scale deflection). Once
the potentiometer has been calibrated, it should be set to the limiting cathode potential desired. Attention is now directed to the electro-deposition cell. The solution to be electrolysed is placed in the cell. The tip of the saturated calomel electrode is placed as close as possible to the cathode and at about its middle. If the cathode happens to be positive to the reference electrode, the reversing switch $S_{13}$ on the valve voltmeter must be thrown into the correct position. Switch $S_{16}$ (Fig. IV, 88, 7) is turned to “D.C. Input” and switch $S_{15}$ to $E_{INPUT}$.

The ammeter switch $S_{3}$ (Fig. IV, 88, 2) should be set to the 10-amp. range (full scale), and the voltmeter switch $S_{2}$ to the 20-volt range (full scale). The stirrer motor for the electrolysis cell is set in motion, and the voltage selector switch $S_{1}$ (Fig. IV, 88, 2) rotated to 12 volts. The “stand-by” switch $S_{9}$ on the Variac unit (Fig. IV, 88, 3) is turned on, and the voltage selector switch $S_{1}$ re-adjusted so that the A.C. output of the Variac unit as indicated on the A.C. voltmeter $M_{3}$ is between 200 and 210 volts. [If this voltage is exceeded, one of the safety switches, $S_{0}$ or $S_{4}$ (Fig. IV, 88, 3), may come into operation and switch off the motor.] If the Variac is functioning in the upper part of its range (and, in consequence $S_{1}$ set at a low value), it will exert a smoother and more accurate control on the D.C. output voltage of the low-tension unit. This will permit the sensitivity control $V_{2}$ (Fig. IV, 88, 5) to be more fully advanced without “hunting” occurring. The voltage-selector switch $S_{1}$ should therefore be adjusted so as to keep the A.C. output of the Variac unit between 200 and 210 volts whenever possible. Soon after the electro-analysis has commenced, the control $V_{2}$ should be advanced as far as is compatible with the absence of “hunting”; the latter will be shown by a gentle oscillation of the needle of the A.C. voltmeter $M_{3}$ (Fig. IV, 88, 3). Towards the end of the electro-deposition the A.C. voltage output of the Variac will fall below 200–210 volts, notwithstanding the fact that the voltage-selector switch $S_{1}$ is set at its maximum value of 15 volts.

When the cathode-reference-cell potential attains the limiting value set on the potentiometer, the relay and amplifier will be brought into operation and, in consequence, the Variac motor will begin to turn, thus decreasing the electrolysis current. The operation of the Variac unit is intermittent, due to the dependence of the cathode overvoltage upon the current, and for other reasons. When the electrolysis current has fallen below 1·0 amp., the ammeter range is changed to 0–1·0 amp. by switch $S_{a}$, and again later to the 0–100-mA range. The electrolysis is discontinued when the current has fallen to 10–30 mA. The electrolyte is removed (e.g., by lowering the electrolysis vessel) and the electrodes are simultaneously washed without interrupting the current.

The valve voltmeter, amplifier, low-tension D.C. unit, and finally the main “on/off” switch $S_{9}$ are then switched off. If another electro-analysis is to be carried out immediately afterwards, the sequence of operations is: turn switch $S_{9}$ to the “on” position; set switch $S_{8}$ (Fig. IV, 88, 3) to the “stand-by” position; adjust the potentiometer to the limiting voltage desired; set $S_{3}$ to the 10-amp. range; set $S_{2}$ to the 20-volt range; and check the zero of the valve voltmeter. The apparatus is then ready for use as already described, viz., place the solution to be analysed round the electrodes; start the stirrer motor; set $S_{1}$ at 12 volts; turn $S_{8}$ to the “working” position,
Gravimetric Analysis

541

switch on the vibrator by means of \( S_1 \); adjust \( S_1 \) so that the a.c. voltmeter reads 200–210 volts; adjust \( V_2 \) to the maximum value before "hunting" appears, etc.

**DETAILED LIST OF COMPONENTS**

For the convenience of those wishing to construct the apparatus, the details of the various components will be given to correspond with the figures. The components are those employed in the author's apparatus and are intended as a guide; equivalent components may, of course, be used.

---

**Fig. IV, 88, 2. D.C. low-tension unit.**

\( R_1 = \) shunt supplied with Pullin voltmeter \((M_1)\).

\( R_2 = \) shunt supplied with Pullin ammeter \((M_2)\).

\( C_1 = 3000 \mu F\) 24-volt paper condenser \((M.R. Supplies)\).

\( C_2 = 9000 \mu F\) \((3 \times 3000)\) 24-volt paper condenser \((M.R. Supplies)\).

\( L_1 = 40\)-millihenry 10-amp. smoothing choke \((M.R. Supplies)\).

\( T_1 = \) mains step-down transformer; primary windings, 10/0/200/220/240 volts; secondary windings, 0/3/6/9/12/15 volts at 15 amps. \((M.R. Supplies)\).

\( SE = \) selenium bridge rectifier, funnel type, rated at 16 volts, 15 amps. \((M.R. Supplies)\).

\( M_1 = \) Pullin voltmeter, C30/IV, knife-edge pointer and mirror scale, scaled to read 0–1-0, 0–5-0, and 0–20-0 volts \((Measuring Instruments (Pullin), Ltd.)\).

\( M_2 = \) Pullin ammeter, C30/100M, knife-edge pointer and mirror scale, scaled to read 0–0-1, 0–1-0, and 0–10-0 amps.

\( S_1 = \) two-pole, six-way, six-bank double-contact rotary switch, wired as one-pole six-way \((Oak or Yaxley)\).

\( S_2 = \) six-pole, three-way switch, wired as one-pole, three-way \((Bulgin, S.438)\).

\( S_3 = \) identical with \( S_2 \).

\( S_4 = \) two-pole on/off switch \((Bulgin, S.267)\).

A mains socket and plug \( (\text{not shown in the figure}) \) was used to connect the low-tension unit with \( P_2 \) on the Variac unit \((Bulgin, P.162)\).

---

**Fig. IV, 88, 3. Motor-driven Variac unit.**

\( L_6 + L_7 = \) windings of four-pole, two-phase reversible induction motor, geared down to 1 r.p.m., attached to Variac of 5-amp. capacity \((Zenith)\).

It will be necessary to rewire the motor as supplied by the manufacturers to conform with **Fig. IV, 88, 3.**

\( C_3 = 0.25-\mu F\) 500-volt paper condenser \((Webb's Radio)\).

\( C_4 = 0.4-\mu F\) condenser, supplied with motor unit \((Zenith)\).

\( S_5 = \) four-pole change-over switch, required for alternative circuit with manual control \((Bulgin, S.301)\).

\( S_6 = \) safety switch supplied with motor.

\( S_7 = \) safety switch supplied with motor.

\( S_8 = \) two-pole on/off switch \((Bulgin, S.267)\).

\( M_3 = \) Pullin 0–300 volts A.C. voltmeter, R30/300V, knife-edge pointer and mirror scale \((Measuring Instruments (Pullin), Ltd.)\).

\( P_1 = \) six-pin socket \((Bulgin, P.166)\).

\( P_2 = \) three-pin socket, one pin not used \((Bulgin, P.162)\).

---

**Fig. IV, 88, 4. Motor direction control unit (manual).**

This consists of one press-button two-way switch as supplied by Zenith Electrical Co., Ltd., with the motor-controlled Variac. It was necessary to drill another hole at the end opposite to the one already present; the latter hole was utilised for the wires to the six-way plug, which was inserted.
into $P_1$ (Fig. IV, 88, 3), and the other hole carried the two wires to the A.C. mains.

Fig. IV, 88, 5. Valve amplifier unit.

The resistances and condensers, unless otherwise indicated, were Erie or Dubilier products.

$R_3 = 100$ ohms, wire wound, 1 watt minimum.
$R_4 = 15,000$ ohms, carbon, 0·5 watt.
$R_5 = 7000$ ohms, carbon, 0·5 watt.
$R_6 = 1$ megohm, carbon, 0·5 watt.
$R_7 = 1$ megohm, carbon, 0·5 watt.
$R_8 = 1$ megohm, carbon, 0·5 watt.
$R_9 = 47,000$ ohms, carbon, 1 watt.
$R_{10} = 100,000$ ohms, carbon, 0·5 watt.
$R_{11} = 250,000$ ohms, carbon, 0·5 watt.
$R_{12} = 300$ ohms, wire wound, 1 watt minimum.
$C_5 = 1$-µfd. 500-volt working paper condenser.
$C_6 = 0·1$-µfd. 300-volt working paper condenser.
$C_7 = 0·1$-µfd. 300-volt working paper condenser.
$C_8 = 0·1$-µfd. 300-volt working paper condenser.
$C_{10} = 12$-µfd. (3 × 4 µfd.) 300-volt working paper condenser (M.R. Supplies).
$C_{11} = 12$-µfd. (3 × 4 µfd.) 300-volt working paper condenser (M.R. Supplies).

$T_1$ = mu-metal screened-input transformer; 1 : 100 step-up ratio; primary winding—400 turns, centre-tapped, D.C. resistance 34 ohms; secondary winding—10,000 turns, D.C. resistance 2700 ohms; inductance ca. 2·15 henrys (Sowter).

$T_2$ = mains transformer; primary winding—10/0/200/220/240 volts; secondary winding—350/0/350 volts at 100 mA. and additional winding 20 volts at 1 amp. for polarised relay (M.R. Supplies).

Relay: polarised relay, large type, two-way switch action, resistance of coil, or series resistance of coils, preferably between 200 and 800 ohms when connected with 20-volt winding on transformer $T_3$ (Standard Telephone, type 4141AG, or Alec Davis Supplies).

$V_a = 0·5$ megohm carbon potentiometer (Erie or Dubilier).

$V_1 = 680$ ohms wire-wound potentiometer (Bulgin, I.VC.12).

Note. The value of $V_1$ is dependent upon the resistance of the winding of the polarised relay. The winding of the relay used had a resistance of 650 ohms and thus passed about 31 mA. at 20 volts; with $V_1 = 680$ ohms, the voltage could be reduced to 10 volts with $V_1$ rated at about 0·3 watt.

Valves: two 6SL7 and two 6SN7 (Webb’s Radio).

Valve-holders: four of the amphenol octal type are required (Webb’s Radio).

Fuses: twin fuse-holder with cover (Bulgin, F.19).

$M_4$ = Pullin A.C. ammeter, 0–10 amps., R30/10A, knife-edge pointer and mirror scale (Measuring Instruments (Pullin), Ltd.).

Mains plug and socket to connect apparatus to A.C. mains (Bulgin, P.162).

Fig. IV, 88, 6. Valve voltmeter.

Unless otherwise stated all resistances are carbon, high stability and 1 per cent tolerance, and of Erie or Dubilier manufacture.

$R_{13} = 20,000$ ohms, 1 watt.
$R_{14} = 20,000$ ohms, 1 watt.
Gravimetric Analysis

\[ R_{15} = 3 \text{ megohms, 1 watt.} \]
\[ R_{16} = 3 \text{ megohms, 1 watt.} \]
\[ R_{17} = 3 \text{ megohms, 1 watt.} \]
\[ R_{18} = 3 \text{ megohms, 1 watt.} \]
\[ R_{19} = 1 \text{ megohm, 1 watt.} \]
\[ V_7 = 2200 \text{ ohms wire-wound potentiometer (Bulgin, 1.VC.15).} \]
\[ V_7 \text{ and } V_5 = \text{two-gang, 7000 ohms each section, wire-wound potentiometer (Reliance Manufacturing).} \]
\[ V_9, V_A, V_B, V_C = 22,000 \text{ ohms wire-wound potentiometer each (Bulgin, 1.VC.21).} \]

\[ M_5 = \text{Pullin microammeter, } 0-25 \mu A.; \text{ internal resistance less than 1400 ohms; knife-edge pointer, mirror scale, illuminated; scaled } 0-0.5 \text{ volt, } 0-1.0 \text{ volt, } 0-2.5 \text{ volts, and } 0-5.0 \text{ volts (Measuring Instruments (Pullin), Ltd.).} \]
\[ S_{12} = \text{three-pole four-way switch, wired as one-pole four-way (Oak or Yaxley).} \]
\[ S_{13} = \text{two-pole change-over switch (Bulgin, S.270).} \]

Valve holders: two of the amphenol octal type are required.

Fig. IV, 88, 7. Potentiometer.

\[ S_{14} = \text{eighteen-way single-pole rotary switch (Bulgin, S.436).} \]
\[ S_{15} = \text{Six-pole three-way switch, wired as two-pole three-way (Bulgin, S.438).} \]
\[ S_{16} = \text{two-pole change-over switch (Bulgin, S.270).} \]
\[ S_{17} = \text{Weston standard cell (Cambridge Instrument Co.).} \]
\[ E = \text{2-volt accumulator (connected externally).} \]
\[ V_9 = 100 \text{ ohms nominal, } 98.0 \text{ ohms actual by independent measurement (Bulgin, 1.VC.7).} \]
\[ V_5, V_6 = 330 \text{ ohms (Bulgin 1.VC.10).} \]
\[ V_4 = 10 \text{ ohms (Bulgin, 1.VC.1).} \]
\[ R_1, R_2, R_3 = \text{fixed resistances, each of 98-0 ohms (equal to } V_4), \text{ wound on paxolin formers with eureka or manganin wire (40 gauge) with an accuracy of 0.5 per cent.} \]

Fig. IV, 88, 8. High-tension power pack.

\[ T_1 = \text{mains transformer; primary windings—10/0/200/220/240 volts;} \]
\[ \text{secondary windings—200/0/200 volts at 60 mA., also 5 volts at 1 amp. and 6.3 volts at 3 amps., centre tapped (M.R. Supplies).} \]
\[ \text{One U50 valve rectifier (Webb's Radio).} \]
\[ \text{One VR 150/30 regulator valve (Webb's Radio).} \]
\[ C_{19} = 12-\mu \text{fd. (3 } \times \text{ 4 } \mu \text{fd.) 300-volt working paper condenser (M.R. Supplies).} \]
\[ C_{18} = 12-\mu \text{fd. (3 } \times \text{ 4 } \mu \text{fd.) 300-volt working paper condenser.} \]
\[ L_4 = 30-\text{henry 40-mA. choke (M.R. Supplies).} \]
\[ V_{10} = 2200 \text{ ohms wire-wound potentiometer (Bulgin, 1.VC.15).} \]
\[ R_{37} = 1000 \text{ ohms, wire-wound resistance, 3 watts (Webb's Radio).} \]
\[ R_{38} = 0.25 \text{ megohm carbon resistance, 1 watt (Webb's Radio).} \]
\[ S_{17} = \text{thermal delay switch (Bulgin, S.363).} \]

Valve-holders: two of the amphenol octal type will be required for each of the two power packs (Webb’s Radio).

Miscellaneous Components

Wooden cabinets. Variac motor unit: 7 x 15 x 9 in. Amplifier, etc., unit: 24 x 15 x 10 in. Low-tension D.C. unit: 22 x 15 x 17 in., asbestos lined (incorporating an air-cooled selenium rectifier; the size can be slightly reduced by employing a motor-driven blower to cool the rectifier).
Quantitative Inorganic Analysis

Chassis, 16 gauge mild steel, plated finish (Imhoff, type F and type H).
Panels, 16 gauge mild steel, cut to specification (Imhoff) or of 16 gauge aluminium.
Three dial lamps and holders (Bulgin, D.280).
Three sockets and two plugs (Bulgin, P.166).
Three sockets and three plugs (Bulgin, P.162).
Terminals, five black and three red (Belling and Lee).
Silvered copper wire, 18 gauge (Webb's Radio).
Wire covered with "Systoflex": A.C. leads = yellow; positive leads = red; negative leads = black; signal leads = green (Webb's Radio).
Multicore solder, No. 16014 or No. 16018 (Ersin Multicore).

NOTES ON WIRING

All connexions were made with 18 gauge silvered copper wire except in the low-tension electrolysis unit, where 15-amp. single-covered cable was used. The connexions from the electro-deposition cell and the D.C. output terminals on the low-tension unit should also be of 15-amp. wire. Ersin's multicore solder was used throughout the apparatus.

In the wiring of the valves, the A.C. wires (heater leads) should be twisted together and kept as far away as possible from the wires carrying the signal voltages; the latter should be as near the earthed chassis as practicable and should be screened and of minimum length. The anode leads of one valve should not be in the vicinity of the control grids of a previous valve, as this may lead to instability. It is particularly important to prevent hum (50 cycles A.C.) pick-up; operation of the motor could occur from the 50-cycle hum (sine wave) as well as from the 50-cycle square-topped wave produced by the vibrator (Fig. IV, 88, 6) on the appearance of a D.C. "error input."

A mains dial light and holder (Bulgin, D.280) may be wired across the mains lead (Fig. IV, 88, 5) to indicate when the apparatus is switched on. Similarly, dial lights may be fitted across the terminals 3 and 5 of the six-pin-socket P of the Variac unit (Fig. IV, 88, 3), and also across the input leads of the low-tension D.C. unit (Fig. IV, 88, 2).

The efficiency of the valves may be checked (e.g., when a breakdown occurs) by inserting a 100-ohm resistance in the cathode leads of all the valves and then switching a milliammeter (0-10 mA.) across each resistance in turn using a nine-way, two-pole selector switch (Bulgin, 8.436); the latter will give an "off" position and a check on eight cathodes. The failure of a rectifier valve will be apparent by a reduced or zero reading on all valves supplied by it.

The A.C. ammeter $M_4$ (constituting an additional refinement; visible on the panel of the amplifier unit, etc., of Fig. IV, 88, 9) is wired in the mains-input leads immediately following the fuses. This ammeter will record the total current consumed by the apparatus. It will indicate any overload such as would be produced, for example, if the mains windings of any of the transformers burnt out or if one of the U50 rectifier valves developed an internal short circuit.

Belling and Lee, Ltd., Cambridge Arterial Road, Enfield, Middlesex.
A. F. Bulgin and Co., Ltd., Bye Pass Road, Barking, Essex.
Alec Davis Supplies, Ltd., 18 Tottenham Court Road, London, W.1.
Erie Resistors, Ltd., Beevor Road, Great Yarmouth.
Measuring Instruments (Pullin), Ltd., Winchester Street,Acton, London, W.3.
Multicore Solders, Ltd., MELLIER HOUSE, ALBEMARLE STREET, LONDON, W.1.
IV, 89. Determination of metals in alloys using controlled potential of the cathode.—A. Copper in bronze. Weigh out accurately 0·5–1·0 g. of the bronze,* add 10 ml. of concentrated hydrochloric acid, heat, and introduce concentrated nitric acid dropwise until the alloy just passes into solution. Avoid an excess of nitric acid. When the sample has dissolved, add 20 ml. of concentrated hydrochloric acid and 4 g. of hydroxylamine hydrochloride, and heat the solution just below the boiling point until the dark-green colour becomes much lighter, indicating considerable reduction to the chlorocuprous complex ion. Dilute the solution to 200–250 ml., and electrolyse with vigorous stirring, using a saturated calomel auxiliary electrode and a limiting cathode potential of —0·35 volt, i.e., the reading of the valve voltmeter should be 0·35 volt. [If the assembly for automatic cathode potential control is used, set the apparatus to limit the cathode-calomel voltage to 0·35 volt; electro-deposition will then proceed automatically.] The auxiliary electrode of Fig. IV, 87, 1, may be used, with the tip placed outside and as close as possible to the cathode cylinder at about its middle. Alternatively, a 6-mm. tube filled with a 3 per cent agar solution in saturated potassium chloride solution may be employed as a salt bridge; the tip of the salt bridge is similarly placed relative to the cathode. The initial value of the current should be 2–5 amps. so that the cathode potential at first quickly acquires a value of at least —0·3 volt. Copper may not deposit for several minutes after the electro-analysis is commenced, and indeed the saturated calomel electrode may first be negative to the cathode: copper will commence to plate out when the cathode potential is about —0·2 volt. Wash down the walls of the beaker several times during the electrolysis. Continue the electrolysis until the current has decreased to about 0·03 amp. Complete the determination in the usual manner, removing the electrolyte and washing off the cathode before turning off the current. Wash the deposit of copper well with water, and dry at a temperature not exceeding 100° C. for 10 minutes.

Calculate the percentage of copper in the bronze.

B. Copper in copper-base and tin-base alloys. The procedure to be described is applicable to the determination of copper in copper-base and tin-base alloys; it may be applied in the presence of lead, tin, antimony, zinc, and various other elements commonly present in these alloys, but bismuth and silver interfere and are co-deposited with the copper. Brasses and bronzes may also be analysed by this method. The copper is deposited at controlled potential from an acidic tartrate solution.

* Either Riddsdale's "Gunmetal, No. 6c" (one of the Analyzed Samples for Students) or the Bureau of Analyzed Samples "Bronze, No. 207C" (one of the British Chemical Standards) is suitable for practice in this determination.
Weigh out accurately a 0.5-2.0 g. sample of the alloy* into a covered 250- or 400-ml. beaker, and dissolve it in a warm mixture of 8 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid. Introduce the nitric acid dropwise as required. Boil the solution very gently for a minute or two to remove most of the oxides of nitrogen and chlorine. Then add 100 ml. of a solution containing 23 g. of pure sodium tartrate dihydrate, 1 g. of urea, or, better, 0.5 g. of sulphamic acid (to remove oxides of nitrogen), and 10 ml. of 5N-sodium hydroxide solution.† Dilute the solution to about 200 ml., introduce 1-2 g. of hydroxylamine hydrochloride as an anodic depolariser, and electrolyse, whilst stirring efficiently, with a cathode potential relative to the saturated calomel electrode at $-0.36 \pm 0.02$ volt. The automatic cathode control potential apparatus, set at $0.35$ volt, is recommended. The initial current is about 3 amps. and drops to a few milliamperes in about 60 minutes. Lower the beaker away from the platinum-gauze electrodes, wash the cathode with a little water, then twice with pure acetone, dry for 3 minutes at 70°C, and weigh after cooling in air for at least 20 minutes.

If the proportion of lead in the alloy is small (≥ 5-10 per cent) and, provided it does not separate as lead hydrogen tartrate in the preparation of the solution, it may be determined by a further application of controlled potential electro-analysis. After the copper deposit has been weighed, replace the copper-placed cathode in the solution and electrolyse at a potential of $-0.55$ to $-0.60$ volt vs. S.C.E. Weigh the lead deposit on the cathode after completing the determination in the usual way. No lead dioxide is deposited on the anode, but the results are 2-3 per cent low, due probably to the partial re-solution of the lead during the washing process.

Calculate the percentage of copper in the alloy.

C. Antimony, copper, lead, and tin in bearing metal. Weigh out accurately 0.2-0.4 g. of the alloy‡ (as drillings or fine filings) into a small beaker. Dissolve the alloy by warming with a mixture of 10 ml. of concentrated hydrochloric acid, 10 ml. of water, and 1 g. of ammonium chloride (the last-named to minimise the loss of tin as the tetra-chloride). Complete solution may be hastened by the addition, drop by drop, of a saturated solution of potassium chlorate. When all the alloy has dissolved, boil off the excess of chlorine, add 5 ml. of concentrated hydrochloric acid, dilute to 150 ml., and then add 1 g. of hydrazine hydrochloride. Electrolyse at 70-75°C, limiting the potential to $-0.4$ volt relative to a saturated calomel electrode; the electrodes depicted in Fig. IV, 77, 9, or in Fig. IV, 77, 12, may be employed. Copper and antimony are deposited together. After 15-20 minutes (when the current has fallen to a low value),§ flush out the liquid in

---

* Any of the following may be used. Copper-base alloys: Ridsdale's "Gunmetal, No. 8b" or "Phosphor bronze, No. 7"; Bureau of Analyzed Samples "Bronze, No. 2070" or "Phosphor bronze, No. 133A"; U.S. Bureau of Standards, "Owens Metal, No. 124b" or "Phosphor bronze, No. 63b." Tin-base alloys: Ridsdale's "White Metal, No. 8b"; Bureau of Analyzed Samples, "White Metal, No. 178B"; U.S. Bureau of Standards, "Tin-base bearing metal, No. 54e."

† If lead hydrogen tartrate separates at this stage, filter the solution before finally diluting to 200 ml.

‡ Either Ridsdale's "White Metal, No. 8b" (one of the Analyzed Samples for Students) or the British Chemical Standard "White Metal, No. 178B" is satisfactory for practice in this analysis.

§ The current is employed not only for the deposition of the antimony but also for the reduction of stannic to stannous ions. This reduction is catalysed by metallic
the tip of the reference electrode vessel (compare Fig. IV, 67, 1) into
the electrolysis beaker and continue the electrolysis for a further 5-10
minutes. Dry and weigh the copper-antimony deposit on the cathode.
Separate the copper and antimony by dissolving the deposit in a
mixture of 5 ml. of concentrated nitric acid, 5 ml. of 40 per cent hydro­
fluoric acid, and 10 ml. of water: boil off the oxides of nitrogen, dilute
to 150 ml., and add dropwise a solution of potassium dichromate until
the liquid is distinctly yellow. Deposit the copper by electrolysing the
solution at room temperature and limiting the cathode-S.C.E. potential
to — 0·4 volt. Evaluate the weight of antimony by difference.
To the solution from which the copper and antimony have been
separated as above, add 1 g. of hydrazine hydrochloride. Electrolyse
the solution at room temperature, limiting the cathode-S.C.E. potential
to — 0·7 volt. The lead and tin are deposited together. Dissolve the
deposit in a mixture of 15 ml. of concentrated nitric acid, 5 ml. of
concentrated hydrofluoric acid, and 15 ml. of water, and boil off the
oxides of nitrogen. For high-lead alloys (about 25 per cent of lead),
dilute to 150 ml., and deposit the lead as peroxide by electrolysing at
90—95° C. for 20 minutes with a current of 6-6·5 amps. With low­
lead alloys, add 20 ml. of a standard 0·5 per cent solution of lead (as
nitrate), dilute to 150 ml., and electrolyse as before. Weigh the deposit
of lead dioxide. Calculate the weight of lead, using the factor 0·864
for Pb/PbO₂; if lead nitrate solution was added, deduct the weight of
lead which was introduced prior to the electrolysis. Obtain the weight
of tin by difference.
Calculate the proportions of Sb, Cu, Pb, and Sn in the alloy.
D. Copper, lead, tin, and zinc in brass or bronze. Dissolve 0·2-0·4 g.,
accurately weighed, of the alloy * in a mixture of 10 ml. of concentrated
hydrochloric acid, 2 ml. of concentrated nitric acid, 10 ml. of water,
and 1 g. of ammonium chloride. Add a further 5 ml. of concentrated
hydrochloric acid, dilute to 150 ml., introduce 1 g. of hydrazine hydro­
chloride and electrolyse for 20 minutes at 50° C., limiting the cathode
potential to — 0·4 volt relative to a saturated calomel electrode. Use
an initial current of 3-4 amps.; this falls rapidly to about 0·1 amp.
All the copper is thus deposited, together with any arsenic which may
be present. To free the copper from the arsenic, dissolve the deposit
in a mixture of 5 ml. of concentrated sulphuric acid, 5 ml. of concen­
trated nitric acid and 10 ml. of water. Boil off oxides of nitrogen,
dilute the solution to 150 ml., and electrolyse for 20 minutes at room
temperature at a cathode potential of — 0·4 volt vs. S.C.E.: copper
alone is now deposited.
Deposit the tin and lead from the original solution (from which the
copper has been removed) and subsequently separate them as described
under C.
Oxidise the solution remaining after the removal of the tin and lead
by boiling with a little bromine water until colourless. Add concen­
trated ammonia solution until the solution is just alkaline to phenol­
phthalein, heat to the boiling point, and filter off any small precipitate

antimony, and hence, after the cathode has become covered with this element, a
considerable increase in current takes place. The reduction must be allowed to proceed
until a residual current of about 0·3 amp. has been in operation for about 10 minutes.
* Risdale's "Brass, No. 50" or "Phosphor Bronze, No. 7" (Analysed Samples
for Students) or the British Chemical Standard "Bronze, No. 207C" may be used for
practice in this separation.
of ferric hydroxide. This precipitate may be dissolved in dilute hydrochloric acid and the iron determined colorimetrically. Cool the filtrate, add 10 ml. of concentrated ammonia solution and 10 ml. of 10 per cent potassium cyanide solution. Electrolyse for 20 minutes at room temperature with a current of 3 amps. Weigh the deposit of zinc.

Finally, calculate the percentage of Cu, Pb, Sn, and Zn in the alloy.

IV, 90. SIMPLE GRAVIMETRIC SEPARATIONS

Discussion. The author has found it a good practice in his own classes for students to undertake simple gravimetric separations before embarking upon the analysis of complex materials. This scheme may not commend itself to all teachers, chiefly on the ground that the mixtures are artificial and are therefore not likely to be encountered as such in practice; however, the analysis of simple artificial mixtures is a valuable preliminary training before proceeding to the analysis of complex materials.

Many separations have been briefly indicated in the text; a few are given in detail. With his knowledge of the determination of the component elements, the student should experience no difficulty in carrying out the undermentioned separations and estimations.

Procedure. A. Iron and aluminium. Method 1. Dissolve the mixture provided (1) in water or in dilute hydrochloric acid in a Pyrex beaker, and dilute to 75 ml. (2). Heat to about 70° C., and add an excess (8–10 fold) of 0·2N-sodium hydroxide (A.R.) slowly and with constant stirring (3). The excess of alkali will dissolve the precipitated aluminium hydroxide as sodium aluminate. Dilute to 150 ml. with boiling water, boil for several minutes, and filter. Wash the beaker, precipitate, and filter with hot water until the washings are at most faintly alkaline. Reserve the filtrate and washings (i). Place the original beaker under the filter, dissolve the precipitated ferric hydroxide by pouring warm 2N-hydrochloric acid upon it (4), and then re-precipitate the iron with ammonia solution (Section IV, 3), or by any of the methods given in Section IV, 31. Ignite and weigh as Fe₂O₃.

Determine the aluminium in the filtrate (i) either by acidifying with dilute hydrochloric acid, adding several grams of ammonium chloride, and precipitating with dilute ammonia solution (Section IV, 9), or by just acidifying with dilute hydrochloric acid and precipitating with sodium thiosulphate solution (Section IV, 28A); in both cases the precipitate is ignited to and weighed as Al₂O₃. Alternatively, the oxine method (Section IV, 28D) may be used.

Notes. 1. A suitable mixture for practice may be prepared by intimately mixing known weights of A.R. iron alum and A.R. ammonium alum.
2. If ferric iron is present, oxidise it with a little concentrated nitric acid.
3. Improved results may be obtained by the following method of precipitation. Nearly neutralise the dilute acid solution of iron and aluminium with aqueous sodium hydroxide, heat to boiling, and add the solution slowly and with constant stirring to 75 ml. of hot 5 per cent sodium hydroxide (A.R.) solution. Boil the mixture for 2–3 minutes with gentle stirring, and filter.
4. It is difficult to completely free the precipitate from sodium hydroxide, etc.; this is most simply achieved by re-precipitation.

Method 2. This procedure depends upon the precipitation of iron by ammonium sulphide in ammonium tartrate solution: aluminium
Gravimetric Analysis

(Also chromium, vanadium, titanium, zirconium, and beryllium) is not precipitated under these conditions.

Dissolve the mixture provided in water or in dilute hydrochloric acid in a conical flask, and dilute to 75–100 ml. Add four times as much pure tartaric acid as the dissolved metals would weigh as oxides, render alkaline with ammonia solution (the solution should remain clear if enough tartrate is present), acidify with 1 : 1 hydrochloric acid, and add 2 ml. in excess. Saturate with hydrogen sulphide to reduce the iron (also to take advantage of the fact that ferrous sulphide is filtered more easily than ferric sulphide). Add a slight excess of dilute ammonia solution, introduce more hydrogen sulphide, and allow the precipitate to settle in the closed flask. Filter off the precipitated ferrous sulphide, wash thoroughly with water containing a little ammonium sulphide and ammonium tartrate, and keep the filtrate and washings (i). Dissolve the precipitate in 1 : 1 hydrochloric acid. Alternatively, place the precipitate and paper in a beaker of suitable size, cover with a clock-glass, and cautiously dissolve the sulphide in 1 : 1 hydrochloric acid: heat until all the black particles have disappeared, and shred the paper by vigorous stirring with a policeman. Oxidise the iron by the addition of 1 ml. of concentrated nitric acid, boil, dilute, and precipitate the iron as in Method 1. Weigh as Fe₂O₃.

To determine the aluminium, concentrate the filtrate and washings (i) to about two-thirds of the original volume, allow to cool, render neutral, and precipitate as the “oxinate” (Sections III, 138A and IV, 28D). Weigh as Al(C₆H₄ON)₃ after drying to constant weight at 130–140° C.

Method 3. This method illustrates the use of cupferron in separating iron (and also titanium, zirconium, and vanadium) from aluminium (and also from chromium, manganese, and nickel). Precipitation is made in strongly acid solution.

Dissolve the mixture provided in water or in dilute sulphuric acid. Dilute to 150 ml., and add cautiously 15 ml. of concentrated sulphuric acid. Cool to 10° C., and then introduce a freshly prepared, cold 6 per cent aqueous solution of cupferron slowly and with constant stirring until an excess * is present. A reddish-brown flocculent precipitate is produced; precipitation is complete when a white, finely crystalline precipitate of cupferron appears. Add a Whatman accelerator (or one-third of an ashless tablet), allow to settle for 2–3 minutes, and filter with gentle suction through a quantitative filter-paper supported on a filter-cone (Whatman, hardened, No. 52). Wash the precipitate with cold 10 per cent by volume sulphuric or hydrochloric acid, then twice with 5N-ammonia solution to remove excess of the reagent, and finally once with water. Reserve the filtrate and washings (i). Complete the determination as in Section IV, 31B. Weigh as Fe₂O₃.

To estimate the aluminium, concentrate the filtrate and washings (i) to 25 ml., add 20–25 ml. of concentrated nitric acid, and evaporate slowly to fumes of sulphuric acid. Treat with more nitric acid if organic matter is still present. Finally, evaporate just to dryness, dissolve the residue in water, and complete the determination as in Method 2.

For other methods of separation, see Section IV, 99, C1 and C2.

B. Iron and chromium. Method 1. Dissolve the mixture (i) in water or in dilute hydrochloric acid, almost neutralise with A.R. sodium

* About 33 per cent excess, i.e., 0.82 g. of cupferron for 0.1 g. of Fe.
hydroxide solution, and heat to boiling. Pour this solution slowly and with constant stirring into 100 ml. of a hot, 5 per cent A.R. sodium hydroxide solution, boil for 2–3 minutes, and cool to the laboratory temperature. Treat with bromine water until the solution is yellow (alternatively, add a few ml. of 100-volume hydrogen peroxide); boil to decompose the excess of hypobromite (or of hydrogen peroxide). The chromium will now be in solution as chromate. Add a Whatman accelerator (or one-third of an ashless tablet), allow the precipitate to settle, and filter through a quantitative filter-paper. Wash the precipitate with hot water, and reserve the filtrate and washings (i). It is advisable to dissolve the precipitate in 2N-hydrochloric acid, and to re-precipitate the ferric hydroxide as in A, Method 1. Weigh as Fe₂O₃.

If sulphate is absent, the chromium may be determined as barium chromate. Render the filtrate (i) acid with acetic acid, and add an excess of barium acetate solution. Complete the estimation as in Section IV, 30C. Weigh as BaCrO₄.

If sulphate is present, acidify the filtrate (i) with hydrochloric acid, reduce the solution by the addition of 15 ml. of alcohol, and boil. Precipitate the chromium as chromic hydroxide as in Section IV, 9, or Section IV, 30A. Weigh as Cr₂O₃.

Note. 1. A suitable mixture for practice may be prepared by intimately mixing known weights of A.R. iron alum and A.R. chrome alum.

Method 2. Here the chromium is oxidised in acid solution by perchloric acid to chromate (1).

Weigh out a suitable quantity of the mixture into a conical flask, add 5 ml. of water and 5 ml. of A.R. 60–70 per cent perchloric acid (DANGER; see Section IV, 70), and place a short funnel in the mouth of the flask. Heat in the fume cupboard until the solution has evaporated to half its original volume, and has assumed a deep orange colour for at least 5 minutes; oxidation is then complete. Allow to cool, add 40–60 ml. of water, and boil for 2–3 minutes to drive off any free chlorine which may be present (test with starch-iodide paper). Transfer quantitatively to a 250-ml. beaker, and precipitate the iron by the addition of ammonia solution in the usual manner (Section IV, 8). Keep the filtrate and washings (i). The ferric hydroxide should be dissolved in 2N-hydrochloric acid and re-precipitated. Weigh as Fe₂O₃.

Determine the chromate in the filtrate and washings (i) as in Method 1 or by the following volumetric process. Acidify with 1 : 1 hydrochloric acid, transfer quantitatively to a 350- or 500-ml. glass-stoppered bottle, and treat with 30 ml. of 10 per cent potassium iodide solution and 5 ml. of concentrated hydrochloric acid. Add 50 ml. of water, and allow to stand for 1 minute. Titrate the liberated iodine with standard 0.1N-sodium thiosulphate; add starch solution towards the end, and continue the titration until the blue colour just disappears.

\[1 \text{ ml. } N\text{-}N\text{a}_2S_2O_3 = 0.02533 \text{ g. } \text{Cr}_2O_3\]

The above procedure may be applied also to the separation of aluminium and chromium.
Note. 1. The following reactions probably occur:

\[
Cr_2O_3 + 3HClO_4 = 2CrO_3 + 3HClO_3
\]
\[
3HClO_3 = HClO_4^- + Cl_2 + O_2 + H_2O
\]

or

\[
Cr_2O_3 + 2HClO_4 = 2CrO_3^- + Cl_2 + O_2 + H_2O
\]

C. Manganese and zinc. This separation depends upon the solubility of manganese quinaldinate in dilute acetic acid, the corresponding zinc complex being insoluble.

Dissolve the mixture (1) in 200 ml. of water, heat, and add 2 ml. of glacial acetic acid. Treat the boiling solution slowly and with stirring with a slight excess of sodium quinaldinate reagent (Section IV, 34c). Allow the precipitate to settle, filter it through a weighed sintered-glass or porous-porcelain crucible, and wash successively with hot 1:40 acetic acid and hot water. Reserve the filtrate and washings (i). Dry the precipitate at 125°C to constant weight, and weigh as Zn(C_10H_8ON_2)_2H_2O.

Determine the manganese in the filtrate (i) as the pyrophosphate (Section IV, 35).

Note. 1. A suitable mixture for practice may be prepared by intimately mixing known weights of A.R. manganese sulphate with A.R. zinc sulphate or pure zinc ammonium sulphate (Section IV, 34A).

D. Nickel and zinc. Weigh out accurately a suitable quantity of the mixture (1) containing not more than 0.2 g. of the total metals, dissolve it in 200 ml. of water, and add 1 ml. of concentrated hydrochloric or sulphuric acid. Heat the solution to boiling, add a large excess of the dimethylglyoxime reagent (Section I, 62A) followed by a concentrated solution of ammonium acetate until a precipitate appears and the equivalent of about 2 g. in excess. Digest for 30–60 minutes, and filter. Complete the estimation as in Section IV, 12A. Weigh as Ni(C_4H_7O_2N_2)(1/2). Reserve the filtrate and washings (i).

For the estimation of zinc it is necessary to destroy the excess of dimethylglyoxime. To do this, acidify the filtrate (i) with concentrated hydrochloric acid, and add 5 ml. of the concentrated acid in excess. Then introduce 25 ml. of concentrated nitric acid, and evaporate on a hot-plate in the fume cupboard to dryness or to fumes of sulphur trioxide. Allow to cool, add 5 ml. of concentrated hydrochloric acid, warm the mixture, and dilute to 50 ml. Complete the determination as in Section IV, 34A (compare Section IV, 38 (i))—remember that the proportions of the reagents apply to about 0.1 g. of Zn. Weigh as both the ammonium phosphate and the pyrophosphate.

Note. 1. A suitable mixture for practice may be prepared by intimately mixing known weights of pure (e.g., A.R.) nickel ammonium sulphate and A.R. zinc sulphate.

E. Calcium and magnesium. The calcium is separated by double precipitation as calcium oxalate, whilst magnesium is determined by double precipitation as the ammonium phosphate. An alternative method which permits of the quantitative separation of the calcium in one operation is to precipitate it as calcium molybdate: magnesium is then determined in the filtrate as magnesium ammonium phosphate.

For full experimental details, see Section IV, 98D, E and Section IV, 98H respectively (compare Section IV, 43A).
Quantitative Inorganic Analysis

A suitable mixture for practice may be prepared from A.R. calcium carbonate and A.R. magnesium sulphate.

**F. Calcium and barium.** This separation is based upon the difference in solubilities of calcium and barium chromates in acetic acid.

Weigh out a suitable quantity of the mixture (1), dissolve it in the minimum quantity of dilute hydrochloric acid in a covered beaker, boil to expel carbon dioxide, if present, and allow to cool. Neutralise with dilute ammonia solution, acidify with a few drops of acetic acid, and dilute to 50–100 ml. Introduce 10 ml of a 30 per cent solution of A.R. ammonium acetate (this should be faintly ammoniacal), heat to boiling, and add dropwise and with constant stirring an excess of 10 per cent A.R. ammonium dichromate solution (5–10 ml.). Allow to cool for 1 hour, decant the clear yellow liquid through a quantitative filter-paper (or through a porous-porcelain crucible), and wash the precipitate by decantation with 2 per cent ammonium acetate solution until the filtrate is no longer perceptibly coloured (ca. 100 ml. of the wash liquid). Complete washing is unnecessary at this stage (2). Reserve the filtrate and washings (i). Transfer the precipitate by a jet of water from the wash-bottle to the beaker containing the bulk of the precipitate, place the beaker under the funnel, and dissolve the residual precipitate in warm 2N-nitric acid, and wash the filter with hot water until free from acid. Add more dilute nitric acid, if necessary, until the precipitate dissolves. Treat with 10 ml of 30 per cent ammonium acetate solution, heat the liquid to boiling and stir steadily all the while, and allow to cool slowly during 1 hour. (The supernatant liquid should be yellow; if this is not the case, add a few ml. of ammonium dichromate solution.) Filter the precipitate through a weighed silica, Gooch, or porous-porcelain crucible; wash first by decantation, then on the filter with 2 per cent ammonium acetate solution, and finally with cold water until the filtrate gives only a slight opalescence with 2 drops of 0·1N-silver nitrate. Reserve the filtrate and washings (ii). Dry the crucible and precipitate to constant weight at 500–600° C. or within a larger crucible at a dull red heat. Weigh as BaCrO₄.

Treat the combined filtrates and washings (i and ii) with a little dilute nitric acid, evaporate to a small volume, and precipitate the calcium as carbonate by the addition of ammonia and A.R. ammonium carbonate solutions. Filter off the precipitate of calcium carbonate, wash it with a little hot water, dissolve it in the minimum volume of 1:1 hydrochloric acid, and precipitate the calcium as oxalate (Section IV, 10) and weigh either as CaCO₃ or as CaO, or precipitate as molybdate (Section IV, 9SH) and weigh as CaMoO₄.

**Notes.**

1. For practice in this analysis, an intimate mixture of A.R. barium chloride and A.R. calcium carbonate may be employed.

2. The subsequent re-precipitation is unnecessary where results of only moderate accuracy are required. For the separation of barium and strontium this method may be used, but re-precipitation is essential.

**G. Calcium and strontium.** The method is based upon the fact that calcium nitrate is soluble in anhydrous acetone, whilst strontium nitrate is almost insoluble (0·02 per cent at 25° C.).

Weigh out a suitable quantity of the mixture (1), dissolve it in the minimum volume of dilute hydrochloric acid in a covered beaker, boil to expel carbon dioxide (if present), and allow to cool. Warm to 50° C.,
and precipitate the two elements as carbonates by the addition of excess of ammonia and A.R. ammonium carbonate solutions. Digest the precipitate on a steam-bath or on a hot-plate for 10 minutes, and allow to cool. Filter off the precipitate, and wash it with a little water. Dissolve the precipitate in dilute nitric acid, and evaporate the solution to dryness on a water-bath. Allow to cool, add 25 ml. of anhydrous acetone, and cover with a clock-glass; leave the solvent in contact with the mixed nitrates for 1 hour with occasional agitation. Transfer the residual strontium nitrate to a weighed filter-crucible, wash with more acetone, dry at 100° C., and weigh as Sr(NO₃)₂. Determine the calcium in the filtrate as CaSO₄ (the details are similar to those given under H below).

**Note.** 1. For practice in this analysis, an intimate mixture of known weights of A.R. strontium chloride or carbonate and A.R. calcium carbonate may be used.

**H. Calcium, strontium, and barium.** Although this analysis is hardly suitable for elementary students of gravimetric analysis, it is given here as an illustration of the separation and determination of three similar elements.

Precipitate the three elements as carbonates by the addition of excess of ammonia and A.R. ammonium carbonate solutions. Filter off the precipitate, and wash it with a little hot water. Dissolve the precipitate in dilute nitric acid, and evaporate the solution to dryness on the water-bath; heat for 30 minutes in an air-bath (Section II, 12F or Fig. II, 13, 1) at 135-140° C., and for 30 minutes at 180° C. Extract the powdered residue twice with 2.5-ml. portions of absolute ethyl alcohol, and once with 5 ml. of dry isobutyl alcohol (1). Dissolve the residue in water, evaporate to dryness on the water-bath, and heat as above. Extract again with two 5-ml. portions of isobutyl alcohol. Evaporate the alcoholic filtrates cautiously in a weighed crucible (preferably of the Main-Smith type), and convert the residual calcium nitrate into calcium sulphate as follows. Add 1 or 2 drops of water, then five times the weight of finely powdered A.R. ammonium sulphate, and dry at 100-110° C. for 30 minutes. Place the crucible inside a larger porcelain crucible provided with an asbestos supporting ring (Fig. II, 31, 4) and heat with a small flame until fuming commences, then increase the size of the flame. Continue the heating for ½ hour after all fuming has ceased. Allow the crucible to cool, and weigh as CaSO₄. (Too strong heating—above dull redness—causes loss of sulphur trioxide.)

Dissolve the residue containing the nitrates of strontium and barium in water or in dilute acetic acid, and determine the barium as chromate as detailed in F. Precipitate the strontium in the filtrate as the carbonate (the experimental procedure is similar to that given for calcium in F), filter, and wash with a little hot water; dissolve the precipitate in a small volume of dilute hydrochloric acid and wash the filter with a little hot water. Add slowly a 10-fold excess of dilute sulphuric acid and then a volume of alcohol equal to that of the solution. Complete the determination as in Section IV, 44A, and weigh as SrSO₄. (Here also too strong heating—above dull redness—results in loss of sulphur trioxide.)
Note. 1. Commercial isobutyl alcohol is refluxed over dry baryta or over a little potassium hydroxide pellets, and then fractionated to separate the fraction of boiling point 107–108° C. Two drops should not give a cloudiness when mixed with 5 ml. of pure n-hexane.

I. Sodium and potassium. The potassium in the mixture of chlorides determined as potassium perchlorate and therefrom the equivalent amount of potassium chloride is computed. The sodium is obtained by difference. For experimental details, see Section IV, 48B.

A suitable mixture for practice may be prepared by intimately mixing A.R. sodium and potassium chlorides.
IV, 91. ANALYSES OF COMPLEX MATERIALS *

**ANALYSIS OF BRASS**

**Discussion.** The chief components of the alloy brass are copper and zinc, but small quantities of tin, lead, and iron, and sometimes very small quantities of other elements as well, are usually present. The percentages of the important constituents rarely fall outside the following values:

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>50-90%</td>
</tr>
<tr>
<td>Zn</td>
<td>20-40%</td>
</tr>
<tr>
<td>Sn</td>
<td>0-6%</td>
</tr>
<tr>
<td>Pb</td>
<td>0-2%</td>
</tr>
<tr>
<td>Fe</td>
<td>0-1%</td>
</tr>
</tbody>
</table>

The analysis involves, therefore, the separation and determination of tin, lead, copper, iron, and zinc.

**Outline of procedure.** The sample is treated with nitric acid to precipitate the hydrated tin oxide SnO₂·nH₂O and to bring copper, zinc, iron, and lead into solution: the insoluble stannic acid is filtered off, ignited, and weighed as stannic oxide, SnO₂.† The filtrate from the tin precipitate is evaporated with an excess of sulphuric acid to fumes of sulphur trioxide in order to expel nitric acid. The residual liquid is treated with water and the insoluble lead sulphate is filtered off, and weighed as PbSO₄ after ignition at about 500° C. (see, however, Section IV. 14A). The copper in the filtrate from the lead sulphate is determined electrolytically by deposition on a platinum cathode, or is estimated as cuprous thiocyanate, Cu₂(CNS)₂.† The solution from which the copper has been separated is treated with brome water or with nitric acid to oxidise iron to the ferric state, and this metal is separated from the zinc by double precipitation with ammonia solution: the ferric hydroxide is ignited and weighed as Fe₂O₃. Finally, the zinc is precipitated as zinc ammonium phosphate, and weighed either as zinc ammonium phosphate, ZnNH₄PO₄, or, after ignition, as zinc pyrophosphate, Zn₂P₂O₇.

An alternative procedure for the electrolytic determination of lead by deposition as lead dioxide at the anode is described. If any antimony is present, it will be weighed with the tin; any aluminium present will separate with the iron.

Details for the analysis of brass by electrolytic methods utilising controlled potential at the cathode are given in Section IV, 89D.

* Space does not permit the inclusion of the experimental details for more than a few typical complex materials. For an excellent and authoritative account of many others the reader is referred to Lundall, Hoffmann, and Bright, *Chemical Analysis of Iron and Steel* (J. Wiley, 1931). This treatise contains details for, *inter alia*, iron ores; manganese ores; chrome ores; fluorspar; refractories of high alumina content and bauxite; slags; moulding sands; iron and coke; sphaguleisen, ferromanganese and manganese metal; ferrosilicon and refined silicon; ferrochromium and chromium metal; ferrovanadium; ferromolybdenum and calcium molybdate; forrotungsten; ferrocobalt and cobalt metal; ferrotitanium; ferroaluminaum and ferrotantalum; and ferroboron. Standard reference works dealing with the analysis of complex materials include W. D. Scott and N. H. Furman, *Standard Methods of Chemical Analysis*, Vols. I and II (D. Van Nostrand Co.; The Technical Press, Ltd., 1930); J. W. Mellor and H. W. Thompson, *A Treatise on Quantitative Inorganic Analysis* (C. Griffin, 1938); Lunge and Keane, *Technical Methods of Chemical Analysis*, Second Edition, four volumes (Gurney & Jackson, 1954–40); *A.S.T.M. Methods of Chemical Analysis of Metals* (American Society for Testing Materials, 1910 Race Street, Philadelphia 8, Pa., 1946); and E. C. Pigott, *The Chemical Analysis of Ferrous Alloys and Foundry Materials* (Chevening and Hall, 1942).

† Tin in brass, bronze, etc., may also be determined with phenylarsonic acid (see Section IV, 220).
Procedure. If the sample, which should be in the form of drillings or turnings, is not quite clean and dry, wash it with a little ether, and dry it by exposure to air on a watch-glass for a short time.

(a) Tin. Weigh out accurately about 1 g. of the brass (1) into a 150-ml. beaker, add 10 ml. of water followed by 15 ml. of concentrated nitric acid; keep the beaker covered with a clock-glass or, better, a Fisher "speedyvap" beaker-cover. When the vigorous reaction is over, evaporate on a water-bath to a volume of 5–10 ml., but not to dryness. The evaporation should require at least an hour to ensure that all the stannic acid has precipitated (2); longer digestion does no harm. Dilute to 50 ml., and heat on the water-bath for 10–20 minutes in order that all soluble salts may dissolve. Then add one Whatman "accelerator," and stir. Filter hot through a small Whatman No. 42 or 542 paper, and collect the filtrate (i) in a 150-ml. beaker. (If the filtrate is not clear, re-filter it, and add more macerated filter-paper if the precipitate persists in running through.) Wash the precipitate at least ten times with hot 1 per cent nitric acid solution. Reserve the filtrate and washings. Fold up the filter-paper and its contents into a weighed porcelain crucible, dry and char the filter at as low a temperature as possible, and finally ignite the residue for 30 minutes over a Meker or similar type burner under good oxidising conditions (compare Section IV, 22A). Allow to cool in a desiccator and weigh. Repeat the ignition until constant weight is obtained.

Calculate the percentage of tin in the sample.

If the residue is coloured, foreign oxides are present. The amount of stannic oxide present may be determined by the excellent ammonium iodide method (Section IV, 22A) or, less rapidly, by the following procedure. Mix the weighed residue with eight times its weight of a mixture of equal parts pure sodium carbonate and pure sulphur, cover the crucible with a lid, and heat with a low flame in the fume cupboard until the sulphur ceases to burn from under the crucible cover. Allow to cool, and then place the crucible and its cover in a beaker containing sufficient water to cover both, and warm to dissolve the melt. (During this process sodium polysulphide is formed, which reacts with the stannic oxide to give the soluble sodium thiosulphate, Na₂SnS₄, and forms insoluble sulphides with the other metals. The latter sulphides, particularly that of copper, are appreciably soluble in polysulphide solutions, but not in solutions of normal sulphides; hence it is necessary to decompose the polysulphide by the addition of sufficient sodium sulphite to form the colourless sulphide, for example:

$$Na_2S_2 + Na_2SO_3 = Na_2S_2O_3 + Na_2S$$

After the melt has dissolved, remove the crucible and lid from the solution, and wash them free from the adhering solution. Then add excess of sodium sulphite solution, and boil for 10–15 minutes. Filter off the residue, which may contain the sulphides of copper, lead, and iron, through a quantitative filter-paper, wash with 0.1 M colourless ammonium sulphide solution, and ignite in a weighed porcelain crucible. The weight of the ignited residue, which may consist of CuO, PbO, and Fe₂O₃, is subtracted from the weight of impure stannic oxide. The ignited residue should be dissolved in 1–2 ml. of 1 : 1 nitric acid, and added to the main filtrate containing the copper, lead, and zinc.

Notes. 1. The determination should be conducted in duplicate. Ridgdales’s "Brass No. 5e" (one of the Analysed Samples for Students) is suitable for this estimation.
2. If no precipitate has appeared at the end of 1 hour, no appreciable quantity of tin is present.

(b) Copper and lead. There are three alternative methods of dealing with the main filtrate and washings from the tin separation (i). In Method A the lead is separated and weighed as lead sulphate, and the copper is separated and weighed as cuprous thiocyanate. In Method B the lead is separated as lead sulphate, and the copper determined electrolytically. In Method C both the lead and copper are determined electrolytically, the lead as lead dioxide at the anode, and the copper as metallic copper at the cathode.

Method A. Add to the main filtrate (i) from the metastannic acid or, if tin was absent, to the nitric acid solution of the brass, 3–4 ml. of concentrated sulphuric acid, and evaporate the solution carefully (e.g., on a low-temperature hot-plate) until white fumes are evolved. Allow the solution to cool, wash down the sides of the beaker (or the casserole, if employed) with 10–20 ml. of water, and again evaporate to white fumes in order to ensure the expulsion of all the nitric acid. Cool, add 25 ml. of water cautiously, heat nearly to boiling, and stir for several minutes until all soluble salts pass into solution. Then add 50 ml. of water, stir thoroughly, and allow to stand for at least 1 hour. Filter off the precipitate through a weighed silica (Vitreosil) or porous-porcelain filter-crucible, and wash thoroughly with cold 1 : 50 sulphuric acid. Reserve the filtrate and washings (ii). Ignite the lead sulphate to constant weight at 500–600° C. (see Section IV, 14A, in which other methods for weighing the PbSO₄ are described).

Calculate the percentage of lead.

Evaporate the filtrate (ii) from the precipitation of lead sulphate to about 50 ml., almost neutralise the free acid with 1 : 1 ammonia solution, and precipitate the copper as cuprous thiocyanate (Section IV, 19A). Reserve the filtrate and washings (iii) for the determination of iron and zinc. Weigh as Cu₃(ONO₂)₂ after drying at 110–120° C.

Calculate the percentage of copper.

Method B. Determine the lead as lead sulphate as described under Method A. Concentrate the filtrate and washings (ii) from the lead sulphate to about 75 ml., add 4 ml. of concentrated ammonia solution to reduce the acidity, and then 2 ml. of concentrated nitric acid, followed by 1 drop (not more) of 0.1 N-hydrochloric acid. Estimate the copper electrolytically; use the slow or rapid method described in Section IV, 78. Keep the combined solution and washings (iii') after the deposition of copper for the determination of iron and zinc.

The solution (iii') may contain a small amount of copper. Test an aliquot portion, say 2 ml., by passing hydrogen sulphide into it for a few minutes. If only white sulphur is formed, no copper is present: boil off the hydrogen sulphide and return the test solution to the main filtrate. If a dark precipitate is formed, treat the entire solution with hydrogen sulphide, filter through a small filter-paper, wash with 1 per cent ammonium nitrate solution, and ignite to the oxide in a weighed porcelain crucible. Add the weight of copper contained in the cupric oxide to the weight obtained on the electrode. Evaporate the filtrate to remove hydrogen sulphide (iii), and use it for the determination of iron and zinc.

Method C. Evaporate the filtrate and washings from the metastannic acid (i) to 50–75 ml. Transfer quantitatively to an electrolytic
beaker of 150 ml. capacity, add 1·5 ml. of concentrated nitric acid for each 10 ml. of solution, and then 0·3 ml. of concentrated sulphuric acid (to make the deposit more adherent). Introduce two clean and weighed electrodes into the solution. These may consist of a platinum-gauze electrode (Fig. IV, 77, 7, a), which is connected to the positive terminal of the source of current, and a heavy platinum wire spiral (Fig. IV, 77, 7, f) or a platinum-gauze electrode (Fig. IV, 77, 7, b), which is connected to the negative terminal and therefore acts as cathode. Alternatively, Sand’s electrodes (Fig. IV, 77, 8, or Fig. IV, 77, 9), similarly connected, may be used. When all is ready, bring the 150-ml. beaker containing the solution beneath the electrodes, and adjust the height so that the electrodes extend nearly to the bottom, and the anode is at least three-quarters immersed. Switch on the current, and adjust the resistance to give 1·5-2 amps. at 2 volts (4). Electrolyse for 1·5 hours (5). Test for completeness of deposition by adding about 20 ml. of water, and observing whether any deposit is formed on the freshly immersed gauze or stem of the anode when the electrolysis is continued for 15-20 minutes. When the electrolysis is complete, lower the beaker gently or slowly raise the electrodes out of the solution whilst rinsing the electrodes thoroughly by a stream of water from a wash-bottle, and take care that all the washings fall without loss into the electrolytic beaker; the current should not be interrupted during the washing. When the electrodes are out of the solution and have been washed, turn off the current. Rinse the anode well in a beaker of water, then with acetone to remove water. Dry the anode at 120° C., cool in a desiccator, and weigh (compare Section IV, 79). Calculate the percentage of lead. Clean the electrode as described in Section IV, 77.

Some copper may have been deposited on the cathode. If this is the case, place the cathode in the electrolysed solution, and allow it to stand therein until the copper has been dissolved off. Then remove the cathode, rinse it with water, and reserve the solution for the determination of copper.

For the estimation of copper, it is necessary first to remove the large excess of nitric acid present in the solution. Add 3 ml. of concentrated sulphuric acid, and evaporate the solution until fumes of sulphur trioxide appear. Cool, dilute with water to 75-100 ml., add 1 ml. of concentrated nitric acid, 1 drop (not more) of 0·1N-hydrochloric acid, and determine the copper as described in Section IV, 78. Calculate the percentage of copper. Reserve the liquid and washings (iii).

Notes. 3. Nitric acid increases the solubility of lead sulphate, and hence must be completely removed.

4. Excellent results are obtained by electrolyzing overnight with 0·5 amp. at 2 volts.

5. If a trace of manganese is present, it will be oxidised to permanganic acid; this colours the solution, but causes no interference.

(c) Iron. The exact procedure will depend upon whether the copper has been separated electrolytically (Method B) or as cuprous thiocyanate (Method A). In the former case the iron will be present in the ferrous state. In the latter case the excess of thiocyanate and sulphite must be removed by evaporation with nitric and hydrochloric acids, which treatment also removes ammonium salts.
Gravimetric Analysis

Method D (copper separated electrolytically). Heat the solution (iii) from the electrolysis to boiling, add 3–4 ml. of saturated bromine water or 1 ml. of concentrated nitric acid, and boil for 2–3 minutes. Add concentrated ammonia solution until a precipitate is obtained, and then 10 ml. in excess. Allow the precipitate to settle, filter it through a small filter-paper into a 400-ml. beaker, and wash the precipitate three times with 1:100 ammonia solution. Replace the 400-ml. beaker by the beaker in which the precipitation was made. Pour 20 ml. of hot 1:3 hydrochloric acid through the filter to dissolve the precipitate, wash the filter first with 1:100 hydrochloric acid and then with water to remove acid. Precipitate the iron in the filtrate as before, using 5 ml. excess of concentrated ammonia solution. Filter the precipitate through the same filter-paper into the first filtrate, and wash the precipitate thoroughly with hot water containing a little ammonium nitrate and a drop or two of concentrated ammonia solution. Reserve the combined filtrates (iv) for the determination of zinc. Ignite the precipitate to ferric oxide (Section IV, 8) and weigh. Calculate the percentage of iron.

Method E (copper separated as cuprous thiocyanate). To the filtrate from the thiocyanate precipitation (iii) add 35 ml. of concentrated nitric acid and 15 ml. of concentrated hydrochloric acid, and evaporate the solution nearly to dryness. Treat the cold residue with 3 ml. of concentrated hydrochloric acid, warm to dissolve the residue, and dilute to 50–75 ml. If there is a precipitate (silica), filter it off on a small filter-paper, and wash thoroughly with 1:100 hydrochloric acid. Determine the iron in the solution as in Method D.

(d) Zinc. This constituent of brass is usually determined by precipitation as zinc ammonium phosphate, which is subsequently ignited to and weighed as zinc pyrophosphate. Excessive amounts of ammonium salts must be removed by oxidising them with hydrochloric and nitric acids. If the thiocyanate method for copper was used, the ammonium salts were removed before the iron was separated. If, however, the lead or copper was determined electrolytically, the solution will contain a considerable quantity of ammonium salts. Remove them as follows. To the filtrate from the ferric hydroxide (iv) add 25 ml. of concentrated hydrochloric acid and concentrated nitric acid, and evaporate the solution to dryness or to fumes of sulphur trioxide. Treat the cold residue with 3 ml. of concentrated hydrochloric acid, warm for a few minutes, dilute with water to 50 ml., and filter off any silica which may have separated, collecting the filtrate in a 400-ml. beaker.

Transfer the filtrate quantitatively to a 250-ml. volumetric flask, make up to the mark, and shake well. Remove 100 ml. of the solution,* nearly neutralise with ammonia solution, add 5 g. of ammonium chloride, 10 ml. of 2N-sodium acetate, and dilute to 140 ml. Heat on the water-bath and, when hot, treat with 10 ml. of 10 per cent A.R. ammonium phosphate \((\text{NH}_4)\text{H}_2\text{PO}_4\) added slowly from a pipette or burette. Complete the determination as described in Section IV, 34A. Weigh the zinc first as \(\text{ZnNH}_4\text{PO}_4\) after drying at 105°C for about 1 hour, and then as \(\text{Zn}_2\text{P}_2\text{O}_7\) after ignition. Calculate the percentage of zinc. Finally, sum up the percentages of tin, lead, copper, iron, and zinc.

* This volume contains about 0.1 g. of Zn.
Quantitative Inorganic Analysis

**Note.** If the estimation of zinc has been spoilt because of some accident, it is desirable in a repeat analysis to avoid the time required for the separation of the other metals. The following method is applicable in the presence of large amounts of copper and small amounts of tin and lead, and is based upon the use of the tartrate ion to prevent the precipitation of the phosphates of these metals.

Dissolve 1 g., accurately weighed, of brass in 30 ml. of 1:1 nitric acid, and exactly neutralise the solution with 1:5 ammonia solution, using litmus-paper as indicator. Heat the solution to about 90° C., add 25 g. of ammonium tartrate dissolved in 75 ml. of water, heat again to 90° C., and add slowly and with constant stirring a solution of 7 g. of A.R. (NH₄)₂HPO₄ in 35 ml. of water. Keep the solution at 80-90° C. for 1 hour, decant the supernatant liquid through a quantitative filter-paper, transfer the precipitate to the paper, and wash it with 1 per cent ammonium tartrate solution. Dissolve the precipitate in 1:3 hydrochloric acid, and wash the filter first with 1 per cent hydrochloric acid and finally with water. Neutralise the filter and washings very carefully with 1:5 ammonia solution, using litmus-paper, add 15 g. of ammonium tartrate dissolved in 50 ml. of water, and re-precipitate the zinc with ammonium phosphate.* Filter the precipitate through a weighed sintered-glass or porous-porcelain filter-crucible, and wash it with cold water. Dry at 100-105° C., and weigh as zinc ammonium phosphate, ZnNH₄PO₄. (Section IV, 84A).

**IV, 92. ANALYSIS OF BRONZE**

**Discussion.** The chief components of the alloy bronze are copper (60-97%) and tin (1-35%), but small amounts of lead, iron, and zinc may be present. Gun-metal is composed nominally of 90% of copper and 10% of tin, but small amounts of zinc (up to 2%), lead and iron together with traces of phosphorus are always present. Phosphor bronze is similar in general composition to gun-metal, but contains also 0.2-1.5% of phosphorus and, sometimes, small amounts of antimony. English bronze coins contain about 95% of copper, 4% of tin, and 1% of zinc. Aluminium bronze usually consists of about 90% of copper and 10% of aluminium, but may also contain small amounts of iron and other metals. Manganese bronze † contains 55-60% of copper, 30-40% of zinc, 0-2% of tin, 0-1.5% of lead, 1-2% of iron, 0-3% of aluminium, and about 1% of manganese.

Only the analysis of gun-metal and of phosphor bronze will be described here. Experimental details for the analysis of bronze by electrolytic methods utilising controlled potential at the cathode are given in Section IV, 89D. The student should employ his own ingenuity in devising schemes for the analysis of the other bronzes, and should check up the procedure by reference to any of the standard texts on metallurgical analysis.

For the analysis of gun-metal and of phosphor bronze, the experimental details are similar to those already given under Brass (Section IV, 87) for the determination of copper, lead, iron, and zinc. The precipitated metastannic acid will carry down considerable quantities of lead, copper, and iron, and also phosphorus, if present, presumably as stannic phosphate. It is therefore essential to determine the amount of tin present in the impure precipitate. Three methods may be used.

**Method A.** Transfer the precipitate of metastannic acid and macerated filter-paper to a beaker, add 10 ml. of ammonium hydrogen sulphide (NH₄HS) solution, prepared by saturating concentrated ammonia solution with hydrogen sulphide, and warm until the precipitate largely dissolves. The sulphides

* For the most accurate results, it is desirable to dissolve the precipitate and re-precipitate again.

† This is sometimes termed high-tensile brass.
of copper, lead, and iron will remain unattacked. Filter through a hardened quantitative filter-paper, and wash with dilute ammonium hydrogen sulphide water. Dissolve the sulphides on the paper in a small volume of 1 : 1 nitric acid and a little bromine water, and add the solution to the main filtrate from the metastannic acid. Heat the ammonium sulphide solution of tin to boiling until a precipitate commences to form, add 10–15 ml. of concentrated nitric acid, and evaporate to dryness. Add 50 ml. of 1 : 10 nitric acid, heat to boiling, add one Whatman accelerator, filter through a Whatman No. 42 or 542 paper, and wash the precipitate with 1 per cent nitric acid. Complete the estimation as described in Section IV, 91 (a), and weigh the tin as stannic oxide.

Method B. Ignite the impure metastannic acid, and weigh as SnO₂ + P₂O₅ + foreign oxides. Heat the impure weighed oxides with eight to ten times its weight of ammonium iodide at 425–475° C., treat the residue with nitric acid, ignite, and weigh. By subtracting the latter weight from that previously obtained the weight of (SnO₂ + P₂O₅) * is secured. A separate portion is analysed for phosphorus (see below) and the weight of P₂O₅ is subtracted from that of (SnO₂ + P₂O₅). If phosphorus is absent, the method is, of course, much simplified.

Method C. Transfer the precipitate of metastannic acid and macerated filter-paper, preferably dried at 100° C., to a Kjeldahl flask (see Section III, 20), treat with 15 ml. of concentrated sulphuric acid and 5 g. of anhydrous sodium sulphate, and boil gently until the organic matter is destroyed. Dilute cautiously, transfer to a flask fitted with carbon dioxide tubes (Section III, 116, Procedure B), add 2–3 g. of pure lead, excess of concentrated hydrochloric acid, and boil gently in an atmosphere of carbon dioxide. The quadrivalent tin is reduced by the lead to the bivalent state:

\[ \text{SnCl}_4 + \text{Pb} + (2\text{HCl}) = \text{SnCl}_2 + \text{PbCl}_2 + (2\text{HCl}) \]

Allow to cool in a stream of carbon dioxide, and then titrate the stannous tin with standard iodine solution (Section III, 116, Procedure B). From the volume of standard iodine solution required, calculate the percentage of tin.

For the determination of the other metals, treat another sample of the alloy with 1 : 1 nitric acid, etc., and dissolve the impure metastannic acid in a mixture of concentrated sulphuric acid and sodium sulphate as above. Transfer the mixture quantitatively to a beaker, treat cautiously with excess of sodium hydroxide solution followed by excess of sodium sulphide, and digest for some time. The tin thus passes into solution as sodium thiosuannate, Na₂SnS₃, and the sulphides of the other metals (e.g. iron, copper, zinc, etc.) are precipitated. Allow to cool, dilute somewhat, and filter. Dissolve the residue in hot 1 : 2 nitric acid, and add the solution to the main filtrate for the estimation of the other metals.

Analysis of gun-metal. Procedure. Use 0·5–1 g., accurately weighed, of the clean dry alloy (1), and proceed as detailed in Section IV, 91 for Brass. The tin should be determined by any of the three methods given above, but preferably by Method B (2). Finally, sum up the percentages of tin, copper, lead, iron, and zinc in the sample.

Notes. 1. Ridsdale’s “Gun-metal No. 6e” (one of the Analysed Samples for Students) is suitable for this analysis.
2. Perhaps the simplest method for the determination of tin is with phenylarsenic acid (Section IV, 22C).

* See Section, IV, 22A. The phosphorus and stannic tin are volatilised as the iodides. The residue in the crucible may be dissolved in hot concentrated hydrochloric acid, and added to the main filtrate for the determination of the other metals.
Analysis of phosphor bronze. Procedure. Use 0·5–1 g., accurately weighed, of the alloy (3), and follow the method used for gun-metal (4). Determine the phosphorus in a fresh sample as follows.

Weigh out accurately about 2 g. of the sample into a 300–350-ml. conical flask, and dissolve it in 20–25 ml. of aqua regia. When all the alloy has dissolved, add 10 ml. of water, and digest at 90° C. for 10 minutes. Dilute to 50–60 ml., and adjust the temperature to 40–50° C. Add 100 ml. of the ammonium molybdate reagent, previously heated to 40–50° C., slowly and with constant stirring. Complete the estimation as described in Section IV, 65B. Dissolve the precipitated ammonium phosphomolybdate in 5N-ammonia solution, and precipitate the phosphate with magnesia mixture as magnesium ammonium phosphate. From the weight of the latter, calculate the percentage of phosphorus in the sample.

Finally, sum up the percentage of tin, copper, lead, iron, zinc, and phosphorus in the phosphor bronze.

Notes. 3. Riddale’s “Phosphor Bronze, No. 7” (one of the Analysed Samples for Students) or the Bureau of Analysed Samples “Bronze, No. 183A” (one of the British Chemical Standards) is suitable for this analysis.

4. If the ammonium iodide method for tin is used, it must be remembered that both tin and antimony (the latter is often present in samples of phosphor bronze) are volatilised. The tin alone may be determined by the phenylarsenic acid method (Section IV, 22C), or by Method C (above), and hence the antimony content estimated by difference.

IV, 93. ANALYSIS OF NICKEL SILVER

Discussion. The chief components of nickel silver (sometimes termed German silver) are copper (45–75%), zinc (10–25%), and nickel (6–25%); small quantities of iron, lead, tin, and occasionally manganese may also be present. The procedure described allows for the determination of all these elements (with the exception of manganese), and is given in outline only, since most of the essential details have already been given under Brass (Section IV, 91).

Procedure. Weigh out accurately about 0·5 g. of nickel silver * in the form of clean drillings or turnings into a tall 150–200-ml. beaker. Cover the beaker and add slowly 10 ml. of concentrated nitric acid. When the reaction is almost over, warm the mixture on a hot-plate until the alloy has completely dissolved. Add 10 ml. of water, and allow the solution to digest for 10–15 minutes.

(a) Tin. If a white residue is present, it is metastannic acid. This should be separated and determined according to the procedure for tin in Brass (Section IV, 91 (a)).

(b) Lead. Add 2–3 ml. of concentrated sulphuric acid to the filtrate from the metastannic acid or, if tin is absent, to the original solution. Evaporate the solution to a pasty mass and fumes of sulphur trioxide (not to dryness) to remove all the nitric acid. To the cold residue add 30 ml. of water cautiously, stir thoroughly, and allow to stand for at least an hour in order that the precipitation of lead sulphate may be

* The U.S. Bureau of Standards “Nickel silver, No. 157” is suitable for practice in this analysis. “Ounce metal, No. 124h,” which contains ca. 1% of Ni, may also be employed for the determination of Sn, Pb, Cu, Fe, Ni, and Zn.
complete. From this point follow the experimental details given for lead in Method A under Brass.

(c) Copper. The filtrate from the lead sulphate, or the original solution if both tin and lead are absent, is employed for the electrolytic determination of copper. Determine the copper electrolytically; use either the slow or rapid method described in Section IV, 76 (see Method B in Section IV, 81 (b)).

(d) Iron. Add 1 to 2 ml. of hydrogen peroxide to the solution from the copper determination in order to re-oxidise the iron to the ferric state. Add a large excess of concentrated ammonia solution, and heat to boiling. Filter off the precipitated ferric hydroxide, and wash it with hot water. Dissolve the precipitate in the minimum volume of hot 1 : 1 hydrochloric acid, and receive the acid solution in a small beaker. Pour in enough 1 : 2 ammonia solution to re-precipitate the ferric hydroxide, heat to boiling, filter, and wash the precipitate. Add the filtrate and washings to the main filtrate containing the zinc and nickel. Ignite the precipitate, and weigh the ferric oxide.

(e) Nickel. Add hydrochloric acid to the combined filtrates from the determination of iron until neutral (to litmus-paper), and add 5 ml. in excess. Add ammonia solution slowly until the solution is faintly ammoniacal. Ammonium chloride is formed by this neutralisation process, and this must be present in order to hold the zinc in solution; the same result is achieved by adding 5 g. of ammonium chloride to the faintly ammoniacal solution. For each 0·1 g. of nickel that is expected to be present, add to the hot solution 0·5 g. of dimethylglyoxime (1) dissolved in rectified spirit, and make certain that the solution is slightly ammoniacal (add more dilute ammonia solution, if necessary). Allow the beaker to stand on the steam-bath for 15–20 minutes, and test the solution for complete precipitation after the red precipitate has settled out. Complete the determination as described in Section IV, 12A.

Note. 1. Too large an excess of dimethylglyoxime must be avoided, as otherwise it, too, may be precipitated since it is not very soluble in water.

(f) Zinc. Acidify the filtrate from the determination of nickel with concentrated hydrochloric acid, and add 5 ml. of the concentrated acid in excess. Then add 25 ml. of concentrated nitric acid, and evaporate on a hot-plate in the fume cupboard either to dryness or to fumes of sulphur trioxide if much sulphuric acid is present. This evaporation removes the organic matter and the large amount of ammonium salts present in solution. Treat the cold residue with 5 ml. of concentrated hydrochloric acid, warm the mixture for a few minutes, dilute to 50 ml., and, when the salts have dissolved, filter the solution if not perfectly clear. Complete the determination as described for zinc in Brass (Section IV, 91 (d)). Weigh the zinc as both the ammonium phosphate and as the pyrophosphate.

IV, 94. ANALYSIS OF SOLDER

Discussion. Ordinary solder is an alloy of approximately 3 parts of lead and 2 parts of tin, but it usually contains also from 1–3 per cent of antimony as impurity. When such an alloy is disintegrated by nitric acid, the insoluble residue consists of metastannic acid and antimonic acid, together with some co-precipitated lead compound. The ignited residue will consist of
SnO₂ + Sb₂O₃ + PbO. The amount of lead present in the residue is most simply determined by the ammonium iodide volatilisation method (Section IV, 22A); the tin and antimony are volatilised as the iodides, and the lead remains behind as a mixture of oxyiodide and oxide. The residue in the crucible is treated with 2-3 ml. of concentrated nitric acid (a Main-Smith crucible is very suitable for this process), evaporated to dryness on the hot-plate, the nitrate cautiously decomposed, and finally ignited to oxide at a low red heat. The loss in weight gives (SnO₂ + Sb₂O₃). The tin may be determined as in Method 0, Section IV, 92 (antimony does not interfere with this process), and the antimony obtained by difference. The residual PbO in the crucible may be dissolved in a little concentrated hydrochloric or nitric acid, and added to the main filtrate from the metastannic acid. The lead is determined as sulphate (Section IV, 14A) or as chromate (Section IV, 14B); in the latter case, about 12 g. of sodium acetate are added to replace the free nitric acid by acetic acid.

An alternative procedure is to transfer the impure metastannic acid precipitate and filter-paper, preferably dried at 100°C., to a Kjeldahl flask, add a mixture of 12 ml. of concentrated sulphuric acid and 5 g. of potassium hydrogen sulphate, and boil gently until the organic matter is destroyed. The carbonaceous matter from the filter-paper reduces the antimony to Sb⁺. The mixture is evaporated to fumes of sulphur trioxide, allowed to cool, cautiously transferred quantitatively to a conical flask with the aid of about 50 ml. of water, 5 ml. concentrated hydrochloric acid is added, cooled to 10°C., and titrated with standard 0.1N-potassium permanganate (see Section III, 117):

$$5\text{Sb}^{+++} + 2\text{MnO}_4^- + 12\text{H}_2\text{O} = 5\text{H}_3\text{SbO}_4 + 2\text{Mn}^{++} + 9\text{H}^+$$

The percentage of antimony can then be calculated. Excess of concentrated hydrochloric acid is then added, followed by 2-3 g. of pure lead, and the mixture boiled gently in an atmosphere of carbon dioxide (see Method C in Section IV, 92). The quadrivalent tin is reduced by the lead to the bivalent state, and the antimony is precipitated as the metal. The stannous tin is titrated with standard 0.1N-iodine, and from the volume of the latter required the percentage of tin may be calculated (Section III, 117). The procedure is much simplified if antimony is absent, as in the case of a pure solder or a pure lead-tin alloy. Such alloys are available commercially, and are useful for practice in the quantitative separation and determination of lead and tin. Here the amount of lead oxide present in the impure stannic oxide may be determined either by the ammonium iodide process or by the sodium carbonate-sulphur fusion process (Section IV, 91 (a)). The lead is determined in the filtrate from the impure metastannic acid, to which the small amount of recovered lead has been added, as the sulphate.

**Analysis of pure solder or a pure lead-in alloy. Procedure.** Weigh out accurately about 0.5 g. of the finely divided alloy (turnings, drillings, etc.) (1) into a 150-200-ml. beaker, and cover with a clock-glass or Fisher “speedyvap” cover. Add 5 ml. of water, followed by 15 ml. of concentrated nitric acid: keep the beaker covered during the ensuing violent reaction. When the vigorous reaction is over, evaporate on a water-bath to a volume of about 5 ml., but not to dryness. Dilute to 50 ml., heat on a water-bath for 10-15 minutes, then add one Whatman accelerator (or half of an ashless tablet), and stir. Filter through a Whatman No. 42 or 542 paper, and collect the filtrate in a 250-400-ml. beaker. Wash the precipitate at least ten times with 1 per cent nitric acid. Keep the filtrate and washings for the determination of lead. Fold up the filter-paper and precipitate and place it in a
weighed porcelain crucible (best in a Main-Smith crucible), and complete the estimation as described for tin in Section IV, 91 (a). Weigh the impure stannic oxide. Add to the latter about fifteen times its weight of powdered ammonium iodide, and mix the two in the crucible intimately by means of a small spatula. Heat the crucible in an electric crucible or muffle furnace at 425-475° C. for 15 minutes or until no further fumes are evolved. Allow the crucible to cool, remove it, and add 2-3 ml. of concentrated nitric acid. Evaporate gently to dryness, and cautiously decompose the residual nitrate over a small flame. Then ignite at a low red heat to constant weight. The loss in weight gives the weight of pure stannic oxide present in the residue. Calculate the percentage of tin.

Dissolve the residue in the crucible by digestion with a few ml. of concentrated hydrochloric acid, and add it to the filtrate and washings from the metastannic acid. Add 7-8 ml. of concentrated sulphuric acid, and evaporate the solution carefully (e.g., on a low-temperature hot-plate) until white fumes of sulphur trioxide are freely evolved. Complete the determination of lead as sulphate according to the procedure given for lead in Section IV, 91 (b) (Method A). Calculate the percentage of lead.

Note. 1. Ridsdale’s “Solder, No. 11c” (one of the Analysed Samples for Students) is an almost pure lead-tin alloy, and is suitable for this analysis.

IV, 95. ANALYSIS OF A SILVER COINAGE ALLOY

Discussion. Prior to 1920 British silver coins contained from 90 to 95 per cent of silver, the remainder being copper; subsequently the percentage of silver was reduced to 50, and this was alloyed with nickel and copper. Many silver coinage alloys also contain a little zinc; the procedure to be described will therefore permit of the separation and determination of silver, copper, nickel, and zinc.

Procedure. The alloy should be clean and grease-free. If dirty, the surface may be cleaned with a little fine emery paper or cloth, and then washed with dry acetone. The coin or sheet of alloy may be cut with the shears into pieces, each weighing 0.4-0.5 g.

(a) Silver. Weigh out accurately about 0.4 g. of the alloy into a 600-ml. beaker, which is kept covered with a clock-glass. Add 5 ml. of water, and then concentrated nitric acid slowly (5-10 ml.). Warm on a water-bath or upon a low-temperature hot-plate until solution is complete (the minimum quantity of nitric acid required for dissolution should be used). Dilute to 300 ml., heat to 70° C., and add approximately 0.2N-hydrochloric acid dropwise and with constant stirring until precipitation is complete. Complete the determination as in Section IV, 15, and weigh the silver chloride. Reserve the filtrate and washings (i).

(b) Copper. Add 3 to 4 ml. of concentrated sulphuric acid to the combined filtrate and washings (i) from the silver estimation, and evaporate until dense fumes of sulphur trioxide appear. Allow the solution to cool, wash down the sides of the vessel with 10-20 ml. of water, dilute to 100 ml., and almost neutralise the solution with 1:1 ammonia solution. Then add 5 ml. of cold, freshly prepared, saturated sulphurous acid solution, followed by 10 per cent ammonium thiocyan-
ate solution slowly and with constant stirring from a burette until present in slight excess (ca. 10 ml.). Complete the estimation as in Section IV, 19A, and weigh the precipitate as cuprous thiocyanate. Keep the filtrate and washings (ii) for the estimation of nickel and zinc.

(c) Nickel. Evaporate the combined filtrate and washings (ii) to 50 ml., add 35 ml. of concentrated nitric acid and 15 ml. of concentrated hydrochloric acid, and evaporate the solution nearly to dryness. This will destroy the excess of thiocyanate. Rinse the clock-glass, and evaporate to dryness on the water-bath in order to expel the excess of nitric acid. Add 1 ml. of concentrated hydrochloric acid, 150 ml. of water, and 5 g. of ammonium chloride (to retain the zinc in solution), and then 1 : 1 ammonia solution until slightly ammoniacal. Precipitate the nickel as the dimethylglyoxime complex; follow the procedure given under nickel silver (Section IV, 93 (e)).

(d) Zinc. Determine the zinc as the ammonium phosphate and, if time permits, the pyrophosphate exactly as described in Section IV, 93 (f).

Finally, sum up the percentage, of silver, copper, nickel, and zinc (if present).

IV, 96. ANALYSIS OF STEEL

Discussion. Plain carbon steel contains a certain amount of carbon, silicon, sulphur, phosphorus, and manganese. For special purposes, varying amounts of other elements, such as chromium, vanadium, molybdenum, tungsten, titanium, nickel, cobalt, zirconium, and copper are added. Iron itself is rarely determined in steel; only the subsidiary elements are estimated, for these are of great practical importance. Generally a number of methods are available for the determination of each element. The procedure employed will depend upon the object in view; the more accurate methods are usually less rapid. In this book only a selected number of exact methods for determining the most important elements which are found in steel will be described. These, it is hoped, will provide the student with a sound, fundamental knowledge, both theoretical and practical, of the most important features of the accurate analysis of steel. For a more detailed treatment of the subject, the reader should consult the numerous special works on iron and steel analysis (see bibliography at the end of this chapter).

Procedure. A. Carbon. The total carbon in steel is determined by combustion at 1000–1300° C. in an atmosphere of pure oxygen. The gases resulting from the combustion (CO₂, SO₂, and SO₃) are passed through reagents which absorb everything but oxygen and carbon dioxide, and the carbon dioxide is finally absorbed in a U-tube containing a suitable solid reagent (see Section IV, 76).*

B. Phosphorus. This element occurs as phosphide, and must be oxidised to orthophosphate before it can be determined. Weigh out accurately about 3 g. of the steel (1) into a 250-ml. conical flask, add 75 ml. of water, and treat as follows:

* For full experimental details the reader is referred to any of the following books: Landell, Hofmann, and Bright, Chemical Analysis of Iron and Steel (J. Wiley, 1931); Chemists U.S. Steel Corporation, Sampling and Analysis of Carbon and Alloy Steels (Reinhold Publishing Corporation, 1938); Scott and Furman, Standard Methods of Chemical Analysis, 6th Edition (Van Nostrand, 1939); Pass and Kenny, Inorganic Quantitative Analysis (Appleton-Century, 1930); Pigott, The Chemical Analysis of Ferrous Alloys (Chapman and Hall, 1942); Willard and Diehl, Advanced Quantitative Analysis (Van Nostrand, 1943); and A.S.T.M. Methods of Chemical Analysis of Metals 1946.
ml. of 6N (3 : 8) nitric acid, and warm gently on a hot-plate until the solid has dissolved. Then add 20 ml. of 2 per cent potassium permanganate solution, and boil for a few minutes in order to precipitate the manganese dioxide; add more permanganate solution if no precipitate appears. Dissolve the precipitate by adding a freshly prepared solution of sodium sulphite dropwise; boil for a few minutes to expel sulphur dioxide and oxides of nitrogen. Partially neutralise the nitric acid by the addition of 20-25 ml. of 6N-ammonia solution, and then introduce 75 ml. of ammonium molybdate reagent. Stopper the flask with a rubber bung, and shake for 5-10 minutes. Wash off the stopper, and allow to stand for 2 hours, or preferably overnight. Filter off the precipitate of ammonium phosphomolybdate, and wash it moderately with 5 per cent ammonium nitrate solution or with cold dilute nitric acid (1 : 50). Dissolve the precipitate in 20 ml. of 6N-ammonia solution containing 2 g. of citric acid, and collect the filtrate in a 250-ml. beaker. Wash the filter-paper two to three times with 1 : 20 ammonia solution, and finally twice with 1 : 20 hydrochloric acid. Add a few drops of methyl red, and acidify the solution with dilute hydrochloric acid. Next add 25 ml. of magnesia mixture (Section IV, 20B, Note 2). Complete the estimation as in Section IV, 65B, and weigh the precipitate as magnesium ammonium phosphate, MgNH₄PO₄·6H₂O.

**Note. 1.** Any of the following samples are suitable for this estimation: Ridsdale's "Medium Carbon Steel, No. 2c" (one of the Analysed Samples for Students); the Bureau of Analyzed Samples" Carbon Steel, No. 232 or No. 152" (British Chemical Standards); British Standardised Steel Sample-No. 3 (supplied by the National Physical Laboratory, Metallurgy Department, Teddington, Middlesex, England).

**C. Sulphur.** Two methods for the determination of sulphur in steels are generally employed. In the first, the sulphur is ultimately weighed as barium sulphate, and is the more accurate. In the second, the hydrogen sulphide evolved by the action of hydrochloric acid is absorbed in an ammoniacal solution of cadmium chloride or of zinc sulphate, and the precipitated sulphide is titrated in an acid medium with standard iodine solution in the presence of starch as indicator. The volumetric method tentatively assumes that the sulphur is present in the form of sulphide, and that all the sulphur is evolved as hydrogen sulphide upon treatment with acid. This is not always entirely the case, so that the procedure is not as accurate as the gravimetric method, but owing to its greater rapidity it is very often used, particularly for routine work. The accuracy of the method may be increased by standardising the iodine solution against a steel of known sulphur content similar in characteristics to the sample being analysed. For further details, the student should consult any of the books listed in the footnote to "A. Carbon."

Sulphur may also be determined by burning a known weight of the steel in a stream of oxygen (furnace temperature about 1425° C.), absorbing the oxides of sulphur (ca. 93 per cent SO₂) in dilute neutral hydrogen peroxide solution, and titrating the sulphuric acid formed with standard sodium hydroxide solution, using methyl red as indicator.*

In another method † the gaseous products are absorbed in a solution

† A.S.T.M. Methods of Chemical Analysis of Metals, 1946, p. 91.
containing starch, potassium iodide, and very dilute hydrochloric acid: a small amount of standard potassium iodate solution is added to produce a blue colour. As the stream of gas bubbles through this solution, the standard potassium iodate solution is added continuously from a burette at such a rate so as to maintain as nearly as possible the same intensity of blue colour:

\[
\begin{align*}
KIO_3 + 5KI + 6HCl & = 3I_2 + 6KCl + 3H_2O \\
SO_2 + I_2 + 2H_2O & = H_2SO_4 + 2HI
\end{align*}
\]

When calculating the result, cognisance is taken of the fact that at about 1425°C, most steels yield approximately 93 per cent of their sulphur as sulphur dioxide.

**Procedure. Gravimetric method.** Weigh out accurately about 5 g. of the steel (1) into a covered 350-ml. conical flask or beaker. Add 50 ml. of pure concentrated nitric acid. Warm, if necessary, on the steam-bath until the sample is dissolved: the cautious addition of up to 5 ml. of concentrated hydrochloric acid will facilitate solution in cases where difficulty arises. When the sample has dissolved, add 1 g. of A.R. sodium chloride (2), evaporate to dryness, and bake gently on a hot-plate for about 10 minutes (3). Cool, add 25 ml. of concentrated hydrochloric acid, and evaporate the solution almost to dryness (i.e., until syrupy). Then add 5 ml. of concentrated hydrochloric acid, 25 ml. of water, and 5 g. of A.R. (sulphur-free) zinc granules (4). Warm on the steam-bath until all the ferric iron has been reduced and evolution of hydrogen ceases. Filter the solution through a small filter, and collect the filtrate in a 250–400-ml. beaker. Wash the residue with small volumes of 1:50 hydrochloric acid (use about 50 ml. in all). Warm the filtrate and washings to 70°C, and precipitate the sulphate by the slow addition of 10 ml. of hot 10 per cent barium chloride solution. Allow to stand overnight, and filter through a Whatman No. 40 or 540 filter-paper. Wash first with a solution containing 10 ml. of concentrated hydrochloric acid and 1 g. of barium chloride per litre, then with cold water to remove chlorides (50–75 ml.). Ignite and weigh the precipitate as barium sulphate according to the procedure of Section IV, 6. For the best results a platinum crucible should be used; the ignited residue should be treated with 1 drop of concentrated sulphuric acid and 1 ml. of pure (e.g., A.R.) hydrofluoric acid, evaporated to dryness, and ignited again to constant weight.

**Notes.** 1. Any of the following samples are suitable for practice in this estimation: Ridsdale's "Medium Carbon Steel, No. 2c" (one of the Analyzed Samples for Students); the Bureau of Analyzed Samples "Carbon Steel, No. 161R or No. 215" (British Chemical Standards); British Standardised Steel Sample, No. 1 or No. 2 (supplied by the N.P.L.).

2. The addition of sodium chloride will fix sulphuric acid as sodium sulphate.

3. The nitric acid must be removed, because of the serious co-precipitation of nitrates in the subsequent precipitation of barium sulphate (see Section IV, 6).

4. Ferrous and zinc chlorides are not carried down to any serious extent by barium sulphate: ferric chloride is co-precipitated if present in appreciable concentration.

**D. Silicon.** The steel may be dissolved in nitric acid, dilute sulphuric acid, or in a mixture of nitric and sulphuric acids; the silica is rendered insoluble and purified with the aid of hydrochloric acid as already
described (Section IV, 70). The best procedure is to employ 60−70 per cent perchloric acid for dehydrating the silica; with this acid the silica is more readily filtered, and is practically free from impurities, since the perchlorates of the metals are generally very soluble. Both methods will be given.

**Method 1.** Weigh out accurately about 5 g. of the steel (1) into a porcelain dish or casserole, and cover it with a clock-glass. Add carefully 100 ml. of dilute sulphuric acid (1 : 3), and warm gently until reaction ceases. When the reaction is over, remove and rinse the clock-glass and evaporate the solution carefully until dense fumes of sulphur trioxide are evolved for 2−3 minutes but no longer, since insoluble sulphates may be formed; take precautions to avoid spattering. Cool to 50−60° C., and add 100 ml. of warm water (40−50° C.) all at once. Stir until all salts have dissolved, warming gently if necessary. Filter immediately through a Whatman No. 40 or 540 paper; use a rubber "policeman" to dislodge any precipitate adhering to the sides of the vessel. Wash the precipitate with hot hydrochloric acid (1 : 20) until all iron salts have been removed (so that no injury may result to the platinum crucible), and finally with a little hot water. Place the paper and precipitate in a weighed platinum crucible, heat slowly to char the paper and burn off the carbon, and then apply the full heat of a Meker or Fisher burner for 15−30 minutes (or heat in an electric muffle furnace at 1100−1150° C.). Cool in a desiccator and weigh. In accurate work it is best to treat the residue as follows: add enough dilute sulphuric acid (1 : 1) to moisten the precipitate and then 3−5 ml. of concentrated hydrofluoric acid. Evaporate carefully, preferably by employing a larger crucible as an air-bath, until the sulphuric acid has been expelled (compare Section IV, 70A), ignite for 10−15 minutes, cool in a desiccator, and weigh. The loss in weight represents silica.

**Method 2.** Weigh out accurately 2·5 g. (Si content > 0·5%) or 5 g. (Si content < 0·5%) of the steel into a 400-ml. beaker, provided with a clock-glass cover. Add 50 ml. of dilute nitric acid (1 : 1) and warm cautiously until solution is complete. Rinse and remove the glass cover, add 40 or 60 ml. of A.R. 60−70 per cent perchloric acid (DANGER, see Section IV, 70) according to the weight of sample taken, and evaporate on a hot-plate to copious fumes of perchloric acid. Replace the clock-glass on the beaker, and heat so that the perchloric acid condenses and runs down the sides of the beaker for 15 minutes. Do not allow the contents of the vessel to become pasty or solid, since if this occurs the separation of silica is always incomplete; add more perchloric acid if necessary. Allow to cool somewhat, dilute with 125 ml. of hot water, stir until all salts have dissolved, and crush any lumps of silica with a flattened glass rod; heat gently if necessary. Filter immediately and complete the determination as in Method 1: the washing of the filter-paper must be thorough, for residual perchloric acid held in the silicic acid tends to cause slight loss of material upon subsequent ignition.

If the silicon content exceeds 0·5 per cent, a second dehydration is desirable; no more perchloric acid need be added for this dehydration.

**Note.** 1. The same sample as was employed for the estimation of sulphur may be employed for practice in this determination. If the "British Standardised Steel Sample, No. 12" ("Cast Iron Standard Sample) is utilised, the quantity may be reduced to 1−2 g.
E. Manganese. This element is usually determined by the bis­muthate or the persulphate process (Section III, 60). Excellent results are obtained by potentiometric titration in pyrophosphate solution with standard potassium permanganate solution (Section IV, 12).

For practice in this determination, the student may employ the same sample of steel as was used for the estimation of silicon.

F. Nickel. This element is generally determined by precipitation with dimethylglyoxime (Section IV, 12B). Precipitation with dicyandiamide sulphate also gives satisfactory results (Section IV, 32D).

G. Chromium. All methods for determining chromium in alloys are based upon the oxidation of the element to the chromate, followed by the determination of the latter by volumetric methods. Chromium is usually associated with vanadium in steels, and a procedure for the estimation of both elements is given under Vanadium. Two methods for chromium will be described here; they are applicable both to Chromium–vanadium steels (tungsten absent) and to ferro-chromium.

Method I. Weigh out accurately about 2 g. of the chromium–vanadium steel (1), in the form of turnings or drillings, into a 600-ml. beaker and add 60 ml. of a H₂SO₄-H₃PO₄ mixture (prepared in quantity by adding slowly and with stirring 160 ml. of 1 : 1 sulphuric acid to 300 ml. of water, cooling, and mixing with 40 ml. of syrupy phosphoric acid) (2). Heat until effervescence nearly ceases, then add cautiously 3–5 ml. of concentrated nitric acid (3), and boil until solution is complete and oxides of nitrogen are expelled. Dilute to about 300 ml. with hot water, add a few pieces of porous porcelain to prevent bumping at a later stage, followed by 5–10 ml. of dilute silver nitrate solution (5 g. of AgNO₃ per litre), and 15–20 ml. of a freshly prepared 10 per cent solution of ammonium persulphate. Boil the solution (4) for 10 minutes. If a permanganate colour, due to the presence of manganese in the steel, does not develop within a few minutes, add more silver nitrate and ammonium persulphate solution, and boil again for 10 minutes to decompose the excess of persulphate (5). Use either of the following procedures to reduce the permanganic acid still present.

A. Add 0.5 per cent sodium azide solution dropwise from a burette to the boiling solution (fume cupboard!) until all permanganic acid has been reduced (6). Boil for 2–3 minutes to remove the slight excess of hydrazoic acid. A reddish colour may develop in the solution during the boiling; this can be disregarded. A large excess of sodium azide should be avoided. B. Add 5 ml. of dilute hydrochloric acid (1 : 3) to the hot solution and boil for 10 minutes (7) after the permanganate colour, or any precipitated manganese dioxide, has disappeared. If any manganese dioxide remains, add 2–3 ml. more of the dilute hydrochloric acid, and boil as before.

Cool the solution obtained by either procedure A or B, dilute to 400 ml. with boiled-out water, add 0·1N-ferrous ammonium sulphate until all the yellow colour disappears, thus indicating the complete reduction of the chromic and vanadic acids (8), and add a further 10 ml. : note the exact volume of ferrous solution added. Stir and titrate the excess of ferrous solution with standard 0·1N-potassium permanganate until a faint pink colour is obtained which persists for one minute with constant stirring (9). From the volume of ferrous ammonium sulphate solution used, calculate the percentage of chromium in the steel.
Gravimetric Analysis

The end point may also be determined potentiometrically. Treat the solution obtained by method A or B with 25 ml. of dilute sulphuric acid (1:1), and cool to room temperature or below. Titrate with 0·1N-ferrous ammonium sulphate solution using a platinum-saturated calomel or a platinum-tungsten electrode system (see Chapter VI). The vanadium content is included in this titration; if present, it must be determined independently and subtracted from the apparent chromium value.

It must be emphasised that the above procedure is applicable to chromium-vanadium steels containing little or no tungsten. If the proportion of tungsten is small, a residue of tungstic acid will be present after the nitric acid treatment; it should be filtered off and washed thoroughly with dilute nitric acid. For larger proportions of tungsten, it is best to hold the tungsten in solution whilst the determination of chromium is carried out. The steel is dissolved directly in sulphuric acid and the residual metallic tungsten brought into solution by the addition of concentrated hydrofluoric and nitric acids, followed by boiling and vigorous stirring or swirling of the solution. The tungsten is present in the resulting green solution as fluorotungstic acid $\text{H}_2\text{WOF}_4$.

After dilution, the persulphate-silver nitrate procedure may be applied.

Notes.

1. The Bureau of Analysed Samples "Chromium-Vanadium Steel No. 224" is suitable for practice in this determination. If ferro-chromium is used (see Method 2), only about 0·25 g. should be weighed out.
2. The object of the phosphoric acid is to decolourise the iron salts that are formed.
3. Evaporation with nitric acid is necessary in order to break up the black insoluble carbides of chromium and vanadium which are left after the non-oxidising attack with the mixed acids.
4. Persulphate oxidises chromium in the presence of silver nitrate (catalyst)

$$\text{Cr}_2(\text{SO}_4)_3 + 3(\text{NH}_4)_2\text{S}_2\text{O}_8 + 8\text{H}_2\text{O} = 2\text{H}_2\text{CrO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + 6\text{H}_2\text{SO}_4,$$

any unoxidised vanadium

$$2(\text{VO})\text{SO}_4 + (\text{NH}_4)_2\text{S}_2\text{O}_8 + 4\text{H}_2\text{O} = 2\text{HVO}_3 + (\text{NH}_4)_2\text{SO}_4 + 3\text{H}_2\text{SO}_4,$$

and manganese

$$2\text{MnSO}_4 + 5(\text{NH}_4)_2\text{S}_2\text{O}_8 + 8\text{H}_2\text{O} = 2\text{MnO}_2 + 5(\text{NH}_4)_2\text{SO}_4 + 7\text{H}_2\text{SO}_4.$$

5. Partial decomposition of the permanganic acid may also occur:

$$4\text{HMnO}_4 + z\text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + y\text{H}_2\text{O} + 3\text{O}_2$$

6. Sodium azide reacts with the hot acid solution containing permanganic acid as follows:

$$2\text{HMnO}_4 + 10\text{HN}_3 + 2\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + 15\text{N}_2 + 8\text{H}_2\text{O}$$

Hydrazoic acid, derived from the slight excess of sodium azide, is very poisonous and also very volatile. It is therefore readily removed by boiling for a few minutes in the fume cupboard.

7. The permanganic acid is also reduced by heating with hydrochloric acid:

$$2\text{HMnO}_4 + 14\text{HCl} = 2\text{MnCl}_2 + 5\text{Cl}_2 + 8\text{H}_2\text{O}$$

Boiling removes the chlorine formed in the reaction. The precipitated silver
Quantitative Inorganic Analysis

chloride acts as a catalyst in this reduction; it has no effect upon the estimation and may be left in the solution.

8. \[2H_2CrO_4 + 6H_2SO_4 + 6FeSO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O\]
   \[2HV_2O_3 + 3H_2SO_4 + 2FeSO_4 = 2(VO)SO_4 + Fe_2(SO_4)_3 + 4H_2O\]

In the back titration with permanganate solution, the reduced vanadium is re-oxidised:

\[2KMnO_4 + 10(VO)SO_4 + 22H_2O = K_2SO_4 + 2MnSO_4 + 10H_3VO_4 + 7H_2SO_4\]
as is also the excess of ferrous solution. It is therefore clear that the sole function of the permanganate solution is to react with the excess of ferrous iron and of the vanadium that has been reduced, and consequently if the permanganate and ferrous solutions are of equal normality, the difference between the volumes used represents the volume of ferrous ammonium sulphate solution required to reduce the chromic acid formed from the chromium present in the sample.

Method 2. Weigh out accurately about 0.2 g. of ferro-chromium (10) into a tall 600-ml. beaker, add 20 ml. of concentrated hydrochloric acid, cover with a clock-glass, and heat for 15 minutes. Add 20-25 ml. of pure 60-70 per cent perchloric acid (DANGER, see Section IV, 70), and boil for 30 minutes after the hydrochloric acid has been expelled. Cool somewhat, add a few ml. of water to dissolve the chromium trioxide, and re-oxidise by boiling for 15 minutes after the water is expelled. If any undissolved particles of metal remain, pour off most of the solution, add a few ml. of 60-70 per cent perchloric acid to the residue, and boil until solution is complete. Add the main decanted liquid, evaporate off the water, and boil for 5 minutes. Cool somewhat, add an equal volume of water, and boil for 3 minutes to remove chlorine. Cool, dilute to 200 ml., add excess of 0.1N-ferrous ammonium sulphate, and titrate back the excess of the latter with standard 0.1N-potassium permanganate, allowing 1 minute for the end point.

Note. 10. The Bureau of Analysed Samples “Ferro-Chromium, No. 203” (one of the British Chemical Standards) is suitable for this estimation. If Cr-V steel is used, weigh out accurately about 2 g., and dissolve it directly in 20-25 ml. of 60-70 per cent perchloric acid. With ferro-chromium, the chromium trioxide initially formed tends to cover the particles of ferro-chromium and thus prevent complete oxidation.

H. Vanadium. The determination of this element is most often required for chromium-vanadium steels; two methods will be described.

Procedure A. The steel is dissolved and treated exactly as in G (Method 1) for the estimation of chromium in chromium-vanadium steel until the solution has been titrated with standard 0.1N-potassium permanganate. Then proceed as follows.

Add a moderate excess of 0.1N-ferrous ammonium sulphate (ca. 10 ml., but note exact volume) (1) to the cold solution. Then introduce 8 ml. of a freshly prepared 15 per cent ammonium persulphate solution, and stir for 1 minute to oxidise the excess of ferrous salt (2). Titrate with standard 0.1N-potassium permanganate until a pink colour persists for 1 minute after stirring (3). Calculate the percentage of vanadium in the alloy.
Notes. 1. The excess of ferrous solution reduces the vanadium to the quadrivalent state:

\[2\text{HVO}_3 + 3\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 = 2(\text{VO})\text{SO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}\]

No changes occur in the valencies of the other elements.

2. The only reaction which occurs in the cool solution in the absence of a soluble silver salt is the quantitative oxidation of the excess of ferrous sulphate solution:

\[2\text{FeSO}_4 + (\text{NH}_4)_2\text{S}_2\text{O}_8 = \text{Fe}_2(\text{SO}_4)_3 + (\text{NH}_4)_2\text{SO}_4\]

The net result of the two treatments is the reduction of the vanadium to the quadrivalent state.

3. The reaction is:

\[2\text{Kl}_2\text{InO}_4 + 10(\text{VO})\text{SO}_4 + \text{H}_2\text{SO}_4 + 12\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 10\text{HVO}_3 + 8\text{H}_2\text{SO}_4\]

No significant oxidation of chromium or decomposition of persulphate occurs during the short time allowed for the development of the end point with permanganate in the cold solution.

Procedure B. The chromium and vanadium are first oxidised to chromic and vanadic acids with perchloric acid or as detailed in G. After removal of the excess of oxidising agent, a measured excess of standard ferrous ammonium sulphate solution is added to reduce the chromic and vanadic acids. With the solution cold and strongly acid, the excess of ferrous salt is titrated with standard potassium permanganate solution, using o-phenanthroline as indicator. The reaction between potassium permanganate and vanadyl ions under these conditions (high acidity and low temperature) is so slow that a good end point is obtained. The reason for the repressing influence of the high hydrogen-ion concentration upon the vanadyl–permanganate reaction is evident from the equation:

\[\text{VO}^{++} + 2\text{H}_2\text{O} = \text{VO}_3^- + 4\text{H}^+ + e\]

whilst the potential of the ferrous–ferric system

\[\text{Fe}^{++} = \text{Fe}^{+++} + e\]

is not appreciably affected by the pH of the solution.

After the titration of the excess of ferrous ammonium sulphate solution, the pH of the solution is raised somewhat by the addition of sodium acetate, and the vanadyl ion may then be titrated with standard potassium permanganate solution at 50°C: at this temperature the reaction between the vanadyl ion and permanganate is rapid, and a second sharp end point is obtained with o-phenanthroline as indicator (vanadic acid does not possess a sufficiently high oxidation potential to affect the indicator).

Weigh out accurately about 2 g. of the chromium–vanadium steel (tungsten-free) into a tall-form Pyrex 300-ml. beaker provided with a clock-glass cover, add 20–25 ml. of A.R. 60–70 per cent perchloric acid and warm gently; if the reaction becomes violent, remove the source of heat. After the steel has dissolved, boil gently for 20 minutes. Cool by immersing the beaker in cold water, stir, add 25 ml. of water (rinse the clock-glass), and boil the solution for 3 minutes to remove chlorine. Dilute to 250–300 ml. and cool to room temperature. Add
20 ml. of 6M-phosphoric acid and run in a measured excess of 0.1N-ferrous ammonium sulphate from a burette. Titrate with 0.05N-potassium permanganate, using three drops of o-phenanthroline indicator, until the colour changes from pink to green.

Now add sufficient A.R. sodium acetate trihydrate to react with the perchloric acid remaining in the solution (assume that 5.4 ml. of 70 per cent perchloric acid are required to dissolve and oxidise each gram of steel, and that 1.6 g. of the salt is necessary for each ml. of acid remaining; alternatively, add sodium acetate in small portions to the warm solution until further addition would lead to the formation of a permanent precipitate of ferric phosphate). Heat the solution to 50° C. (use a thermometer) and titrate with the 0.05N-potassium permanganate until the colour changes from pink to green and is permanent for one minute.

Calculate the percentages of chromium and vanadium in the steel.

I. Molybdenum. The most satisfactory method for the gravimetric determination of molybdenum in steel is to precipitate the molybdenum with α-benzoinoxime, and ignite the resultant complex to, and weigh it as, molybdic oxide MoO₃ (see Section IV, 23B).

Weigh out accurately about 1 g. of the molybdenum steel (1) and dissolve it in 50 ml. of 1:6 sulphuric acid; treat the solution with the minimum volume of concentrated nitric acid (ca. 2 ml.) required to decompose carbides, and to oxidise the iron and the molybdenum. Boil the solution to expel oxides of nitrogen, and filter the liquid if it is not perfectly clear. Dilute to 100 ml., cool, and heat with sufficient ferrous ammonium sulphate solution to reduce vanadic and chromic acids. Cool to 5-10° C., add 10 ml. of the reagent (2 ml. of α-benzoinoxime in 100 ml. of alcohol) with constant stirring, then 5 ml. more for each 0.01 g. of Mo present, followed by the addition of sufficient bromine water to impart a pale-yellow colour to the solution, and finally 3-4 ml. more of the reagent. Allow the mixture to stand for 10-15 minutes with occasional stirring, and then filter off the molybdenum complex. Complete the estimation as in Section IV, 23B; use 150 ml. of the special wash liquid. Ignite to constant weight in an electric muffle or crucible furnace at 500-525° C. If tungsten is suspected, proceed as described in the Discussion to Section IV, 23B.

Note. 1. The Bureau of Analyzed Samples “Alloy Steel No. 214 or No. 225” (one of the British Chemical Standards) is suitable for practice in this estimation.

J. Tungsten. Practice in this estimation may be obtained by the use of a chromium–tungsten steel. The tungsten is precipitated as tungstic acid with the aid of hydrochloric and nitric acids, but it is difficult to collect it quantitatively and wash it completely because of the tendency of tungstic acid to form colloidal solutions. This difficulty may be overcome by the addition of cinchonine–hydrochloric acid solution to the suspension (compare Section IV, 51B). The precipitate is, however, far from pure; it contains co-precipitated silica and other substances. The former is removed by volatilisation with sulphuric and hydrofluoric acids, and the amount of the latter (chiefly ferric oxide) is determined by a double fusion with sodium carbonate, the WO₃ forming soluble sodium tungstate.
Gravimetric Analysis

Weigh out accurately about 1 g. of the steel (1) into a 400-ml. beaker provided with a clock-glass cover, add 50 ml. of concentrated hydrochloric acid, and heat until the alloy is decomposed. Remove the beaker from the source of heat, and add cautiously 5–7 ml. of concentrated nitric acid. Heat to boiling for 5 minutes in order to oxidise all the iron and to convert the tungsten into bright-yellow tungstic acid. The precipitate should be yellow with no trace of dark metallic tungsten; if it is not yellow, boil down to a volume of 5–10 ml., add more hydrochloric acid and a little nitric acid, and continue the boiling. Dilute to 100 ml., introduce 5 ml. of cinchonine solution (2), and digest slightly below the boiling point for 30–45 minutes, stirring occasionally. The addition of a Whatman accelerator is advantageous. Filter off the precipitated tungstic acid through a Whatman No. 40 or 540 filter-paper, and wash the precipitate thoroughly with the cinchonine hydrochloride solution diluted 30-fold. Transfer the precipitate and filter to a platinum crucible, dry the paper, char it, and burn off the carbon at the lowest possible temperature. Cool the crucible, add 1 drop of concentrated sulphuric acid and 2 ml. of A.R. hydrofluoric acid. Evaporate off the hydrofluoric acid cautiously and expel the sulphuric acid; finally dry at 750–850° C. in an electric muffle furnace to constant weight (3). The weighed residue will be free from silica, but will consist of impure WO₃ (ferric oxide and other oxides may be present as impurities). Fuse the weighed residue with 5 g. of A.R. anhydrous sodium carbonate, extract the cold melt with 75–100 ml. of water, and filter off any insoluble matter on a quantitative filter-paper; rinse out the crucible carefully, and wash the paper and residue thoroughly with hot water. Place the filter in the crucible, char the paper, and burn off the carbon; fuse the residue with 1 g. of A.R. sodium carbonate. Extract the cold melt with 25 ml. of water, filter, and wash the crucible and paper with hot water. Keep all filtrates. Place the filter-paper in the crucible, char, and ignite to constant weight; this will give the weight of ferric oxide, etc. Deduct this weight from the weight of impure tungstic oxide.

Divide the combined filtrates from both sodium carbonate fusions into four equal parts. If it is colourless, no chromium is present; if it is pale yellow, determine the chromium colorimetrically (Section V, 17); if the yellow colour is comparatively deep, acidify with dilute sulphuric acid, add excess of 0·1N-ferrous ammonium sulphate, and titrate the excess of ferrous salt with 0·1N-potassium permanganate. Determine in another portion the molybdenum either colorimetrically (Section V, 19) or by the α-benzoinoxime method (see I). Test for vanadium and, if present, determine it colorimetrically (Section V, 18) in an aliquot portion.

Correct the weight of impure tungstic oxide (from which the weight of residual ferric oxide, etc., has been subtracted) for the Cr₂O₃, MoO₃, or V₂O₅ which may be present.

Calculate the percentage of tungsten in the alloy.

Notes. 1. Ridsdale's "H. S. Steel, No. 64a" (one of the Analysed Samples for Students) or the Bureau of Analysed Samples "Alloy Steel, No. 220" is satisfactory for practice in this determination.

2. Prepared by dissolving 12·5 g. of cinchonine in 100 ml. of 6N-hydrochloric acid.

3. Alternatively, heat the covered crucible to redness.
**K. Titanium.** This element may be present in steels up to a few tenths per cent, and is then best determined colorimetrically. Essentially one method consists in adding hydrogen peroxide to a sulphuric acid solution of the steel, and comparing the resultant yellow colour with a standard solution containing known amounts of titanium treated in the same way (compare Section V, 15).

Ferro-titanium usually contains 10-25 per cent of Ti, and a method for its gravimetric determination will be described.

Weigh out accurately 0.5-1 g. of ferro-titanium (1), and dissolve it in 50 ml. of 1:4 sulphuric acid in a 600-ml. beaker. When effervescence ceases, evaporate the solution until fumes of sulphur trioxide appear. Cool, add 100 ml. of water, and heat to dissolve iron salts. Filter, and wash the precipitate thoroughly with dilute sulphuric acid; reserve the filtrate (i). Transfer the filter and precipitate to a weighed platinum crucible, burn off the carbon, then ignite for 10-15 minutes, and weigh. Add a few drops of concentrated sulphuric acid and 2 ml. of A.R. hydrofluoric acid, evaporate to dryness, cool, and weigh. The loss in weight is due to SiO₂. Reserve the residue.

Dilute the filtrate (i) to 400 ml., add ammonia solution until a faint precipitate is obtained, then add successively 2 ml. of 1:1 hydrochloric acid, 10 ml. of glacial acetic acid, and 10 g. of sodium thiosulphate dissolved in 50 ml. of water. Boil for 10 minutes, allow to settle, filter, and wash several times with 2 per cent acetic acid. Transfer the filter and precipitate to the platinum crucible containing the residue from the silica determination, burn off the carbon, then add 5 g. of A.R. anhydrous sodium carbonate, and fuse until a quiet melt is obtained. Allow to cool, transfer the crucible to a beaker, add 50 ml. of water, and heat until the fused mass is disintegrated and no hard particles remain. Remove the crucible and wash it. Filter and wash well with hot water (2). Dissolve the residue on the paper in 25 ml. of hot 1:1 hydrochloric acid, and precipitate in the same way as before by adding ammonia solution, acetic acid, and sodium thiosulphate. Filter and wash with 2 per cent acetic acid until free from chloride. Transfer again to a platinum crucible, heat gently at first to burn off the paper and oxidise the carbon, and finally ignite to constant weight. Weigh as TiO₂ (3).

**Notes.**
1. The Bureau of Analysed Samples "Ferro-Titanium, No. 201" (one of the British Chemical Standards) is suitable for this estimation.
2. Sodium titanite is insoluble, whilst sodium phosphate and aluminate dissolve.
3. The method of precipitation with tannin and antipyrin (Section IV, 40B) is a considerable improvement upon the above procedure. The student should employ this method also, and compare the results obtained. The best method is probably that based upon precipitation with para-hydroxyphenylarsenic acid (Section IV, 40D).

**L. Cobalt.** This element is present in certain Cr-V-W-Co and Cr-V-W-Co-Mo steels. It may be determined with α-nitroso-β-naphthol.

Weigh out sufficient of the steel to contain 0.02-0.03 g. of cobalt (1) into a 400-ml. beaker, add 25 ml. of dilute hydrochloric acid (1:1), heat and, when decomposition is complete, add 5 ml. of dilute nitric acid (1:1) to oxidise the iron. If tungsten is present, continue the digestion with the hydrochloric and nitric acids until all the tungsten has been converted into yellow tungstic acid. Evaporate to a syrupy consis-
Gravimetric Analysis

577
tency (ca. 5 ml.), add 100 ml. of water and digest on a steam-bath for about 5 minutes. Dilute the solution to about 300 ml., add a suspension of zinc oxide (prepared by shaking 10 g. of finely divided zinc oxide with 60 ml. of water) in approximately 5-ml. portions until all the iron is precipitated and a slight excess of zinc oxide is present: shake thoroughly after each addition and avoid a large excess of the precipitant. Allow the precipitate to settle for a few minutes, filter, and wash three times with cold water. Reserve the filtrate and washings.

Treat the combined filtrate and washings with 10 ml. of concentrated hydrochloric acid, adjust the volume to 400 ml., and heat the solution to boiling. Add 3 ml. of the α-nitroso-β-naphthol reagent (2) for each 0.01 g. of cobalt present and then 8 ml. more. Allow the solution to cool for 30 minutes or more, and filter. Complete the determination as detailed in Section IV, 38A. Weigh either as CoSO₄ or as Co.

Notes. 1. For practice in this estimation, the student may employ 0.5 g., accurately weighed, of the Bureau of Standards "Alloy Steel, No. 241" (a Cr-V-W-Co steel).

2. The reagent is prepared by dissolving 1 g. of α-nitroso-β-naphthol in 15 ml. of glacial acetic acid and filtering, if necessary.

M. Zirconium. An excellent reagent for the determination of zirconium in steels is n-propylarsionic acid (Section IV, 41G; compare Section I, 62J). The experimental details for a complex steel, containing 1–2 per cent of Zr, will be given.

Dissolve 3 g. of the steel in 40 ml. of concentrated hydrochloric acid and add sufficient concentrated nitric acid to oxidise the iron. Evaporate to dryness, moisten the residue with concentrated hydrochloric acid, evaporate again to dryness, and heat for 30 minutes at 105–110°C. Treat the residue with 10 ml. of concentrated hydrochloric acid, and warm gently until solution is complete. Dilute to 100 ml., filter whilst hot, and wash the residue (silica, zirconium phosphate, etc.) well with hot water. Reserve the filtrate (i), and treat the residue as follows in order to recover the small quantity of zirconium present.

Ignite the residue in a platinum crucible, and volatilise the silica with sulphuric and hydrofluoric acids in the usual manner (Section IV, 70). Fuse the residue with ten times its weight of sodium carbonate, extract with water, filter, and wash well with water. Discard the filtrate. Ignite the residue in a platinum crucible, and fuse with a little potassium pyrosulphate. Extract with water containing a few drops of dilute sulphuric acid, filter, and wash with hot water. Add the filtrate and washings to the main filtrate (i).

Dilute the combined filtrates to a volume of 300 ml., heat to boiling, and precipitate the zirconium with 15–25 ml. of a 5 per cent aqueous solution of n-propylarsionic acid (1). Digest for 30–50 minutes, filter whilst hot, with gentle suction, through a quantitative filter-paper supported on a filter-cone (Whatman, hardened, No. 51), and wash with hot water. Return the filter-paper and precipitate to the original beaker, and disintegrate by warming gently with 10–15 ml. of concentrated hydrochloric acid. Add 100 ml. of water, and re-precipitate the zirconium by adding 10 ml. of the n-propylarsionic acid reagent. Digest for 30 minutes, filter as before, and wash well with hot water. Transfer to a weighed porcelain or Main-Smith crucible, ignite gently at first and then more strongly over a Méker or Fisher burner to constant
weight. If tin is present, add ammonium iodide, follow the procedure of Section IV, 25A, and ignite to constant weight. Weigh as ZrO₂.

Note. 1. This is an approximately saturated solution. The reagent may be purchased, inter alia, from British Drug Houses, Ltd., Poole, Dorset, or the Eastman Kodak Company, Rochester, N.Y., U.S.A.

N. Copper. This element is usually present to the extent of 0.005-1 per cent in certain steels. Two methods will be described for its determination—a gravimetric and a volumetric procedure. The manner of effecting solution of the steel will depend upon whether tungsten is present or absent.

Gravimetric method. (a) Tungsten absent. Transfer 1-10 g., accurately weighed, of the steel (according to the copper content) to a 800-ml. beaker, add 200 ml. of dilute sulphuric acid (1:9) and heat gently until solution is complete. (If much chromium or vanadium is present, add a few crystals of potassium chlorate and boil to dissolve carbides.) Dilute to 500 ml. with water, heat to boiling, and saturate with hydrogen sulphide for 30 minutes as the solution cools. Digest for about 30 minutes, add a Whatman accelerator (or one-third of an ashless tablet), filter on a quantitative filter-paper, and wash three or four times with dilute sulphuric acid (1:99) which has been saturated with hydrogen sulphide.

(b) Tungsten present. Dissolve up to 10 g., accurately weighed, of the steel in 100 ml. of dilute hydrochloric acid (1:1). Add 25 ml. of dilute nitric acid (1:1) portionwise, and boil gently until the separated tungstic acid becomes bright yellow. Dilute the solution to 150 ml. with boiling water, digest for 5 minutes, filter the solution (which contains practically all of the copper) and wash with dilute hydrochloric acid (1:9). Add 30 ml. of dilute sulphuric acid (1:1) to the filtrate, evaporate just to fumes of sulphuric acid, cool and add 100 ml. of water. If a small residue of tungstic acid separates, filter and wash with dilute sulphuric acid (1:20). To the clear filtrate add 5 g. of tartaric acid, neutralise with ammonia solution, adjust the acidity to 5 per cent by volume of sulphuric acid, heat to boiling and pass a rapid stream of hydrogen sulphide for 10-15 minutes. Digest the precipitate at 50-60° C. for 1 hour, filter and wash the precipitate as under (a).

Transfer the paper containing the copper sulphide precipitate, which may also contain the sulphides of molybdenum, vanadium, arsenic, tin, etc., to a Main-Smith crucible, ignite at a temperature not exceeding 550° C. (1) and fuse with 2-4 g. of alkali pyrosulphate. Dissolve the cooled melt in 25 ml. of dilute hydrochloric acid (1:9), dilute to 100 ml., neutralise with 5 per cent sodium hydroxide solution and add 0.3 ml. in excess. Boil for 3 minutes, digest for ca. 30 minutes, filter, and wash the impure copper hydroxide precipitate five or six times with a cool 0.5 per cent solution of sodium hydroxide. Dissolve the precipitate in dilute hydrochloric acid (1:3) or in dilute sulphuric acid (1:3), add 3-5 g. of tartaric acid, neutralise with ammonia or sodium hydroxide solution, and acidify with dilute acetic acid. Determine the copper with salicylaldoxime as detailed in Section IV, 19C.

Note. 1. The following method may also be used. Heat the cooled residue in the crucible with 10 ml. of concentrated hydrochloric acid, transfer the solution quantitatively to a 400-ml. beaker, add 2-3 drops of concentrated nitric acid, and then treat with excess of concentrated ammonia solution.
Heat to boiling and filter into a 600-ml beaker; wash with hot 1 per cent ammonia solution and discard the paper. Dilute the filtrate to 250 ml., heat to boiling, and precipitate the copper by the dropwise addition of a 2 per cent alcoholic solution of α-benzoinoxime (10–15 ml.). The subsequent experimental details are similar to those given in Section IV, 19B; the copper is best weighed as Cu(C₁₄H₁₁O₂N).

**Volumetric method.** This method yields satisfactory results if the percentage of copper is greater than 0·1. If the steel contains less than 1 per cent of copper, use 5 g. of the sample; if the copper content exceeds 1 per cent, use 2·5 g. of the steel.

Weigh out accurately about 5 g. of the steel into a 750-ml. conical flask, add 125 ml. of dilute sulphuric acid (1 : 9), and heat until reaction ceases. Remove from the source of heat, add ca. 15 g. of A.R. ammonium persulphate, and boil for 15 minutes. Dilute the solution to 400 ml. with hot water, add 70 ml. of sodium sulphite solution (25 g. of sodium sulphite per 100 ml.) and then 25 ml. of potassium thiocyanate solution (5 g. of potassium thiocyanate per 100 ml.). Boil for 5 minutes, allow to stand for 5 minutes, and filter through a quantitative filter-paper. Wash the flask, paper, and precipitate with cold dilute sulphuric acid (2 : 98). Transfer the paper and precipitate to a 250–300-ml. reagent bottle, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of chloroform or carbon tetrachloride. Titrate the copper with standard 0·025M-potassium iodate solution as detailed in Section III, 126.

**O. Lead.** This element is sometimes added in small amounts (about 0·25 per cent) to improve the machinability of both carbon and alloy steels: no alloy is formed, but the lead should be uniformly dispersed in the material.

Place 5–10 g., accurately weighed, of the sample in a 600-ml. Pyrex beaker, and add 50–100 ml. of dilute hydrochloric acid (1 : 1). Cover with a clock-glass and heat until dissolved. Evaporate just to dryness in order to expel excess of acid, but do not bake. Transfer to a conical flask, heat to boiling, and pass a rapid stream of hydrogen sulphide through the solution for at least 10 minutes (the pH should be adjusted to be in the range 2·0–2·5). Allow the precipitate to settle, filter through a hardened paper, and wash with cold saturated hydrogen sulphide water. Dissolve the lead sulphide in hot 1 : 1 nitric acid (sulphur, if present, will remain unattacked) and wash the paper with hot 1 per cent nitric acid. The volume of the filtrate and washings should not exceed 100 ml. Add cautiously with stirring 15 ml. of concentrated sulphuric acid, evaporate to copious fumes, and allow to cool. Add 50–60 ml. of water, heat to the boiling point to dissolve iron salts, add 50 ml. of ethyl alcohol, and set aside for several hours, but preferably overnight. Filter through a paper-pulp pad or a porous-porcelain filter-crucible and wash with dilute sulphuric acid (1 : 20) containing 10 per cent of ethyl alcohol. Dissolve the lead sulphate in three 10-ml. portions of hot 20 per cent ammonium acetate solution, followed by several washings with hot water. Treat the combined filtrate and washings with 5 ml. of glacial acetic acid, heat to the boiling point, add 10 ml. of 5 per cent aqueous ammonium paramolybdate solution, and boil for a few minutes until the lead molybdate precipitate has coagulated. Filter through a porous-porcelain filter-crucible, and wash with slightly ammoniacal ammonium nitrate solution (2 per cent).
Heat to dull redness on a crucible-ignition dish or at 600–650° C. to constant weight (see Section IV, 140). Weigh as PbMoO$_4$.

The chemical reactions involved in the determination may be written:

$$
PbCl_2 + H_2S \rightarrow PbS + 2HCl
$$

$$
PbS \xrightarrow{HNO_3} Pb(NO_3)_2 \xrightarrow{H_2SO_4} PbSO_4
$$

$$
PbSO_4 + 2CH_3COONH_4 \rightarrow Pb(CH_3COO)_2 + (NH_4)_2SO_4
$$

$$
Pb(CH_3COO)_2 + (NH_4)_2MoO_4 \rightarrow PbMoO_4 + 2CH_3COONH_4
$$

**P. Germanium.** Some special steels may contain up to 0.25 per cent of germanium; for such steels a 10-g. sample is used for the determination. Higher germanium contents will necessitate the use of proportionally smaller samples. The method consists in separating the element by distillation from a hydrochloric acid solution as the tetrachloride, precipitation of the germanium in the distillate with tannin, and ignition to the oxide. Interference of tin is avoided by adding sulphuric acid to the solution before distillation.

Weigh out accurately about 10 g. of the germanium steel into a 500-ml. round-bottomed flask fitted with a standard ground-glass joint. Add a mixture of 100 ml. of 1:4 sulphuric acid and 10 ml. of concentrated nitric acid. When reaction has largely ceased, boil the mixture gently for 3 minutes to ensure complete solution of the germanium steel. Cool somewhat, add 5 g. of A.R. copper turnings to destroy the excess of nitric acid, and boil for 3 minutes to expel oxides of nitrogen. Wash down the sides of the flask with sufficient water to make the total volume about 150 ml., and cool the solution in ice. Add 200 ml. of concentrated hydrochloric acid and immediately connect by ground-glass joints to a distillation apparatus incorporating an efficient fractionating column, e.g., of the Widmer type; * the latter is required in order to minimise contamination by metal chlorides of higher boiling point. The distillate is collected through an adapter incorporating a large safety bulb attached to the end of the condenser and dipping into a beaker containing 100 ml. of ice-cold water. A stopcock should be inserted at the top of the column as a precaution against sucking back. Distil and adjust the rate of heating so that constant-boiling-point hydrochloric acid passes over at the rate of one drop in about 5 seconds and collect 20–30 ml. of distillate; all the germanium tetrachloride (b.p. 86° C.) distils over before any of the constant-boiling acid. Disconnect the apparatus, wash the adapter with a jet of water, and add 2 g. of hydroxylamine hydrochloride to the distillate in order to reduce any oxidising substances. Introduce, with stirring, 30 ml. of freshly prepared 5 per cent tannin solution, and then a few drops of methylred indicator. Add ammonium hydroxide solution until alkaline, render the solution barely acid by the dropwise addition of sulphuric acid and add 10 drops in excess, i.e., to a final acidity of about 0.8 N. Heat the mixture to incipient boiling, allow to stand until the flocculent precipitate has settled and the solution is cool. Filter the precipitate through a quantitative filter-paper (e.g., Whatman No. 40 or 540), and wash until free from chloride with a wash water containing 5 g. of ammonium nitrate, 0.5 g. of tannin, and 0.5 ml. of nitric acid.

* See, for example, Fig. II, 17, 5, in the author’s Text Book of Practical Organic Chemistry, Second Edition, 1951 (Longmans, Green).
Gravimetric Analysis

acid per 100 ml. Ignite cautiously at first in a silica crucible, and then at 600° C. for an hour. Allow to cool, treat with 5 drops of concentrated sulphuric acid, and 3 ml. of concentrated nitric acid, and evaporate to dryness to destroy most of the remaining carbon. Ignite again below 600° C. until all carbon is burned off, and finally heat the white residue at 900–1000° C. for 10 minutes. Weigh as GeO₂. Correct for the weight of a blank by repeating the determination with ca. 10 g. of germanium-free steel.

IV, 97. ANALYSIS OF AN ALUMINIUM ALLOY

Discussion. There are numerous kinds of aluminium alloys; thus we have: (i) Ultra-light alloys: these have a moderate aluminium content, a high percentage of magnesium, and small percentages of copper, zinc, silicon, etc.

(ii) Light alloys: these have a high aluminium content, together with small quantities of copper, zinc, magnesium, etc.

(iii) Aluminium-silicon alloys: these may contain up to 20 per cent of silicon, together with small quantities of other elements.

The analysis of a typical alloy of class (ii) will be described.*

Procedure. Weigh out accurately about 2 g. of the alloy (1) and dissolve it in 30 ml. of 20 per cent sodium hydroxide solution, preferably in a Monel beaker (or in a large “nickel” crucible). When the vigorous reaction subsides, heat until solution is complete, dilute with 100 ml. of hot distilled water, filter through a sintered-glass crucible, and wash thoroughly with hot water. The residue (A) contains the copper, lead, iron, nickel, magnesium, etc., whilst the filtrate and washings (B) contain the zinc and aluminium as the zincate and aluminate respectively.

Lead and copper. Dissolve the residue (A) in 1:1 nitric acid, and determine the lead and copper as in the analysis of nickel silver in Section IV, 93 (b) and (c) respectively.

Iron. Proceed as in Section IV, 93 (d).

Nickel. Proceed as in Section IV, 93 (e).

Magnesium. Acidify the filtrate from the determination of nickel with concentrated hydrochloric acid and add 5 ml. of the concentrated acid in excess. Then add 25 ml. of concentrated nitric acid, and evaporate on a hot-plate in the fume cupboard either to dryness or to fumes of sulphur trioxide if much sulphuric acid is present. This evaporation removes the organic matter, and incidentally also the large amount of ammonium salts present in solution. Dilute the solution to about 200 ml., add 10 g. of ammonium acetate, then an excess of a 2 per cent solution of oxine in 2N-acetic acid, followed by concentrated ammonia solution until the liquid is strongly alkaline; stir the mixture vigorously during the addition. Boil the mixture for a few minutes until the precipitate is crystalline, filter it off on a weighed Gooch, sintered-glass, or porous-porcelain crucible, and wash with hot

* For further details, see, for example, Analysis of Aluminium and its Alloys (British Aluminium Co., Ltd., 1947); Modern Methods for the Analysis of Aluminium Alloys, compiled by Alar, Ltd. (Chapman and Hall, 1949); A.S.T.M. Methods of Chemical Analysis of Metals, 1946.

The determination of Cu, Pb, Sn, Ni, and Zn in a “light aluminium alloy” by electro analysis involving controlled potential at the cathode is described in Sand Electrochemistry and Electrochemical Analysis, Volume II, p. 105 (Blackie, 1941).
water or, better, with 1 per cent ammonia solution. Dry at 130–140°C to constant weight, and weigh as \( \text{Mg(C}_6\text{H}_5\text{ON)}_2 \). Alternatively, dissolve the washed precipitate in 2N-hydrochloric acid, and titrate the magnesium with standard potassium bromate solution as in Section III, 138, Procedure B.

Zinc. Determine the zinc electrolytically in the filtrate and washings (B) obtained by solution of the alloy; * use the method described in Section IV, 84.

Alternatively, acidify the solution (B) with dilute sulphuric acid, and determine the zinc volumetrically by titration with standard potassium ferrocyanide solution using diphenylbenzidine as indicator (Section III, 145) or by potentiometric titration (see Chapter VI).

Silicon. Dissolve 0·5–1·0 g., accurately weighed, of the alloy in 15 ml. of 30 per cent sodium hydroxide solution (prepared from the A.R. solid) contained in a covered Monel metal beaker or in a large "nickel" crucible. When the vigorous reaction subsides, evaporate slowly on a hot-plate to a volume of about 5 ml. If the solution is dark, add 2–3 ml. of 10-volume hydrogen peroxide to accelerate oxidation, and again reduce the volume to 5 ml. Neutralise the concentrated alkaline solution cautiously with 1:1 hydrochloric acid, and transfer quantitatively to a Pyrex beaker. Add 20 ml. of 60–70 per cent perchloric acid solution (CAUTION, see Section IV, 70), evaporate to copious fumes, dilute with 50 ml. of hot water, add a Whatman "accelerator" (or one-third of a Whatman ashless tablet), heat to the boiling point, and filter immediately: wash the precipitate with warm 1 per cent hydrochloric acid. Add 10 ml. of 60–70 per cent perchloric acid solution to the filtrate, "fume," and filter as before. Dry the filter-papers and precipitates at 100°C, transfer to a platinum crucible, and ignite at ca. 1000°C. Add a few drops of concentrated sulphuric acid, and ignite to constant weight. Treat the residue with sulphuric and hydrofluoric acids as in Section IV, 70, and ignite again to constant weight. The loss in weight will give the silica content of the residue.

Note. 1. Ridsdale's "Aluminium Alloy, No. 20" (one of the Analysed Samples for Students) is suitable for practice in this analysis. The alloy contains 80–90 per cent of aluminium and small quantities of copper, lead, iron, nickel, zinc, and magnesium. The British Chemical Standard "Aluminium Alloy, No. 181A" may also be used.

IV, 98. ANALYSIS OF A LIMESTONE OR DOLOMITE

Discussion. Limestone consists essentially of calcium carbonate, but it often contains magnesium in amounts which vary from traces to that present in dolomite; the latter is strictly the equimolecular compound of calcium and magnesium carbonates, \( \text{CaCO}_3\text{MgCO}_3 \). It is, of course, impossible to differentiate sharply between the various varieties, but it is usual to apply the name dolomite to all carbonate rocks that contain sufficient magnesium carbonate to approximate to the above theoretical composition more or less

* The metallic residue (A) may contain a little zinc. If it is desired to recover this, use another sample of the alloy for the determination of zinc. Dissolve the residue (A) in a little hot 1:1 nitric acid, filter, wash with hot water, render the filtrate and washings alkaline with aqueous sodium hydroxide, boil for 10 minutes, filter off the hydroxides of iron, nickel, etc., and add the filtrate to the main solution (B) for the determination of zinc.
Gravimetric Analysis

Gmvimctl'ic Analysis

583

closely. The procedure to be described is applicable to the analysis of any of the carbonates from CaCO₃ to CaCO₃,MgCO₃.

The usual minor constituents of limestone or dolomite are iron, aluminium, titanium, manganese, silica (either free or combined as clay or felspar), sulphur (as pyrites, FeS₂, or gypsum, CaSO₄), sodium, potassium, and organic matter. The minerals themselves have many industrial uses, and for judging their suitability for any particular purpose a complete analysis, involving the determination of all the substances just mentioned, is rarely necessary: a shorter analysis will supply all the information that is required. The shorter technical analysis includes the following determinations, all of which are usually made on the same sample:

A. Loss on ignition.
B. Impure silica or insoluble matter.
C. Combined oxides “R₂O₃.” This is the residue obtained upon ignition of the precipitate produced by ammonia solution, and consists chiefly of Al₂O₃ + Fe₂O₃, together with some TiO₂, Mn₂O₄, and P₂O₅ (chiefly as AlPO₄ and FePO₄).
D. Calcium oxide.
E. Magnesium oxide.
F. Carbon dioxide (a separate sample is used for this determination).

The experimental details to be described below will not, however, be confined to the determination of the constituents of technical interest; the mode of estimation of some of the other components will also be indicated.

Attention should be directed to the method sometimes employed for expressing the results of a mineral analysis. It is usual to express the amount of each metal as its oxide, almost always in its higher state of oxidation, and the amount of each anion as the anhydride of the most common acid. Thus magnesium is given in terms of MgO, and phosphorus as percentage of P₂O₅. The fact that the percentage of the constituent is given as the oxide does not, however, imply a determination of oxygen; rather, the constituent is determined in the customary manner, and the amount present is calculated as if it were the oxide. The method is of particular value with minerals to which no simple chemical formula can be assigned.

Procedure. A. Loss on ignition. Weigh out accurately about 1 g. of the ground, air-dried sample (1) into a weighed, covered crucible (porcelain or platinum), and dry at 110° C. for 1 hour. Cool and weigh. The loss in weight represents hygroscopic or superficially adsorbed moisture. Calculate the percentage of moisture. Then ignite the crucible and its contents slowly (use an electric muffle or crucible furnace at 1000–1100° C., or over a Méker-type burner). The sample must be heated slowly at first to prevent mechanical loss arising from the sudden evolution of carbon dioxide. Heat for 1 hour at the maximum temperature, cool, and weigh. Repeat the ignition for half-hour periods until the weight of the residue is constant to 0·2 mg. Remember calcium oxide is hygroscopic, and observe the precautions given in Section IV, 10. Calculate the percentage loss upon ignition.

Note. 1. Ridsdale’s “Dolomite No. 9b” or “Limestone, Nos. 15b or 15d” (these are Analyzed Samples for Students) are suitable for practice in this analysis.

B. Impure silica, or insoluble matter. Transfer the residue after ignition (A) to a small covered porcelain dish or casserole, add to the small residue in the crucible a few ml. of 1 : 1 hydrochloric acid, and
rinse the solution into the porcelain dish.* Add 5 ml. of concentrated hydrochloric acid and 1 ml. of concentrated nitric acid, and stir until the solid has dissolved. Evaporate the solution to dryness on the steam-bath or upon a low-temperature hot-plate at 110-120° C.; observe the precautions given in Section IV, 70A. Moisten the dry mass with 5 ml. of concentrated hydrochloric acid, warm, and allow to stand for 5 minutes to dissolve basic salts. Add 20 ml. of water, and warm on the steam-bath for 10 minutes; use a glass rod to break up any lumps present. When all the soluble matter has dissolved, filter through a Whatman No. 41 or 541 paper. Wash the precipitate thoroughly with 1:100 hydrochloric acid, and finally once or twice with water to remove most of the hydrochloric acid. Evaporate the filtrate and washings to dryness in the original porcelain vessel,† heat the residue to 110-120° C.; then take up in hydrochloric acid and digest as before, using, however, smaller volumes of hydrochloric acid and water. Filter off the precipitate on a fresh filter, and wash as before. Reserve the combined filtrate and washings (i) for C. Place the two silica precipitates in a weighed crucible, dry and ignite at the full temperature of a Meker-type burner. Allow to cool and weigh. Calculate the percentage of impure silica or insoluble matter present.

Note. The dehydration is most simply effected by boiling with 12-15 ml. of 60-70 per cent perchloric acid instead of evaporation to dryness (compare Section IV, 70, Discussion).

C. Combined oxides. Dilute the filtrate (i) from determination B to 200 ml., add 5 g. of ammonium chloride (to prevent precipitation of magnesium hydroxide), heat nearly to boiling, add 2 drops of methylred indicator, then 1:1 ammonia solution until the solution is just alkaline (yellow); boil for 1-3 minutes, filter the precipitate at once, and collect the filtrate in a 600-ml. beaker; wash the beaker and precipitate twice with hot 2 per cent ammonium chloride solution. Set the filtrate and washings (ii) aside. If the precipitate is small and well washed, re-precipitation can be omitted. If it is large, place the original beaker under the funnel, dissolve the precipitate in a small volume of hot 1:1 hydrochloric acid, and wash the paper thoroughly with hot water. Dilute the solution to about 75 ml., add a few drops of methylred indicator, re-precipitate with ammonia solution as before, add a Whatman accelerator, and filter. Transfer the precipitate completely to the filter, and wash with hot 2 per cent ammonium nitrate solution. Combine the filtrate and washings (ii') with that of (ii). Place the paper in a crucible, dry and ignite the residue as detailed in Section IV, 8. Calculate the percentage of mixed oxides "R₂O₅." 

D. Calcium oxide. Acidify the combined filtrates (ii') from the ammonia precipitation slightly with dilute hydrochloric acid, and evaporate them to about 250 ml. Add 1 ml. of concentrated hydro-

* Alternatively, weigh out accurately about 1 g. of the powdered mineral into a covered porcelain dish or casseroles, and dissolve it in 1:1 hydrochloric acid. When effervescence has ceased, evaporate to dryness on the steam-bath or low-temperature hot-plate with stirring by means of a glass rod until the residue is just dry. Continue as in B.

† The second evaporation is unnecessary if the silica content is small, and results of only moderate accuracy are required.

‡ If manganese is present or is suspected, add about 5 ml. of bromine water prior to the addition of ammonia solution: the manganese will then precipitate as hydrated manganese oxides.
chloric acid, and precipitate the calcium by adding slowly to the boiling solution 50 ml. of a hot 4 per cent solution of ammonium oxalate, followed by 1:10 ammonia solution until the solution is neutral or slightly alkaline (to methyl red). Test for complete precipitation by adding a little more of the oxalate solution. Allow the precipitate to settle for an hour. Filter off the precipitate, and wash it two or three times with a cold, 0·1 per cent ammonium oxalate solution. Set aside the filtrate (iii). Place the original beaker under the funnel, dissolve the precipitate in 25–50 ml. of hot 1:9 hydrochloric acid, and wash the paper with hot water.* Dilute to 100 ml., if necessary, add 5 ml. of the 4 per cent ammonium oxalate solution, boil, then add ammonia solution dropwise until the solution is just alkaline. Set aside for 1 hour, thus allowing the precipitate to settle. Either of two procedures may now be used according as to whether the precipitate is to be weighed as calcium carbonate or as calcium oxide.

**Weighing as calcium carbonate.** Filter the precipitate through a weighed porous-porcelain crucible (previously heated at 500° C.), wash with a 0·1 per cent ammonium oxalate solution until free from chloride (ca. 50 ml.; acidify with dilute nitric acid before testing for chloride). Mix the filtrate and washings (iii') with that from the first precipitation (iii), and reserve the liquid (iv). Dry the crucible and contents at 110° C. for 30–60 minutes (the composition will approximate to CaC₂O₄·H₂O), and then place it in an electric muffle furnace regulated to within ±25° of 500° C. Heat for 1–2 hours and weigh as CaCO₃. Repeat the heating to confirm that constant weight has been attained. Calculate the percentage of CaO in the sample.

**Weighing as calcium oxide.** Filter the precipitate through a quantitative filter-paper and wash it with a 0·1 per cent ammonium oxalate solution until free from chloride (ca. 50 ml.). Mix the filtrate and washings (iii') with the previous one (iii), and reserve the liquid (iv). Dry the paper and precipitate, and ignite in a platinum crucible to constant weight. Weigh as CaO, following the procedure of Section IV, 10. Calculate the percentage of CaO present in the sample.

**Note.** The urea hydrolysis method (Section III, 154), which is superior to that given above, may be used for the precipitation of calcium as oxalate. A better separation from magnesium results. If the proportion of magnesium is relatively high, a second precipitation must be made. The calcium oxalate may be titrated with 0·1 N-potassium permanganate, or it may be weighed as CaCO₃.

**E. Magnesium oxide.** The combined filtrates (iv) contain excess of oxalate ion and large amounts of ammonium salts; these, as already pointed out (Section IV, 11), cause the results for magnesium, when precipitated as magnesium ammonium phosphate, to be high. This error may be avoided by double precipitation or by the removal of the interfering elements. In the latter procedure any silica which may be present is also removed. By oxidation of the hot solution with nitric acid in the presence of chloride ions, oxalate is oxidised to carbon.

---

* If difficulty is experienced in dissolving the precipitate directly on the filter, wash as much as possible of the precipitate into the original beaker, and dissolve the small amount of the precipitate adhering to the paper by pouring hot 1:9 hydrochloric acid repeatedly through the filter. Then add a drop of methyl red, heat until the precipitate has dissolved, adding more dilute hydrochloric acid if necessary.
dioxide and water, and the ammonium salts principally to nitrous oxide, nitrogen, and water. Both methods will be described.

**Method 1.** Acidify the filtrate (iv) from the determination of calcium, and evaporate to 300 ml. Cool, add a few drops of methyl-red indicator, followed by 20 ml. of freshly prepared ammonium phosphate reagent (25 g. of A.R. (NH4)2HPO4 in 100 ml. of water). Then add pure concentrated ammonia solution slowly whilst stirring the solution vigorously until the indicator turns yellow; continue the stirring for 5 minutes, keeping the solution alkaline by the addition of more ammonia solution if necessary, and finally add 10 ml. of concentrated ammonia solution in excess (i.e., approximately one-thirteenth of the volume of the solution). Allow the solution to stand for at least 4 hours, but preferably overnight. Filter off the precipitate and wash it two or three times with 1 : 20 ammonia solution: discard the filtrate. Place the beaker under the funnel, and dissolve the precipitate in 25–50 ml. of hot 1 : 10 hydrochloric acid. Add 0·2–0·3 g. of (NH4)2HPO4, and precipitate the magnesium as before in a volume of 150 ml. Allow to stand overnight, filter off the precipitate, and wash it with cold 1 : 20 ammonia solution until free from chloride. Complete the determination as described in Section IV, 11, and weigh as magnesium ammonium phosphate hexahydrate or as magnesium pyrophosphate. Calculate the percentage of MgO present.

**Method 2.** To the combined filtrates (iv) from the calcium estimation, add 50 ml. of concentrated nitric acid, and evaporate carefully to dryness on a steam-bath or upon a low-temperature hot-plate. Only a small residue (largely magnesium salts) should remain. Add 2–3 ml. of concentrated hydrochloric acid and 20 ml. of water, warm the mixture for a few minutes until the solid has dissolved; if a little silica remains, filter it through a small paper and wash the residue thoroughly. Determine the magnesium in the filtrate, after diluting to 150 ml., as in Method 1; only one precipitation of magnesium ammonium phosphate is necessary in this case. Calculate the percentage of MgO present.

**F. Carbon dioxide.** Follow the procedure given in Section IV, 76, using 0·5–0·6 g., accurately weighed, of the sample. Calculate the percentage of carbon dioxide present in the mineral.

**Additional determinations.** It is sometimes required to estimate the iron content of the original mineral. As a first approximation we may assume that the "combined oxides" are composed of Fe₂O₃ + Al₂O₃. This is not strictly true, as TiO₂ and P₂O₅ (as metallic phosphates) may be present, but the error introduced by making this assumption is usually small. The Fe₂O₃ may be determined directly as detailed below, and the Al₂O₃ may then be obtained by difference. The Al₂O₃ may be written, if desired, as Al₂O₃ ( + TiO₂ + P₂O₅, etc.), if the constituents inside the parentheses are known to be present. Alternatively, the alumina content may be determined directly with 8-hydroxyquinoline (for details, see Section IV, 99, 91; this procedure applies in the presence of titanium).

**G. Ferric oxide.** The impure silica (B) may, and usually does, contain a little of the mixed oxides. Treat the impure silica, contained in a platinum crucible, with 0·5 ml. of concentrated sulphuric acid and 2–3 ml. of A.R. hydrofluoric acid, evaporate the whole cautiously, and ignite (see Section IV, 70A); the loss in weight gives the amount of pure silica present. Fuse the residue with 3–4 g. of A.R. anhydrous
sodium carbonate, dissolve the melt cautiously in dilute hydrochloric acid, boil, then precipitate with ammonia solution as detailed in C. Filter off the precipitate, re-dissolve it in dilute hydrochloric acid, and again precipitate with ammonia solution. Filter the latter precipitate through a small filter-paper, and transfer the paper and precipitate to the original (platinum) crucible containing the “combined oxides,” and ignite in the usual manner. It is evident that if only a small residue is obtained after treatment with sulphuric and hydrofluoric acids, the sodium carbonate fusion is unnecessary except for the most accurate work.

Add 5–7 g. of pure anhydrous potassium pyrosulphate to the platinum crucible containing the ignited mixed oxides, and heat slightly above the melting point of the pyrosulphate; keep the crucible covered. After about 20 minutes raise the temperature slowly until eventually the bottom is at low redness and no dark particles are visible (ca. 1 hour): there must be no spattering. Allow the crucible to cool, place it in a 250–400-ml. beaker, add 100 ml. of water and 3 ml. concentrated sulphuric acid, and warm until all the solid has dissolved with the exception of a few flakes of silica. Remove the crucible with a glass rod and wash it thoroughly with water. Filter off the silica on a small filter-paper, and collect the filtrate in a 350-ml. conical flask; wash the paper thoroughly with hot water. Reduce the solution in a Jones or cadmium reductor (Sections II, 39, and III, 51B) or with stannous chloride (Section III, 51A) and determine the resultant ferrous iron by titration with standard 0·1N-potassium permanganate. Calculate the percentage of Fe$_2$O$_3$, and by subtracting the weight of the latter from that of the “combined oxides,” evaluate the percentage of “Al$_2$O$_3$.”

H. Alternative procedure for the determination of calcium and magnesium (molybdate method). The procedure given in D and E involving double precipitation of the calcium as oxalate, followed by double precipitation of the magnesium as the ammonium phosphate, is accurate but time-consuming. The following method is rapid, and is based upon the comparative insolubility of calcium (also strontium and barium) molybdate, and the solubility of magnesium molybdate under the given experimental conditions ($p$H > 7). The results are satisfactory for a Mg/Ca ratio of 5/1, but the concentration of the magnesium must be less than 0·1N, which may be achieved by dilution. If the magnesium-ion concentration exceeds 0·1N, the precipitate must be dissolved in hydrochloric acid and the calcium re-precipitated.

Treat the neutral solution of calcium and magnesium salts (volume reduced by evaporation to, say, 40–50 ml.) with excess of the ammonium or sodium molybdate reagent (1). The latter should be added at the rate of one drop per second until excess is present (2); a moderate excess of the reagent is not harmful. If the rate of addition is exceeded or if a stirring-rod is used, the precipitate may adhere tenaciously to the glass and will require a rubber “policeman” for its removal. Adjust the $p$H of the solution to about 7–8 (methyl-red indicator) by the addition of filtered ammonia solution. Boil until the supernatant
liquid is perfectly clear (about 15 minutes), and allow to stand until cold (30–40 minutes). Filter through a weighed porous-porcelain filter-crucible, wash with a minimum volume of hot water, dry at 130° C. for 30 minutes, ignite upon a crucible-ignition dish or in a larger crucible (Fig. II, 37, 4) or at 700° C. to constant weight. Weigh as CaMoO₄, and calculate the percentage of CaO present in the sample.

Concentrate the filtrate and washings to about 125 ml. and precipitate the magnesium as magnesium ammonium phosphate in the usual way. Weigh as MgNH₄PO₄·6H₂O or as Mg₂P₂O₇, and calculate the percentage of MgO present. The excess of alkali molybdate does not interfere.

Notes. 1. The ammonium molybdate reagent is prepared by dissolving 35 g. of A.R. ammonium paramolybdate and 96 g. of A.R. ammonium nitrate in 40 ml. of 6N-ammonium hydroxide solution, and diluting to 1 litre. Another method is given in Section IV, 18A.

The sodium molybdate reagent is prepared by dissolving 50 g. of A.R. sodium molybdate (Na₂MoO₄) in 1 litre of water.

Both reagents should be acidified to pH 4 by the addition of hydrochloric acid in order to reduce the absorption of carbon dioxide from the atmosphere.

2. To detect excess of the reagent, use the solution adjusted to the correct pH and which has been boiled for 10 minutes. Allow to settle, remove a drop of the supernatant liquid, and add a saturated solution of pyrogallol in chloroform: it. brown coloration indicates the presence of molybdate.

IV, 99. ANALYSIS OF A FELSPAR*

Discussion. The chief constituents that are normally sought for in an ordinary analysis of a felspar, expressed in petrological nomenclature, are SiO₂; Al₂O₃; Fe₂O₃; TiO₂; CaO; MgO; Na₂O; K₂O; the loss upon heating to 105–110° C. is also sometimes determined. Methods for determining all these constituents are given below. The mineral should be in the form of a fine powder (ca. 100 mesh). If it is in the form of lumps, the method described in Section II, 15, employing a hardened steel plate, a percussion mortar, and an agate mortar successively may be used. However, for practice in analytical methods, the sample is usually supplied in a finely divided form suitable for immediate analysis.

Procedure. A. Solution of the sample. Weigh out accurately 1–1.5 g. of the finely powdered mineral (1) into a platinum crucible (30-ml. size), and, by means of a short, thin glass rod, mix it intimately with 6–7 g. of A.R. anhydrous sodium carbonate. Remove any powder from the rod by brushing it with a camel hair brush. Cover the crucible, and heat, at first very carefully, over a low Bunsen flame, then gradually over the full Bunsen flame, and finally over the full flame of a Méker-type burner until quiet fusion results and decomposition is complete. Take care that the melt does not “boil over.” When cold, place the crucible and lid in a covered, deep, 7-in. porcelain or platinum basin or in a casserole, cover it with distilled water, and leave overnight, or warm on the water-bath until the contents are well disintegrated. When this is the case, add concentrated hydrochloric acid in small portions until an excess is present, and warm on the water-bath until the evolution of carbon dioxide ceases. Remove and rinse the cover-
Gravimetric Analysis

589
glass, crucible, and lid, and evaporate the contents of the dish or casserole
to complete dryness on the water-bath, crushing all lumps with a glass
rod.

Note. 1. Ridsdale's "Felspar No. 29" (one of the Analysed Samples
for Students) is suitable, but the U.S. Bureau of Standards "Feldspar
(potash), No. 70" or "Feldspar (soda), No. 99" is to be preferred, since a
complete analysis is supplied.

B. Silica. Heat the residue from A for an hour at 110-120° C. to
dehydrate the silica, and then complete the determination as in Section
IV, 70B. At least two evaporations are required to dehydrate
the silica completely. Treat the ignited residue with sulphuric and
hydrofluoric acids, and determine the SiO₂ by difference. After
weighing, set aside the platinum crucible without cleaning and use it
in this condition for C.

O. Ferric, aluminium, and titanium oxides. Dilute the filtrate from
the precipitation of silica to 200 ml., add 5 g. of ammonium chloride
(to prevent precipitation of magnesium hydroxide), then about 3 ml.
of bromine water, and boil.* Boil the solution to expel excess of
bromine. Add 2 drops of methyl-red indicator to the boiling solution
followed by pure 1 : 1 ammonia solution until just alkaline; boil for
1 or 2 minutes. Filter off the precipitate at once and collect the filtrate
in a 600-ml. beaker; wash the beaker and precipitate with 2 per cent
ammonium chloride solution. Set aside the filtrate and washings (i).
Place the original beaker under the funnel, dissolve the precipitate
in hot 1 : 1 hydrochloric acid, and wash the paper thoroughly with hot
water. Dilute the filtrate to 150 ml., re-precipitate by ammonia solu­
tion as before, add one Whatman accelerator, and filter. Transfer
the precipitate completely to the paper, and wash thoroughly with 2
per cent ammonium nitrate solution. Combine the filtrate and
washings (i') with those of (i). Transfer the precipitate and paper to
the platinum crucible containing the residue from the impure silica
after treatment with sulphuric and hydrofluoric acids, and ignite the
residue as detailed in Section IV, 8. Weigh to obtain the weight of
Fe₂O₃ + Al₂O₃ + TiO₂. The percentage of TiO₂ is usually very small,
and, for many purposes, the residue may be regarded as a mixture of
Fe₂O₃ + Al₂O₃. If time is limited, the percentage of the mixed oxides
alone may be returned.

For the determination of the individual elements in the residue,
proceed as follows.

C1. Aluminium oxide. Dissolve a portion of the residue, accurately
weighed, in sulphuric acid, dilute, and add excess of 10 per cent sodium
hydroxide solution. Filter and wash. Acidify the filtrate with hydro­
chloric acid, and determine the aluminium by the addition of an
acetic acid solution of oxine, followed by 2N-ammonium acetate (for
details, see Section IV, 28D). Weigh as Al(C₉H₅ON)₃. Calculate the
percentage of Al₂O₃ present.

C2. Ferric oxide. Use the potassium pyrosulphate fusion method
described in Section IV, 986, with a known weight of the residue.
Reduce with hydrogen sulphide as follows. Adjust the sulphuric acid

* This will oxidise iron to the ferric state; it will also precipitate any manganese
present as hydrated manganese oxide and thus prevent contamination in the subsequent
precipitation of magnesium.
content to 2–2.5 per cent by volume, and pass a stream of washed hydrogen sulphide for 30 minutes and then continue the stream of gas for 15 minutes as the solution is heated to boiling. Add about one-fifth of the volume of sulphuric acid and pass in a stream of oxygen-free carbon dioxide for 30 minutes whilst boiling the solution. Allow to cool in the gas, and titrate the ferrous salt with 0.1N-potassium permanganate.

Alternatively, the product of the pyrosulphate fusion may be treated with excess of ammonia solution, the precipitate collected, and dissolved in hydrochloric acid. The hydrochloric acid solution may then be reduced with a silver reductor (Section II, 38), and the reduced solution titrated with 0.1N-potassium permanganate.

C8. Titanium oxide. Dissolve a known weight of the mixed oxides in sulphuric acid, and determine the titanium colorimetrically with hydrogen peroxide (Section V, 15). If appreciable quantities of titanium are present, precipitate the titanium from the acid solution with tannin and antipyrin (for details, see Section IV, 40B), or with p-hydroxyphenylarsionic acid (Section IV, 40D), and weigh as TiO₂. Calculate the percentage of titanium oxide present.

D. Calcium oxide. Acidify the combined filtrate and washings (i + ii) from the ammonia precipitation with hydrochloric acid, evaporate to about 150 ml., heat to boiling, and precipitate the calcium by means of ammonium oxalate and ammonia solution. Filter. Dissolve the precipitate in dilute hydrochloric acid, heat and re-precipitate the calcium by the addition of ammonia and a little ammonium oxalate solution. Filter and wash with dilute ammonium oxalate solution. Weigh the calcium either as CaCO₃ or as CaO. Follow the experimental procedure given in Section IV, 98D. Calculate the percentage of CaO present. Reserve all the filtrates and washings (ii).

E. Magnesium oxide. Acidify the combined filtrates and washings (ii) from the determination of calcium, evaporate to 150 ml., and estimate the magnesium by double precipitation with diammonium hydrogen phosphate (Section IV, 98E) as the ammonium phosphate. Since the percentage of magnesium is small, precipitation with 8-hydroxyquinoline may be employed with advantage (for details, see Sections IV, 46B and Section IV, 100E). Calculate the percentage of MgO present.

Note. For an alternative and more rapid method for the determination of calcium oxide and of magnesium oxide, see Section IV, 98H.

F. Potassium and sodium oxides. Discussion. The J. Lawrence Smith method (1871) will be described. The very finely divided sample is decomposed by heating it with its own weight of pure ammonium chloride and eight times its weight of pure calcium carbonate. The sintered mass is leached with water to extract the alkalis and filtered; much of the calcium passes into solution as the hydroxide or chloride, and silica, aluminium, magnesium, iron, etc., remain undissolved. The extract is treated with ammonium carbonate solution to precipitate calcium, and the ammonium salts are removed by volatilisation. The alkali chlorides alone remain, and are weighed. Then sodium or potassium in the mixture is determined by any of the usual methods, and the other alkali is estimated by difference.

Procedure. Weigh out accurately about 0.7 g. of the very finely divided mineral (ca. 200 mesh) into an agate mortar, add an equal weight
Gravimetric Analysis

of A.R. ammonium chloride (weighed to the nearest 2 mg.), and grind the two substances together, using a small agate pestle. Weigh out to the nearest desigram 5·6 g. of A.R. calcium carbonate on to a watch-glass, and add three-fourths of this, a little at a time, to the mortar and mix thoroughly after each addition. When the mixing is complete, lay the pestle down on the watch-glass containing the remainder of the calcium carbonate, and transfer the mixture to a 30-ml. platinum crucible, fitted with a cover, with the aid of a spatula (preferably of platinum): it is advisable to place a little of the calcium carbonate at the bottom of the crucible in order to prevent adhesion of the sintered material at the end of the subsequent ignition. Rinse out the mortar with the remaining calcium carbonate, and transfer to the crucible. The whole operation should be carried out on a sheet of glazed paper, and thus avoid the possibility of any loss in filling the crucible. Cover the crucible with the lid, and tap the crucible gently to cause the powder to settle. Insert the crucible in a hole in a sheet of asbestos (or of "uralite"); about one-third of the crucible should extend below the asbestos. Heat the crucible with a very small flame until the odour of ammonia is no longer perceptible (about 30 minutes—if fumes of ammonium chloride are evolved, the flame should be turned down). Then heat the crucible over a Bunsen flame for 1 hour, regulating the temperature so that only the lower half of the crucible is at a red heat. Allow to cool, rinse off the cover, add sufficient water to cover the sintered cake, and heat for 10 minutes on the water-bath, adding more water if necessary. Wash the contents of the crucible into a dish (porcelain, silica, but preferably of platinum); crush any lumps present to powder with the agate pestle or a thick glass rod.

Add enough water to the residue in the dish to give a volume of 50-75 ml., and digest on the steam-bath for 30 minutes. Filter by decantation through a 9-cm. fast-filtering paper into a 600-ml. Pyrex beaker or into a large silica or platinum dish. Add 50 ml. of hot water, heat to boiling, rub the insoluble mass with the pestle for some minutes, and again decant. Repeat the extraction four or more times, depending upon the alkali content of the mineral. Wash the paper with 50 ml. of hot water or, better, with hot, saturated pure calcium hydroxide solution. Test the residue for complete decomposition by warming it with dilute hydrochloric acid; it should dissolve completely except, possibly, for a few white flocks of silica: no gritty particles should remain.

Treat the filtrate with a few ml. of pure concentrated ammonia solution, and precipitate the calcium present by the addition of excess of ammonium carbonate solution (3 g. of the A.R. salt in 40 ml. of water). Heat the solution to boiling, allow the precipitate to settle, filter, and wash the precipitate with hot water. Re-dissolve the precipitate in the minimum volume of dilute hydrochloric acid, and re-precipitate with ammonia and ammonium carbonate solutions; this re-precipitation will recover the small amounts of alkali chlorides which have may been co-precipitated. Filter again, and wash with hot water. Combine the filtrates and washings, and evaporate them to complete dryness in a porcelain or silica basin on the steam-bath.*

* It is better for the subsequent removal of ammonium salts to transfer the solution quantitatively, when it has been reduced to a small volume, to a small platinum dish, and to complete the evaporation in the latter.
Heat the dry residue in the covered basin until all ammonium salts are expelled; take care to avoid too strong heating. The residue will be dark-coloured, but this does not matter. Dissolve the residue in 25 ml. of hot water, and add, first, a few drops of dilute barium chloride solution to remove traces of sulphate and, secondly, a few drops of ammonium oxalate solution to precipitate the remaining calcium. Allow to cool, and treat with a few ml. of ammonium carbonate solution in order to remove the excess of barium; allow to stand overnight.

Filter off the precipitate through a small paper, evaporate the filtrate to dryness as before, and ignite gently in a covered basin to volatilise the last traces of ammonium salts. Dissolve the residue in water, and filter if necessary. Add 0.5 ml. of concentrated hydrochloric acid to the filtrate, and evaporate to dryness in a small weighed platinum dish or in a large platinum crucible. Heat the dry residue carefully until the chlorides just commence to melt at the edges, then cool for 25 minutes in a desiccator, and weigh as rapidly as possible; the sodium chloride of the residue is somewhat hygroscopic. Repeat the ignition until constant weight is obtained. This gives the weight of the sodium and potassium chlorides.

Determine the potassium in the mixed chlorides by the perchlorate method (Section IV, 48B), or by the periodate method (Section IV, 48E), and the sodium by difference. Alternatively, estimate the sodium as sodium magnesium uranyl acetate (Section IV, 47C), and the potassium by difference. Calculate the results as percentages of $K_2O$ and $Na_2O$ respectively.

The reagents may contain traces of alkali metals, and the use of glass or porcelain vessels may introduce further small quantities. It is therefore advisable to run “blank” determinations for both potassium and sodium on the same amount of the ammonium chloride-calcium carbonate mixture and in exactly the same way as in the analysis.

Another method for the determination of the alkali metals, involving decomposition of the insoluble silicate with hydrofluoric acid, has been used with success.

G. Moisture. Dry 1 g., accurately weighed, of the felspar at 105–110° C. until constant in weight. Calculate the percentage loss in weight.

IV, 100. ANALYSIS OF PORTLAND CEMENT

Discussion. Portland cement is an example of an artificial silicate which is almost completely decomposed by means of acid, thus rendering the process of fusion with sodium carbonate unnecessary. The chief constituents, expressed in technical nomenclature, are: silica, lime, alumina and ferric oxide, magnesia, with small amounts of the oxides of the alkali metals; sulphuric anhydride and carbonic anhydride. The following constituents are usually determined in an industrial analysis: A. Insoluble matter; B. Silica; C. Alumina and ferric oxide; D. Lime; E. Magnesia; F. Sulphuric anhydride; G. Alkalis (by difference); H. Loss upon ignition.

It should be pointed out that “insoluble matter” may contain metallic
Gravimetric Analysis

593

elements, and for a complete scientific analysis this should be fused with sodium carbonate or with sodium peroxide, and the portion of the melt insoluble in water analysed for the other components. This procedure is, however, unnecessary for technical analysis. Full details for the complete analysis will be evident upon reference to Sections IV, 98, and IV, 99.

Procedure. A. Insoluble matter. Weigh out accurately about 1 g. of the finely divided Portland cement (1) into a 250-ml. porcelain dish or casserole, add 10 ml. of water, followed by 5 ml. of concentrated hydrochloric acid, and cover immediately with a clock-glass; warm until effervescence ceases. Add 40 ml. of water, digest upon a steam-bath or upon a low-temperature hot-plate until the decomposition is complete. Filter off the precipitate, and wash with hot water. Transfer the filter-paper and contents to a Pyrex beaker, and digest at just below the boiling point with 30 ml. of 5 per cent sodium carbonate solution for 15 minutes. Filter, wash with cold water, then with a few drops of 1:9 hydrochloric acid, and finally with hot water. Transfer the paper and precipitate to a weighed crucible, burn off the paper, ignite at a red heat, allow to cool, and weigh. Calculate the percentage of insoluble matter.

Note. 1. Ridsdale’s “Portland Cement, No. 24a” (one of the Analysed Samples for Students) is satisfactory for practice in this analysis.

B. Silica. Weigh out accurately about 0.5 g. of the sample into a 250-ml. porcelain dish or casserole, add 30 ml. of water, mix with a stirring-rod, and then introduce 10 ml. of concentrated hydrochloric acid; break up any lumps with the stirring-rod. Cover the dish, and heat on a water-bath until the cement is decomposed. Rinse the clock-glass with a little water, and evaporate to dryness on the water-bath. The clock-glass should be supported on a large glass triangle during the evaporation; alternatively, a Fisher “speedyvap” beaker-cover may be used. Complete the determination as in Section IV, 99B. Calculate the percentage of silica present.

Note. In a technical analysis the sulphuric-hydrofluoric acid treatment is not usually employed. The residue is heated for 1 hour at 200-250° C. then treated with 10 ml. of concentrated hydrochloric acid, warmed gently, diluted with hot water, filtered, and washed until free from chlorides. The filter is dried, and ignited for 1 hour in a muffle furnace, cooled and weighed. The weight of insoluble matter is subtracted from the weight of the residue; the difference is taken as that of silica. The filtrates are reserved for C.

C. “Alumina and ferric oxide.” Proceed exactly as in Section IV, 99C. The alumina and ferric oxide (and titanium oxide, if present) may be determined as in Section IV, 99, C1, C2, and C3 respectively.

Note. In a technical analysis, the “alumina and ferric oxide” are determined, as is also the ferric oxide. The latter is estimated in a fresh sample of cement as follows. About 1 g. of the cement, accurately weighed, is stirred with 50 ml. of water, 10 ml. of concentrated hydrochloric acid added, and heated to boiling. The ferric iron is reduced with stannous chloride solution in the usual way (Section III, 51A), treated with orthophosphoric acid and 2–3 drops of diphenylamine sulphonate indicator, and the ferrous iron titrated with standard potassium dichromate solution (Section III, 63, and III, 66; the other indicators given in the latter Section would be more satisfactory).
D. Lime. Follow the procedure of Section IV, 99D.

E. Magnesia. Follow the procedure of Section IV, 99E.

The following method, based upon the precipitation of the magnesium as the 8-hydroxy-quinolate, is rapid and accurate. Heat the filtrate and washings from the calcium determination to boiling, add a moderate excess of a 2 per cent solution of oxine in 2N-acetic acid, followed by 4 ml. of concentrated ammonia solution per 100 ml. of solution; stir the mixture vigorously during the addition. The supernatant liquid must be yellow at this stage, thus indicating the presence of excess of oxine; if not, more oxine solution must be added until the yellow colour is obtained. Boil the mixture for several minutes until the precipitate is crystalline, and allow to settle. Filter the precipitate through a weighed sintered-glass or porous-porcelain crucible, wash it thoroughly with 2 per cent ammonia solution, and dry to constant weight at 150–160° C. Weigh as Mg(C₆H₅O₇)₂. Alternatively, the precipitation may be dissolved in 2N-hydrochloric acid, and the magnesium determined by titration with standard potassium bromate solution as in Section III, 138, Procedure B.

F. Sulphuric anhydride. Two methods may be used. The first is employed for routine analysis in industry, and takes no account of any sulphur which may be present in the insoluble matter, and is also subject to a number of obvious errors. The second method gives the total sulphur content of the cement, and is therefore to be preferred.

Method 1. Weigh out accurately about 0.5 g. of the cement into a 250-ml. porcelain dish or casserole. Follow the procedure given under B to the point where the solution is evaporated to dryness on the water-bath. Extract the residue thoroughly with dilute hydrochloric acid, filter, and wash the precipitate. Determine the sulphate in the hydrochloric acid extract by precipitation with barium chloride solution as described in Section IV, 6. In order to compute the weight of barium chloride required, you may assume that the cement contains about 3 per cent of SO₃. Express your result as percentage of SO₃.

Method 2. Weigh out accurately about 0.5 g. of the cement into an iron or nickel crucible, add 2 g. each of sodium peroxide and of anhydrous A.R. sodium carbonate, mix thoroughly, insert the crucible in a hole in an asbestos or “uralite” shield (this will protect the contents from the sulphur in the flame gases), and heat the crucible gradually at first with a Bunsen burner, and finally over a Meker burner until the contents of the crucible are in quiet fusion. Allow to cool and, when cold, extract the crucible with hot water in a porcelain dish or casserole. Remove the crucible, and wash it thoroughly, allowing the washings to run into the dish. Cover the dish, and acidify cautiously with hydrochloric acid. Evaporate to dryness on the water-bath. Moisten the residue with 5 ml. of 1:1 hydrochloric acid, dilute with 200 ml. of water, and filter; wash thoroughly. Precipitate the sulphate in the boiling solution (300–350 ml.) by the addition of barium chloride solution (Section IV, 6). Filter, ignite, cool, and weigh. Express your result as percentage of SO₃.

G. Alkalis. Use the J. Lawrence Smith method of Section IV, 99F.

Note. In a technical analysis, the alkali content is usually obtained by difference.
**Gravimetric Analysis**

**H. Loss upon ignition.** Weigh out accurately about 1 g. of the cement into a platinum crucible, cover with the lid, and support in a hole in an asbestos or "uralite" board. Heat gradually, and then more strongly with a Meker-type burner until constant weight is obtained (about 30 minutes). Allow to cool in a desiccator for 25 minutes before weighing. Express your result as percentage loss upon ignition.

**Note.** If desired, the percentage of carbonate present may be determined by the method of Section IV, 76; use 2–4 g. for the determination.
SELECTED BIBLIOGRAPHY ON GRAVIMETRIC ANALYSIS


CHAPTER V

COLORIMETRIC ANALYSIS—SPECTROPHOTOMETRY—TURBIDIMETRY
AND NEPHELOMETRY—FLUORIMETRY

V, 1. General discussion.—The variation of the colour of a system with change in concentration of some component forms the basis of what the chemist commonly terms colorimetric analysis. The colour is usually due to the formation of a coloured compound by the addition of an appropriate reagent, or it may be inherent in the desired constituent itself. The intensity of the colour may then be compared with that obtained by treating a known amount of the substance in the same manner.

It must, however, be pointed out that colorimetric analysis is only a special case of the more general photometric chemical analysis. The latter may be defined as the analysis which is based upon the quantity of light absorbed by a coloured solution (spectrophotometry, colorimetry), or by a suspension (turbidimetry, Section V, 8), or by the amount of light scattered by a suspension (nephelometry, Section V, 8), or by the amount of light scattered by a solution with ultra-violet light as the exciting radiation (fluorimetry, Section V, 8). In visual colorimetry, natural or artificial white light is generally used as a light source, and determinations are usually made with a simple instrument termed a colorimeter. When the eye is replaced by a photo-electric cell (thus largely eliminating the errors due to the personal characteristics of each observer), the instrument is termed a photo-electric colorimeter. The latter is usually employed with light contained within a comparatively narrow range of wavelengths furnished by passing white light through filters, i.e., materials in the form of plates of coloured glass, gelatin films, etc., transmitting only a limited spectral region: the name filter photometer is sometimes applied to such instruments. In spectrophotometry, light of definite wavelength (not exceeding, say, 10–35 A. in band width) extending to the ultra-violet region of the spectrum, constitutes the source of light, and thus necessitates the use of a more complicated, and consequently more expensive, instrument: the instrument has been named a spectrophotometer.*

The chief advantage of colorimetric methods is that they provide a simple means for determining minute quantities of substances. The

* A spectrophotometer, as its name implies, is really two instruments in one cabinet—a spectrometer and a photometer. A spectrometer is a device for producing coloured light of any selected colour (or wavelength) and, when employed as part of a spectrophotometer, is usually termed a monochromator and is generally calibrated in wavelengths (μ). A photometer is a device for measuring the intensity of the light, and when incorporated in a spectrophotometer is used to measure the intensity of the monochromatic beam produced by the associated monochromator. Generally the photometric measurement is made first with a reference liquid and then with a coloured sample contained in similar cells interposed in the light beam: the ratio of the two intensity measurements being a measure of the opacity of the sample at the wavelength of the test.
upper limit of colorimetric methods is, in general, the determination of constituents which are present in quantities of less than 1 or 2 per cent. The development of inexpensive photo-electric colorimeters has placed this branch of instrumental chemical analysis within the means of even the smallest teaching institution.

V. 2. Theory of spectrophotometry* and colorimetry.—When light (monochromatic or heterogeneous) falls upon a homogeneous medium, a portion of the incident light is reflected, a portion is absorbed within the medium, and the remainder is transmitted. If the intensity of the incident light is expressed by $I_0$, that of the absorbed light by $I_a$, that of the transmitted light by $I_t$, and that of the reflected light by $I_r$, then:

$$I_0 = I_a + I_t + I_r$$

For air–glass interfaces consequent upon the use of glass cells, it may be stated that about 4 per cent of the incident light is reflected. $I_r$ is usually eliminated by the use of a control, such as a comparison cell, hence:

$$I_0 = I_a + I_t$$

(1)

Lambert (1760) investigated the relation between $I_0$ and $I_t$. Beer (1852) extended the experiments to solutions. Spectrophotometry and colorimetry are based upon Lambert’s and Beer’s laws.

**Lambert’s law.** This law states that when monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the light. This is equivalent to stating that the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically, or that any layer of given thickness of the medium absorbs the same fraction of the light incident upon it. We may express the law by the differential equation:

$$-\frac{dI}{dt} = kI$$

(2)

where $I$ is the intensity of the incident light of wavelength $\lambda$, $t$ is the thickness of the medium, and $k$ is a proportionality factor. Integrating (2) and putting $I_0$ for $t = 0$, we obtain:

$$\ln \frac{I_0}{I} = kt$$

or, stated in other terms,

$$I_t = I_0 \cdot e^{-kt}$$

(3)

where $I_0$ is the intensity of the incident light falling upon an absorbing medium of thickness $t$, $I_t$ is the intensity of the transmitted light, and $k$ is a constant called the absorption coefficient for the wave-length and the absorbing medium used. By changing from natural to Briggsian logarithms we obtain:

$$I_t = I_0 \cdot 10^{-0.4343kt}$$

(4)

* Spectrophotometry proper is mainly concerned with the following regions of the spectrum: ultra-violet, 185–400 mp (millimicrons); visible, 400–760 mp; and infra-red, 0·76–15 µ (microns). In this chapter our attention will be confined to the visible portion of the spectrum.

1 A = 0·1 mp = 10^{-4} = 1 \times 10^{-4} cm.

1 mp = 10 A = 10^{-7} cm.
where $K = k/2.3206$ and is usually termed the extinction coefficient (Bunsen and Roscoe, 1857). The extinction coefficient is generally defined as the reciprocal of the thickness ($t$ cm.) required to reduce the light to $1/10$ of its intensity. This follows from equation (4), since:

$$\frac{I_t}{I_0} = 0.1 = 10^{-Kt} \text{ or } Kt = 1 \text{ and } K = 1/t$$

The ratio $I_t/I_0$ is the fraction of the incident light transmitted by a thickness $t$ of the medium, and is termed the transmission. Its reciprocal $I_0/I_t$ is the opacity, and the optical density $D$ of the medium, sometimes designated the extinction $E$, is given by:

$$D = \log \frac{I_0}{I_t}$$

Thus a medium with optical density 1 for a given wavelength transmits 10 per cent of the incident light at the wavelength in question.

**Beer’s law.** We have thus far considered the light absorption and the light transmission for monochromatic light as a function of the thickness of the absorbing layer only. In quantitative analysis, however, we are mainly concerned with solutions. Beer (1852) studied the effect of concentration of the coloured constituent in solution upon the light transmission or absorption. He found the same relation between transmission and concentration as Lambert had discovered between transmission and thickness of the layer (equation (3)), i.e., the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically. This may be written in the form:

$$I_t = I_0 \cdot e^{-k'c}$$

$$= I_0 \cdot 10^{-0.4343Kc} = I_0 \cdot 10^{-Ect} \ldots \ldots (5)$$

where $c$ is the concentration, and $k'$ and $K'$ are constants. Combining (4) and (5), we have:

$$I_t = I_0 \cdot 10^{-Ect} \ldots \ldots \ldots \ldots \ldots (6)$$

This is the fundamental equation of colorimetry and spectrophotometry, and is often spoken of as the Beer-Lambert law. The value of $c$ will clearly depend upon the method of expression of the concentration. If $c$ is expressed in gram mols per litre and $t$ in centimetres then $c$ is the molecular extinction coefficient. The latter is equal to the reciprocal value of the thickness in centimetres of a 1 molar solution ($c = 1$) at which $I_t = 0.1I_0$, since $I_t = I_0 \cdot 10^{-Ect}$ when $t = 1$ and $c = 1$.

The specific extinction coefficient $E$, may be defined as the extinction coefficient per unit concentration.

Where the molecular weight of a substance is not definitely known, it is obviously not possible to write down the molecular extinction coefficient, and in such cases it is usual to write the unit of concentration as a superscript, and the unit of length as a subscript. Thus

$$E^\text{cm.}_1 = 325 \text{ m} \mu = 30$$

means that for the substance in question, at a wavelength of 325 m$\mu$, a solution of length 1 cm., and concentration 1 per cent (1 per cent
Colorimetric Analysis

by weight of solute or 1 g. of solid per 100 ml. of solution) \( \log I_0/I_t \) has a value of 30.

We may recapitulate some of the various technical terms which are in common use in colorimetric and spectrophotometric measurements:

The optical density \( D \), also called the extinction \( E \), of a medium is the logarithmic ratio of the intensity of the incident light to that of the emergent light, i.e.,

\[
D = E = \log (I_0/I_t) \text{ or } I_t = I_0 \cdot 10^{-D}
\]  

\[ (7) \]

\( D \) is obviously related in a simple way to the molecular extinction coefficient, since:

\[
D = \varepsilon ct
\]

The molecular extinction coefficient is therefore the optical density when the layer of solution is 1 cm. thick and the concentration of the absorbing substance is 1 g.mol. per litre.

The transmission \( T \) is defined as the ratio of the intensity of the transmitted to that of the incident light; thus:

\[
T = I_t/I_0
\]

The term transmittance or transmittancy \( T_c \), widely used in the U.S.A., is defined as the ratio of the transmission of a cell containing the coloured solution to that of an identical cell containing water or a blank solution.

The optical density \( D \) may therefore be put equal to the logarithm of the reciprocal of the transmission:

\[
D = \log (1/T) = - \log T
\]

The scales of spectrophotometers are often calibrated to read directly in densities, and frequently also in percentage transmission. It may be mentioned that for colorimetric measurements \( I_0 \) is usually understood as the intensity of the light transmitted by the pure solvent, or the intensity of the light entering the solution; \( I_t \) is the intensity of the light emerging from the solution, or transmitted by the solution. It will be noted that:

the extinction coefficient is the density for unit path length

\[
K = D/t \text{ or } I_t = I_0 \cdot 10^{-Kt}
\]

the specific extinction coefficient is the density per unit path length and unit concentration

\[
\varepsilon_t = D/ct \text{ or } I_t = I_0 \cdot 10^{-\varepsilon_t ct}
\]

the molecular extinction coefficient is the specific extinction coefficient for a concentration of 1 g.-mol. per litre and a path length of 1 cm.

\[
\varepsilon = D/ct
\]

Application of Beer’s law. Let us consider the case of two solutions of a coloured substance with concentrations \( c_1 \) and \( c_2 \). These are placed in an instrument in which the thickness of the layers can be altered and measured easily, and which also allows a comparison of
Quantitative Inorganic Analysis

the transmitted light (e.g., a Duboscq colorimeter, Section V. 6). When the two layers have the same colour intensity:

\[ I_i = I_0 \cdot 10^{-a_i c_i} = I_i = I_0 \cdot 10^{-a_i c_i} \quad \cdots \quad (8) \]

Here \( t_1 \) and \( t_2 \) are the lengths of the columns of solutions with concentrations \( c_1 \) and \( c_2 \) respectively when the system is optically balanced. Hence under these conditions and when Beer's law holds:

\[ t_1 c_1 = t_2 c_2 \quad \cdots \quad \cdots \quad \cdots \quad (9) \]

A colorimeter can therefore be employed in a dual capacity: (a) to investigate the validity of Beer's law by varying \( c_1 \) and \( c_2 \) and noting whether equation (9) applies, and (b) for the determination of an unknown concentration \( c_2 \) of a coloured solution by comparison with a solution of known concentration \( c_1 \). It must be emphasised that equation (9) is valid only if Beer's law is obeyed over the concentration range employed and the instrument has no optical defects.

When a spectrophotometer is used it is unnecessary to make comparison with solutions of known concentration. With such an instrument the intensity of the transmitted light or, better, the ratio \( I_i/I_0 \) (the transmittance) is found directly at a known thickness \( t \). By varying \( t \) and \( c \) the validity of the Lambert-Beer law, equation (6), can be tested and the value of \( e \) may be evaluated. When the latter is known, the concentration \( c_2 \) of an unknown solution can be calculated from the formula:

\[ c_2 = \frac{\log I_0/I_i}{e t} \quad \cdots \quad \cdots \quad \cdots \quad (10) \]

Attention is directed to the fact that the extinction coefficient \( e \) depends upon the wavelength of the incident light, the temperature, and the solvent employed. In general, it is best to work with light of wavelength approximating to that for which the solution exhibits a maximum selective absorption (or minimum selective transmittance): the maximum sensitivity is thus attained.

For matched cells (i.e., \( t \) constant), the Lambert-Beer law may be written:

\[ c = A \log I_0/I_i = A \log 1/T \]

or

\[ c = B \log T \quad \cdots \quad \cdots \quad \cdots \quad (11) \]

where \( A \) and \( B \) are constants; the concentration is therefore proportional to the logarithm of its transmittance. Hence by plotting \( \log T \) (ordinates) against concentration (abscissae), a straight line will be obtained, and this will pass through the point \( c = 0, T = 100 \) per cent (semi-log paper should be used): if the Lambert-Beer law is valid only one value of \( c \) and the corresponding value of \( T \) is required. Values of \( c \) can be read off from observed values of \( T \) as determined with a spectrophotometer.

Deviation from Beer's law. Beer's law will generally hold over a wide range of concentration if the structure of the coloured ions or of the coloured non-electrolytes in the dissolved state does not change with concentration. Small amounts of electrolytes, which do not react chemically with the coloured components, do not usually affect the light absorption; large amounts of electrolytes may result in a
shift of the maximum absorption, and may also change the value of
the extinction coefficient. Discrepancies are usually found when the
coloured solute ionises, dissociates, or associates in solution, since
the nature of the species in solution will vary with the concentration.
Also discrepancies may occur when monochromatic light is not used.
The behaviour of a substance can always be tested by plotting
log \( I_0/I_1 \), \( E \) or log \( T \) against the concentration: a straight line passing
through the origin indicates conformity to the law.

For solutions which do not follow Beer's law, it is best to prepare
a calibration curve using a series of standards of known concentration.
Instrumental readings are plotted as ordinates against concentrations
in, say, mg. per 100 ml. or 1000 ml. as abscissae. For the most precise
work each colour formation should be calibrated over the dilution
range likely to be met with in the actual comparison.

V. 3. Classification of methods of "colour" measurement or com-
parison.—The basic principle of most colorimetric measurements con-
sists in comparing under well-defined conditions the colour produced
by the substance in unknown amount with the same colour produced
by a known amount of the material being determined. The quantita-
tive comparison of these two solutions may, in general, be carried
out by one or more of six methods. It is not essential to prepare a
series of standards with the spectrophotometer; the molecular
extinction coefficient can be calculated from one measurement of the
optical density or transmittance on a standard solution, and the
unknown concentration can then be computed with the aid of the
molecular extinction coefficient and the observed value of the optical
density or transmittance (cf. Section V, 2, equations (10) and (11)).

A. Standard series method. The test solution contained in a Nessler
tube (Section V, 4) is diluted to a definite volume, thoroughly mixed,
and its colour compared with a series of standards similarly prepared.
The concentration of the unknown is then, of course, equal to that
of the known solution whose colour it matches exactly. The accuracy
of the method will depend inter alia upon the concentration of the
standard series; the probable error is of the order of ± 3 per cent,
but may be as high as ± 8 per cent.

For convenience, artificial standards, e.g., Lovibond glasses, salt
solutions such as ferric chloride in aqueous hydrochloric acid (yellow),
aqueous cobalt chloride (pink), aqueous copper sulphate (blue), and
aqueous potassium dichromate (orange) are sometimes used. It is
essential to standardise the artificial standards against known amounts
of the substance being determined, the latter always being treated
under exactly similar conditions. The disadvantage of this method
is that the spectral absorption curves of the test solutions and of the
sub-standard glasses or solutions may be far from identical; the error
due to this cause is greatly magnified in the case of observers suffering
from partial colour blindness.

B. Duplication method. A standard solution of the component
under determination is added to the reagent until the colour produced
matches that of the unknown sample in the same volume of solution.
This method is less accurate than A.

C. Dilution method. The sample and standard solution are con-
tained in glass tubes of the same diameter, and are observed horizontally
through the tubes. The more concentrated solution is diluted until
the colours are identical in intensity when observed horizontally through the same thickness of solution. The relative concentrations of the original solutions are then proportional to the heights of the matched solutions in the tubes. This is the least accurate method of all, and will not be discussed further.

D. Balancing method. This method forms the basis of all colorimeters of the plunger type, e.g., in the Dubosq colorimeter. The comparison is made in two tubes, and the height of the liquid in one tube is adjusted so that when both tubes are observed vertically the colour intensities in the tubes are equal. The concentration in one of the tubes being known, that in the other may be calculated from the respective lengths of the two columns of liquid and the relation:

\[ c_1 l_1 = c_2 l_2 \] (Section V, 2)

It must be emphasised again that this simple proportionality holds only if Beer's law is applicable, and that the relation holds with greater exactness if a beam of monochromatic light (obtained with the aid of a suitable colour filter) rather than white light is employed. As a general rule, it is preferable that the solutions under comparison should not differ greatly in concentration, and for the most accurate work an empirically constructed calibration curve should be used. As usually employed with white light, the accuracy obtainable with a Dubosq colorimeter is of the order of ± 7 per cent; the accuracy is increased appreciably if monochromatic light (produced with colour filters) is employed.

E. Photo-electric photometer method. In this method the human eye is replaced by a suitable photo-electric cell; the latter is employed to afford a direct measure of the light intensity, and hence of the absorption. Instruments incorporating photo-electric cells measure the light absorption and not the colour of the substance: for this reason the term "photo-electric colorimeters" is a misnomer; better names are photo-electric comparators, photometers, or, best, absorptiometers.

Essentially most such instruments consist of a light source, a suitable light filter to secure an approximation to monochromatic light (hence the name photo-electric filter photometer), a glass cell for the solution, a photo-electric cell to receive the radiation transmitted by the solution, and a measuring device to determine the response of the photo-electric cell. The comparator is first calibrated in terms of a series of solutions of known concentration, and the results plotted in the form of a curve connecting concentrations and readings of the measuring device employed. The concentration of the unknown solution is then determined by noting the response of the cell and referring to the calibration curve.

These instruments are available in a number of different forms incorporating one or two photo-cells. With the one-cell type, the absorption of light by the solution is usually measured directly by determining the current output of the photo-electric cell in relation to the value obtained with the pure solvent. It is of the utmost importance to use a light source of constant intensity, and if the cells exhibit a "fatigue effect" it is necessary to allow the photo-cell to attain its equilibrium current after each change of light intensity. The two-cell type of filter photometer is usually regarded as the more trustworthy.
Colorimetric Analysis

(provided the electrical circuit is appropriately designed) in that any fluctuation of the intensity of the light source will affect both cells alike if they are matched for their spectral response. Here the two photo-cells, illuminated by the same source of light, are balanced against each other through a galvanometer: the test solution is placed before one cell and the pure solvent before the other, and the current output difference is measured.

F. Spectrophotometer method. This is undoubtedly the most accurate method for determining inter alia the concentration of substances in solution, but the instruments are, of necessity, more expensive. A spectrophotometer may be regarded as a refined-filter photo-electric photometer which permits the use of continuously variable and more nearly monochromatic bands of light. The essential parts of a spectrophotometer are: (i) a source of radiant energy, (ii) a monochromator, i.e., a device for isolating monochromatic light or, more accurately expressed, narrow bands of radiant energy from the light source, (iii) glass cells for the solvent and for the solution under test, and (iv) a device to receive or measure the beam or beams of radiant energy passing through the solvent or solution. Further details will be found in Section V, 7.

In the following Sections it is proposed to discuss the more important of the above methods in somewhat greater detail. For a more complete treatment the reader is referred to the special treatises on the subject (see Selected Bibliography, Section V, 32).

V. 4. Standard series method.—In this method colourless glass tubes of uniform cross-section and with flat bottoms are usually employed. These are termed Nessler tubes. The best variety has a polished, flat bottom.* They are made in either the “low” form with a height of 175–200 mm. and a diameter of 25–32 mm. (Fig. V, 4, 1) or as a “high” form with a height of 300–375 mm. and a diameter of 21–24 mm. The solution of the substance being determined is made up to a definite volume, and the colour is compared with that of a series of standards prepared in the same way from known amounts of the component being determined. Fifty or 100 ml. of the unknown and standard solutions are placed in Nessler tubes, and the solutions are viewed vertically through the length of the columns of the liquid. The concentration of the unknown is equal to that of the standard having the same colour.† As a general rule, it will be found that the colour intensity of the unknown lies between two successive standards.

* The “double-plane” Nessler tubes supplied by the Fisher Scientific Co. of Pittsburgh, U.S.A., have bottoms which have been ground and polished optically plane on both sides and then fused to the tubes. They are very satisfactory in use, since they produce a uniform field of colour intensity.

† It is advisable wherever possible to make a preliminary determination of the strength of the unknown solution by adding from a burette a solution of the component in known concentration to a Nessler tube containing the reagents diluted with a suitable amount of water until the depth of colour obtained is practically the same as that of an equal volume of the unknown solution also contained in a Nessler cylinder and standing at its side. A series of standards on either side of this concentration is then prepared.
Another series of standards may then be prepared covering the latter range over smaller concentration intervals. Thus, for example, in the determination of a particular constituent the first series of standards might cover the range 0·1, 0·2, 0·4, 0·6, 0·8, and 1·0 mg. per litre, and it is found that the colour of the unknown lies between 0·4 and 0·6 mg. per litre. The second series of standards may then be prepared containing 0·40, 0·45, 0·50, 0·55, and 0·60 mg. per litre. Further comparison may then show that the value lies between 0·45 and 0·50 mg. per litre, and for many purposes this should be returned as 0·48 mg. per litre. If a more accurate value is required, and provided the colour intensity of the solution and also the apparatus employed will permit of finer comparison, another series of standards covering the range of, say, 0·45, 0·475, and 0·50 mg. per litre may be made up and the unknown compared with these standards.

For the comparison of colours in Nessler tubes, the simplest apparatus consists of a modified test-tube rack (Fig. V, 4, 2). It is constructed of wood, finished dull black, and is provided with an inclined opal glass reflector or mirror, arranged to reflect light up through the tubes. The Nessler tubes rest on a narrow edge, and do not come into contact with the reflector. The unknown and standards are compared by placing them adjacent to each other and looking vertically down through them.

There are a number of devices which employ permanent coloured-glass standards; these are usually prepared from Lovibond or similar type glasses. An inexpensive model is shown in Fig. V, 4, 3. This is the B.D.H. Lovibond nesslerimeter* (for other similar apparatus, such as the Lovibond comparator, see Section V, 9 on the determination of pH). It consists essentially of a Bakelite case for holding vertically two Nessler glasses between a reflector and a detachable rotating disc having nine apertures containing a series of graded, permanent glass colour standards. Each disc incorporates a

* The apparatus is manufactured by The Tintometer Ltd., Milford, Salisbury, in association with British Drug Houses Ltd., Poole, Dorset.
Colorimetric Analysis

series of standards designed for one particular test conducted under specified conditions. Discs are available for many of the common determinations by colorimetric methods, and the manufacturers are constantly extending the range. The discs at present marketed include: ammonia (with Nessler's reagent); bismuth (with potassium iodide); chlorine in water (with o-tolidine); cobalt (with nitroso-R-salt); copper (with dithio-oxamide); iron (with thioglycollic acid); lead (with sodium sulphide); manganese (with sodium bismuthate); nitrate (with phenoldisulphonic acid and also with 2:4-xylen-1-ol); pH (various ranges with different indicators); silicate (with ammonium molybdate); and titanium (with hydrogen peroxide). A wider range of determinations can be made with the discs supplied with the Lovibond comparator (see Fig. V, 9, 2).

The B.D.H. Lovibond nesslerimeter can, of course, be employed as a simple comparative colorimeter as described above; the colour disc is then removed.

V, 5. Duplication method.—This method finds its chief application in the so-called colorimetric titration. A known volume, say 50 or 100 ml., of the solution is placed in a Nessler cylinder (Fig. V, 4, 1) and a measured volume of the reagent or reagents is then added. An equal volume of water (50 or 100 ml.) together with the same volume of the reagent is introduced into another similar Nessler cylinder. For mixing the solutions both cylinders are provided either with a glass tube on which a flattened bulb (ca. 1 cm. diameter) is blown or with a stirring-rod of which the lower end is flattened to a width of 1 cm. and over a length of several centimetres. The tubes should also be provided with black- or brown-paper cylinders to exclude light from the sides. The colour intensities are compared by holding the tubes close together over a white surface, such as a sheet of opal glass or, better, in a Nessler tube-stand (Fig. V, 4, 2). A solution containing a known concentration of the constituent being determined is added to the blank solution from a burette (preferably of the micro type) until the colours of the two solutions viewed by looking down into the tubes match. As a rule, if the volume of the standard solution required to match the colour of the unknown is less than about 2 per cent of the total volume, the volume change due to the addition of the reagent may be neglected. It may, however, be allowed for by a simple calculation, or the determination may be repeated by taking 100 — x (or 50 — x) ml. of water, where x is the volume of the standard solution employed in the first titration. Several determinations should be carried out, and the positions of the tubes should be interchanged—thus that on the right-hand side should be put to the left of the observer and vice versa.

It must be emphasised that this method can be applied only when the colour is independent of the mode of mixing, for in one tube a very dilute solution of the substance to be determined is mixed with the reagent, whilst in the other tube a comparatively concentrated solution of the substance is mixed with a dilute solution of the reagent. The development of colour should be practically instantaneous and remain permanent during the time required for the measurements; foreign substances present in the unknown should not affect the colour. The method is, at best, only an approximate one, but has the advantage that only the simplest apparatus is required.
V, 6. Balancing method. Plunger-type colorimeters.—The plunger-type of colorimeter with two halves of the field of view illuminated by the light passing through the unknown and standard solutions respectively was invented by J. Duboscq of Paris in 1854. Various improved modifications of the instrument were subsequently developed by manufacturers of optical apparatus. Before describing the latter, reference must be made to Hehner cylinders (Fig. V, 6, 1). These are utilised in pairs, and are the simplest form of apparatus employed in matching colours by the balancing method. Each cylinder has a glass stopcock about 2.5 cm. from the bottom through which liquid may be drawn off until the colour in the two cylinders is the same in intensity when viewed vertically. The cylinders are graduated at 1-ml. intervals, and usually have a capacity of 100 ml.; they should have flat, carefully ground and polished bottoms of clear glass and be uniform in bore. It is advisable to place them in a box so arranged that the light is reflected from the bottom of the latter up through the tubes.

A Duboscq colorimeter (the Watts "Microptic" colorimeter *) is shown in Fig. V, 6, 2, and sectional diagrams in Figs. V, 6, 3 and V, 6, 4.


The more conventional types of Duboscq colorimeter, i.e., with scales and verniers which are read at each side of the instrument, include the "Crista" colorimeter from Hawksley and Son, Ltd., 17 New Cavendish Street, London, W.1, and the "biological model" from Bausch and Lomb Optical Co., Rochester, N.Y.
The essential principles of the instrument will be evident from Fig. V, 6, 5. Light from an even source of illumination concealed in the base of the instrument passes through the windows (matt white screens) in the top of the base through the solutions to be tested and through the plungers. Some of the light is absorbed in passing through the liquids, the amount of absorption being dependent upon the concentration and the depth of the solution. The two beams of light from the plungers are then brought to a common axis by a prism system. On looking through the eyepiece, a wide, circular field is visible, light from one cup illuminating one half, and light from the second cup illuminating the other half of the field. The depths of the columns of liquids are adjusted by rotating the milled heads on either side of the instrument, which raises and lowers the cups, until the two halves of the field are identical in intensity, i.e., until the dividing line practically disappears. When this condition holds and Beer's law is applicable, the concentrations of the two solutions are inversely proportional to their depths, which are normally read on the scales on the side of the instrument.

In the "Microptic" colorimeter the two precisely divided glass scales, reading directly to 0.1 mm. and so dispensing with the use of x
Quantitative Inorganic Analysis

A vernier are viewed simultaneously in the reading microscope (situated immediately adjacent to the main eyepiece), which has a magnification of $\times 10$. The scales have a range of 60 cm., and readings can easily be made with the aid of an index pointer to about one-fifth of a division (0.02 mm.). The cups and plungers are all-glass, i.e., the bottoms have ground and polished surfaces, and are fused to the cylinders. Two sizes are supplied with the instrument; the smaller sizes have a capacity of ca. 1 ml. each, and are employed with “micrometer” plungers which are interchangeable with the larger type. Each cup is provided with a special fitting on the bottom, permitting the insertion of either one or two Ilford or Wratten filters. The front metal cover, which forms a light shield and protection for the cups and plungers, slides on a grooved fitting, and is easily removed for access to the cups.

Use of Duboscq-type colorimeter. The colorimeter must be kept scrupulously clean. The cups and plungers are rinsed with distilled water and either dried with soft lens-polishing material or rinsed with the solution to be measured.

Make sure that the readings are zero when the plungers just touch the bottoms of the cups. Place the standard solution in one cup, and an equal volume of the unknown solution in the other; do not fill the cups above the shoulder. Set the unknown solution at a scale reading of 10.0 mm. and adjust the standard until the fields are matched. Carry out at least six adjustments with the cup containing the standard solution, and calculate the mean value.

The plungers should always remain below the surface of the liquid. Since the eye may become fatigued and unable to detect small differences, it is recommended after making adjustment to close the eyes for a moment or to look at something else, and then see if the adjustment still appears satisfactory. It is advisable to approach the match point both from above and from below.

If $t_1$ and $t_2$ are the average readings for the cups containing the solutions of known and unknown concentration respectively, and $c_1$ and $c_2$ are the corresponding concentrations, then if Beer’s law holds:

$$c_1 t_1 = c_2 t_2$$

It will be noted that if $t_2 = 10.0$, the standard scale when multiplied by 10 will give the percentage concentration of the sample in terms of the standard.

Owing to optical and mechanical imperfections of some makes of colorimeters, it is sometimes found that the same reading cannot be obtained in the adjustment for illumination when the cups are filled with the same solution and balanced. In such a case one of the cups (say, the left one) is filled with a reference solution (which may be a solution containing the component to be determined) of the same colour and approximately the same intensity as the unknown
and the plunger set at some convenient point (about the middle) of the scale. Fill the other cup with a solution having a colour corresponding to a known concentration of the component to be determined, and adjust this cup to colour balance. Take the reading and repeat the adjustment, say ten times, in such a way that the balancing point is approached five times from the lower and five times from the higher side. Calculate the average reading \( t_1 \). Remove the cup, rinse it thoroughly, and fill it with the unknown solution. Repeat the balancing exactly as for the standard solution, and find the average of, say, 10 readings \( t_2 \). If \( c_1 \) is the concentration in the standard solution, then the concentration of the unknown solution is given by:

\[
c_2 = c_1 \frac{t_1}{t_2}
\]

(This method is comparable in many respects to the method of weighing by substitution.) If Beer's law is not valid for the solution, it is best to arrange matters so that the colour intensity of the standard lies close to that of the unknown.

Immediately the determination has been completed, empty the cups and rinse both the cups and plungers with distilled water. Leave the colorimeter in a scrupulously clean condition.

### V. 7. Photo-electric filter photometer method

**Photo-electric colorimeters (absorption meters).** One of the greatest advances in the design of colorimeters has been the use of photo-electric cells to measure the intensity of the light, thus eliminating the errors due to the personal characteristics of each observer. Before describing the various types of photo-electric colorimeters, a brief account will be given of the construction and properties of the light-sensitive devices employed. Photo-emissive and particularly barrier-layer-type cells are commonly employed.

**Photo-emissive cells.** In the simplest form of photo-emissive cell (also termed photo-tube in the U.S.A.) a glass bulb is coated internally with a thin, sensitive layer, such as cesium or potassium oxide and silver oxide (i.e., one which emits electrons when illuminated), a free space being left in one part to permit the entry of the light. This layer is the cathode. A metal ring inserted near the centre of the bulb forms the anode, and is maintained at a high voltage by means of a battery. The interior of the bulb may be either evacuated or filled with an inert gas at low pressure (for example, argon at about 0.2 mm.). When light, penetrating the bulb, falls on the sensitive layer, electrons are emitted, thereby causing a current to flow through an outside circuit; this current may be amplified by electric means, and is taken as a measure of the amount of light striking the photo-sensitive surface. Otherwise
expressed, the emission of electrons leads to a fall in potential across a high resistance in series with the cell and the battery; the fall in potential may be measured by a suitable potentiometer, and is related to the amount of light falling on the cathode. The action of the photo-emissive cell is shown diagrammatically in Fig. V, 7, 1.

Barrier-layer cells. A barrier-layer cell (also known as a photovoltaic or photronic cell) is entirely different in design and principle from the photo-emissive cell, and it operates without the use of a battery. The commonest form consists essentially of a metal base plate A (usually of iron) upon which is deposited a thin layer of selenium B (see Fig. V, 7, 2); this is covered, in turn, by a trans-

![Diagram of barrier-layer cell](image)

parent metal layer D, which is lacquered except for a portion mechanically strengthened to form a collecting ring E. The underside of the metal base plate is covered by a non-oxidising metal. When light, passing through the thin metal layer, falls upon the selenium surface, electrons are released, and these penetrate a hypothetical barrier layer C and give the transparent metal layer D a negative charge. Thus, under the action of light, we have a cell of which the negative pole is the metal collecting ring E and the positive pole is the metal base plate. If this cell be connected to a galvanometer, a current will flow which will vary with the intensity of the incident light.

The "Eel" selenium photo-cell* is an excellent example of a highly sensitive barrier-layer cell. Fig. V, 7, 3 shows how the current output of a typical "Eel" 45-mm. cell varies with the intensity of the light falling upon it and with the resistance in the external circuit.

With 100 ohms external resistance the current is almost linear at both high and low illuminations; with 200 ohms the response is linear only up to about 150 ft.-candles. In the single-cell type of photo-electric colorimeter, the galvanometer (or micro-ammeter) reading is taken as a measure of the intensity of the light falling upon the cell. It is important therefore that conditions be so chosen that there is a straight-line relationship between the light intensity and the current output; this may be achieved by having a low resistance in the external circuit (<100–200 ohms) and using a low level of illumination. The linear response is not important for colorimeters of the two-cell type.

The current output of the barrier-layer cell is dependent also upon the wavelength of the incident light, the variation being similar to

Colorimetric Analysis

Fig. V, 7, 3.

Fig. V, 7, 4.
that of the human eye, particularly if a corrective filter is employed. The spectral response of the "Eel" cell compared with that of the eye is shown in Fig. V, 7, 4.

Light filters. Optical filters are used in colorimeters (absorptiometers) for isolating desired spectral regions. They consist of coloured glass or gelatin impregnated with a dye, and possessing the property of transmitting light from a specified region of the spectrum, the other components being preferentially absorbed. Ilford spectrum filters, Chance glass filters, or Corning glass colour filters are largely used. The approximate peak of transmission of a series of Ilford spectrum filters in combination with heat-absorbing filters (as used with the Hilger Spekker absorptiometer—see below) are collected in the following table; Fig. V, 7, 5 gives the transmission curves (as measured with a Hilger "Uvispek") which clearly show the band widths. It will be noted that by the use of these filters a fairly close approximation to monochromatic light may be obtained over the whole of the spectrum range.

<table>
<thead>
<tr>
<th>No.</th>
<th>Colour Name.</th>
<th>Approx. Peak of Transmission (mµ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>601</td>
<td>Spectrum violet</td>
<td>430</td>
</tr>
<tr>
<td>602</td>
<td>Spectrum blue</td>
<td>470</td>
</tr>
<tr>
<td>603</td>
<td>Spectrum blue-green</td>
<td>490</td>
</tr>
<tr>
<td>604</td>
<td>Spectrum green</td>
<td>515</td>
</tr>
<tr>
<td>605</td>
<td>Spectrum yellow-green</td>
<td>545</td>
</tr>
<tr>
<td>606</td>
<td>Spectrum yellow</td>
<td>570</td>
</tr>
<tr>
<td>607</td>
<td>Spectrum orange</td>
<td>600</td>
</tr>
<tr>
<td>608</td>
<td>Spectrum red</td>
<td>680</td>
</tr>
</tbody>
</table>
To determine which filter to use with a coloured solution, it is usually best to take readings with the photo-electric colorimeter with each of the spectrum filters in turn. As a general rule the best filter to use in a particular determination is that which gives the maximum absorption or minimum transmission for a given concentration of the absorbing substance; in practice, it is found that filters which give good proportionality at various concentrations are also satisfactory.

With certain determinations the spectral filters absorb so much of the incident light that it is impossible to obtain a full-scale deflection of the galvanometer. In such cases filters with a high transmission must be used. Although these filters do not possess such a narrow range of transmission as spectral filters, they have proved satisfactory in biochemical practice. Examples of such filters include the Chance glass filters as used with the Hilger Biochem absorptiometer; the transmission curves are shown in Fig. V, 7, 6, and other data are tabulated below.

**CHANCE GLASS FILTERS**

<table>
<thead>
<tr>
<th>No.</th>
<th>Colour</th>
<th>Approx. Peak of Transmission (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OR₁</td>
<td>Violet</td>
<td>440</td>
</tr>
<tr>
<td>OR₂</td>
<td>Blue</td>
<td>470</td>
</tr>
<tr>
<td>OG₁</td>
<td>Green</td>
<td>550</td>
</tr>
<tr>
<td>OY₂</td>
<td>Orange</td>
<td>Over 600 *</td>
</tr>
<tr>
<td>OR₂</td>
<td>Red</td>
<td>Over 650 *</td>
</tr>
</tbody>
</table>

* These two filters exhibit no drop in transmission above these values in the visible spectrum.

A general idea of the filter to use may be obtained from the following table due to Mellon (1945). It is the filter which gives the greatest difference in reading between two concentrations of the unknown solution.
A filter of the complementary colour to the solution is required. The following table, due to Gibb (1942), may be found useful:

**Complementary Colours**

<table>
<thead>
<tr>
<th>Wavelength (μm)</th>
<th>Hue (transmitted)</th>
<th>Complementary Hue</th>
</tr>
</thead>
<tbody>
<tr>
<td>400–435</td>
<td>Violet</td>
<td>Yellowish-green</td>
</tr>
<tr>
<td>435–480</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>480–490</td>
<td>Greenish-blue</td>
<td>Orange</td>
</tr>
<tr>
<td>490–500</td>
<td>Bluish-green</td>
<td>Red</td>
</tr>
<tr>
<td>500–580</td>
<td>Green</td>
<td>Purple</td>
</tr>
<tr>
<td>580–590</td>
<td>Yellowish-green</td>
<td>Violet</td>
</tr>
<tr>
<td>590–610</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>610–750</td>
<td>Orange</td>
<td>Greenish-blue</td>
</tr>
<tr>
<td></td>
<td>Red</td>
<td>Bluish-green</td>
</tr>
</tbody>
</table>

* Manufactured by:

5. Fisher Scientific Company, 717 Forbes Street, Pittsburgh 19, Pa., U.S.A.
**Colorimetric Analysis**

**Fig. V, 7.7.**

**Fig. V, 7.8.**
controlled by a shutter. Eight Ilford filters (Nos. 607-8 and 621-6) are supplied. Matched test-tubes of 3 or 7 ml. capacity are employed.

The scale on the instrument is logarithmic. There is one test-tube holder in the instrument, and the makers term it a single-cell absorptiometer.

**Hilger Biochem absorptiometer.** This instrument is depicted in Fig. 7, 10. The light source is a 6-volt, 18-watt filament lamp operated either from a constant-voltage transformer or an accumulator; a light shutter is also provided. Matched test-tubes (6 in. × $\frac{3}{4}$ in.) or fused-glass cells (0·25–4 cm. in length) may be used. The range of the five glass filters normally supplied with the instrument is shown in Fig. 7, 6. The current produced by the photo-cell is measured by means of a sensitive galvanometer which is fitted with two scales—one a logarithmic scale and the other indicating percentage transmission. A variable resistance is connected in parallel with the galvanometer, so that it controls the total photo-electric current pass-
Colorimetric Analysis

Bausch and Lomb "monochromatic" colorimeter. A diagrammatic representation of this instrument is given in Fig. V, 7, 10A. Light from a 6-volt, 32-c.p. lamp, operated from a constant-voltage transformer, passes through the condensing lens, a heat-absorbing filter, a control diaphragm, a light ("interference") filter, through the sample (contained in a test-tube or cuvette), and finally strikes the barrier-layer cell. The current output of the barrier-layer cell is measured by a sensitive double-suspension galvanometer. The light filters normally supplied (430, 500, 550 and 630 mp) have a narrow band pass of ca. 20 mp and a transmission of about 40 per cent; filters for other wave lengths are available.
Unicam G.P. photo-electric colorimeter. This colorimeter (Fig. V, 7, 11) operates from a 6-volt battery or a constant-voltage transformer. The light is controlled by a shutter mechanism operated by two controls, "coarse" and "fine." Ilford spectrum filters (No. 608 red, 609 deep red, 621 violet, 622 blue, 623 blue green, 624 green, 625 yellow green, and 626 yellow) are supplied. The sensitive galvanometer is calibrated with a linear scale 0–100 and a logarithmic scale; the scale is removable, and can be substituted by others, if desired.

An important feature is the dual cell-holder, which slides each cell in the light path as required (compare Fig. V, 7, 7).

Two-cell instruments. In view of possible variations of the operating current for the light source in one-cell colorimeters, two-cell circuits have been proposed based upon the idea that fluctuations would affect the two cells equally and thus be compensated. In addition, the null-point method of balancing the cells against each other, as indicated by a galvanometer, is supposed largely to eliminate errors arising from cell fatigue or temperature changes. The two photocells should be selected on the basis of similarity in spectral response, and should be matched as closely as possible. Examples of actual circuits will be given in the description of the various instruments.

Hilger Spekker absorptiometer. The actual instrument (type H 760) is shown in Fig. V, 7, 12; the optical arrangements are incorporated in Fig. V, 7, 13, which includes the photo-electric circuit. A 100-watt projection lamp G, mounted in a central lamphouse and run from the electric-supply mains, is the source of light. To the right of G the light first passes through a heat-absorbing filter H, and then through
Colorimetric Analysis

To render it parallel before it passes through a cam-shaped diaphragm $J$, which controls the aperture of the beam and hence its intensity. The light then passes through a cell for the absorbing liquid $L$, a selected colour filter $M$, and a lens $N$, which forms an image of the light source on the surface of the photo-cell $O$. On the left of $G$ the light passes through a heat-absorbing filter $F$, symmetrical with $H$, an iris diaphragm $E$, a lens system $D$ and $B$ (corresponding with that on the right-hand side of the instrument), a selected colour filter $C$, and, finally, an image of the light source $G$ is formed on the photo-cell $A$.

The cam-shaped disc $J$ is connected with a large, calibrated drum, and enables the intensity of the light falling upon the photo-cell $O$ to be varied by known amounts. Since there is an image of the filaments on the cell there is no change in the photo-cell area illuminated when the aperture alters; only the quantity of light reaching the cell is controlled by the variable aperture formed by the upper portion of the circumference of the cam and the diaphragm limiting the area of the light beam. The scale associated with the aperture is so calibrated that if $R$ is the reading corresponding to a degree of opening...
such that the amount of light transmitted is $1/A$ of that admitted
when the aperture is fully open, then $R = \log A$. This function,
known as optical density, was chosen because it is approximately
linear with the concentration of a solution over small ranges. This
function is normally a logarithmic one, but by giving the cam disc $J$
a suitable contour, an evenly divided scale on the drum has been
provided; there is also a scale of percentage transmissions.

The cell at $A$ simultaneously receives light from $G$ of an intensity
controlled by an iris diaphragm $E$; the latter is uncalibrated, and is
used only for adjusting purposes and also as a fine adjustment for the
final setting. The two photo-cells $A$ and $O$ are connected in opposition
across a Cambridge spot galvanometer $P$, so that when the photo-
electric currents given by the cells are equal the galvanometer records
zero deflection. A variable resistance $R$ is arranged to provide variable
sensitivity.

Use of Béleker photo-electric absorptiometer. This is best illustrated
by describing the procedure for making a determination. Let us
suppose that it is desired to compare the depth of colour or, more
precisely stated, the amount of light absorbed by two liquids $s_1$ and $s_2$,
the latter being the more deeply coloured, i.e., the more absorbing.

1. Place $s_2$, contained in the special cell, into the beam, and open
the variable aperture to its full extent by setting the drum at zero.

2. Adjust the iris diaphragm in front of the compensation cell until
the galvanometer shows zero deflection.

3. Substitute $s_1$ for $s_2$, when the galvanometer will be seen to be
deflected.

4. Adjust the calibrated variable aperture by means of the drum until
the galvanometer returns to zero, and take the reading on the drum.

This series of operations takes less than half a minute. The cells
containing the liquids are mounted side by side, and are easily inter-
changed by pushing the slide along an inch or so until it clicks into
the correct position.

If we assume that the light intensity remains constant throughout
the series of operations, then the current given by the indicating cell
at the end of operation 4 is the same as at the end of operation 2
(since in each case it balances the output of the compensating cell).
The difference in the illumination condition in the two cases is that
in the second case the intensity-reduction produced by closing down
the aperture is substituted for the reduction produced by the absorp-
tion of the specimen. The ratio of the area of the partly closed aper-
ture to that of the aperture when fully open is thus a measure of the
absorption of the liquid. Since both photo-cells are affected alike by
changes in the intensity of the lamp, the reading is unaffected by
changes occurring during the series of operations.

The sensitivity of the instrument in detecting small differences
between the absorption of two liquids is greatly increased by the use
of an appropriate light filter; indeed, as indicated in Fig. V, 7, 13,
the use of a suitable light filter should be the normal practice (for a
discussion as to the choice of filter, see previous paragraphs on Light
Filters). A set of eight pairs of Ilford spectrum filters, which have a
narrow band of transmission and a fairly sharp cut-off (see Fig. V, 7, 5),
is normally supplied for use with the instrument. Sliding carriers are
provided for two filters which enable them to be interchanged quickly
in the absorptiometer or changed at will. The all-glass cells for liquids are available in lengths of 0.25, 0.5, 1, 2, and 4 cm.

It is a well-known fact that photo-electric cells under prolonged illumination tend to behave irregularly. This difficulty is overcome by the use of a gravity-controlled shutter which must be held open while the readings are being taken. In this way the steady burning of the lamp itself is ensured, and at the same time it is impossible to expose the cells for any longer than is required for the reading to be made.

For the routine use of the absorptiometer in colorimetric determinations, it is necessary to prepare a calibration curve by taking readings with a number of coloured solutions of known concentration covering the required range. This calibration curve remains valid so long as appreciable changes do not take place in the spectral sensitivity of the photo-electric cells or in the colour of the filter. The changes in the photo-cells and in the glass of the filters are generally very gradual, and the calibration curve need be checked only at wide intervals, say, every few months.

The advantages of the Spekker absorptiometer include:

(a) It runs directly from the electric mains supply; no batteries are required.

(b) Owing to the use of the two balanced photo-cells, the readings are independent of the fluctuations of the mains supply.

(c) The scale of the instrument is approximately linear with the concentration of the solution.

(d) The instrument readings are not affected by variations in the sensitivity of the photo-cells or of the galvanometer, since a null method is employed.

(e) The galvanometer, which indicates the photo-electric current, is a robust but sensitive instrument of the spot type, and is used as a null indicator.

(f) Readings can be taken with as little as 2.5 ml. of liquid with the 2.5-cm. cells; if a micro-cell is employed the volume can be reduced to 0.5 ml. The commonly used cell (1 cm.) has a capacity of approximately 8 ml.

Fisher electrophotometer. The instrument and a schematic diagram of the optical arrangements and the electrical circuit are shown respectively in Figs. V, 7, 14 and V, 7, 15. The light from the photometer lamp, which is transmitted through a coloured solution, falls upon one barrier-layer-type photo-cell, and the current generated is measured in a potentiometer circuit by comparison with the current generated by a second similar photo-cell illuminated directly from the same source. The percentage light transmission of the solution is found by comparison with the light transmission under identical conditions of distilled water or the solvent, the transmission of which is taken as 100 per cent. The lamp is operated well below its normal rating, and a switch is provided for varying the intensity of the light. The lamp is controlled by a button which is left on only during the actual readings. The cells (of circular or rectangular cross-section) have a capacity of 23 or 3 ml., and a special dual-cell slide is provided which permits rapid interchange of the positions of the unknown and of the standard solution in the light beam. Three filters with the following
characteristics are normally supplied: blue, 425 mμ (for red, pink, orange, and yellow solutions); green, 525 mμ (for violet and purple solutions); and red, 650 mμ (for blue, violet, purple, and green solutions). The main scale on the instrument is a logarithmic one.

The manufacturers suggest the following procedure to assist in the correct choice of filter. Prepare the standard solutions of the constituent to be determined, following as closely as possible the analytical procedure, (i) of approximately the maximum concentration c likely to be encountered, (ii) of exactly half this concentration, and (iii) of slightly lower con-
centration than the most dilute solution likely to be examined and preferably an aliquot part of c. Determine the logarithmic scale readings for each of the three filters. Two cases may arise:

(a) If, for a particular filter, the reading for (ii) is exactly one half of that of (i), and that of (iii) is the aliquot part of (i) corresponding to its concentration, the logarithmic scale may be used directly for this concentration range, since the data follow Beer's law. This filter should be used for the determination.

(b) If, for all the filters, the reading for solution (ii) is not one-half that for solution (i), plot the three groups of data separately with scale readings as ordinates and concentrations as abscissae. Each graph will be a curved line. Select the filter corresponding to the curve with the greatest slope, since this will result in the largest "spread" of scale readings.

Coleman colorimeter (model 8). The general appearance of the instrument, which is of the two-cell and potentiometer type, is similar to that of the Coleman spectrophotometer (Fig. V, 7, 24). Six Corning optical filters (peaks at 390, 430, 470, 525, 590, and 655 m\(\mu\)) are supplied with the colorimeter, which can be operated either from the supply mains through a constant-voltage transformer or from a storage battery. Readings may be taken on either of two scales calibrated in transmittance and optical density respectively. Matched cuvettes ranging from 25 mm. depth and requiring 10 ml. of sample to capillaries requiring 5 cu. mm. of solution are standard equipment.

Photo-electric spectrophotometers. Spectrophotometers, from the standpoint of analytical chemistry, are those instruments which enable one to measure transmittance (or optical density) at various wavelengths. Photo-electric spectrophotometers may be regarded as refined-filter photo-electric photometers (absorptiometers) employing continuously variable and more nearly monochromatic bands of light. The less expensive instruments (e.g., the Unicam D.G. or the Coleman) give a band width of about 35 m\(\mu\): this is reduced to 5–10 m\(\mu\) with the more elaborate spectrophotometers.

A brief description will be given of the following photo-electric spectrophotometers: (a) Unicam D.G.,\(^1\) (b) Hilger uvispek (ultraviolet and visible),\(^2\) (c) Unicam quartz (ultraviolet and visible),\(^1\) (d) Coleman universal (model 14) and Coleman Junior (model 6A),\(^3\) (e) Beckman model B,\(^4\) and (f) Beckman quartz, model DU.\(^4\)*

Unicam diffraction grating spectrophotometer. This is an inexpensive instrument\(^†\) and may well be considered as a reasonable alternative to most photo-electric colorimeters for routine work. The spectrophotometer is shown in Fig. V, 7, 16, and the optical arrangements in Fig. V, 7, 17. It has been designed for the measurement of percentage transmission and optical density of solutions over the visible region of the spectrum, 400–700 m\(\mu\); the band width is approximately 35 m\(\mu\). Power is derived from a large-capacity 12-volt storage

---

\(^1\) Unicam Instruments (Cambridge) Ltd., Arbury Works, Cambridge.


\(^3\) Manufactured by Coleman Instruments Inc., Maywood, Illinois, and supplied by Willems–Anderson Co., 111 North Canal St., Chicago, U.S.A.

\(^4\) Manufactured by National Technical Laboratories, South Pasadena, California, and supplied by Will Corporation, Rochester 3, N.Y., U.S.A.

\(^†\) The present price (1950) is about £70.
battery; the instrument may also be operated from the mains if a constant voltage transformer is used. Special test-tubes of \( \frac{1}{2}, \frac{3}{4}, \) or 1 in. diameter or a rectangular fused-glass cell of 10 mm. optical path may be used. Spare cells and a calibrating didymium filter (for the wave-length dial) are housed in a special built-in compartment.

Hilger uvispek (ultra-violet and visible spectrophotometer). The Hilger uvispek must be regarded as a precision instrument suitable inter alia for plotting the absorption curves of liquids throughout the visible and ultra-violet regions, or for determining absorption (or transmission) at any previously chosen wavelengths throughout the region for quantitative analysis, by their visible or ultra-violet absorption, of mixtures of known components, or for accurate absorptiometry (colorimetric analysis). Two light sources are supplied—a hot-cathode hydrogen-discharge lamp for the ultra-violet, and a tungsten lamp for the visible; both are permanently mounted in a metal housing, and a movable mirror (operated by a lever) enables either source to be selected at will. The optical system employs a glass or quartz
Colorimetric Analysis

prism of the Littrow type with a concave mirror of 650 mm. focal length; the relative aperture of the system is F/10, and the slits are adjustable to 0.02 mm. The average band-spread of the monochromator, with the optimum slit width, is about 1 μm over most of the spectral range. Quartz or glass prisms are available; the associated drums are graduated in Angstroms covering the ranges 200–

2000 μm and 380–2000 μm respectively. Two readily interchangeable photo-cells are employed: one covers the range 200–650 μm, and the other 600–1000 μm. A null method for measuring the photo-cell response is employed in which a counter e.m.f. is obtained from a calibrated potentiometer. The potentiometer scale is arranged in five overlapping ranges, and is calibrated in optical densities (0–3.2) and in percentage transmission (100–0). Five sizes of silica or glass cells (1, 5, 10, 20, and 40 mm) can be supplied; at least 3 ml of
liquid are required for the 10-mm. cell, and proportionate amounts for the other cells. The cells are accommodated in a three-compartment sliding tray, moved by means of a notched rod so that any of the cells can be instantly brought into the light path.

The actual instrument is shown in Fig. 5, 7, 18, and a simplified schematic diagram in Fig. 5, 7, 19. Measurements may be made either in the visible or ultra-violet regions of the spectrum; a slight rotation of the concave mirror 3 enables either the hot-cathode, hydrogen lamp 1 or the tungsten-filament lamp 2 to be used. Both sources are fed from a special mains-operated power pack (not shown in the figure). After reflection from the mirror 4, the light passes into the monochromator through a symmetrical slit 5, where it is collimated by the mirror 7, dispersed by the prism 6, and refocused on the exit slit 9 by the concave mirror 7. (For certain optical reasons the prism 6 is actually immediately below the slit 5, but has been shown at one side in the diagram for clarity.) The required radiation (monochromatic beam) is selected by rotating the prism by a screw motion with a directly calibrated drum. The now monochromatic light passes through one of the three liquid cells 10, and is received by one of the two photo-cells 11 or 12 according to the wavelength in use. The e.m.f. generated by the cell is fed to the direct-current amplifier 13, and passes to the needle galvanometer 14, which can be brought to zero by means of the precision potentiometer device 15, the operating dial of which is calibrated in optical densities and in percentage transmission. This part of the apparatus is also supplied with stabilised current from the power pack. Additional controls are provided for setting the zero of the instrument and for adjustment for 100 per cent transmission, independent of the position of the reading scale.

A diffuse-reflection attachment for the measurement of reflectance over the range of spectrum provided by the monochromator and a fluorescence attachment for measuring the relative intensity of the fluorescence produced in a solution under controlled conditions of illumination are in the course of development.

Unicam ultra-violet and visible spectrophotometer (model S.P. 500). This precision photo-electric spectrophotometer is in many respects similar to the Hilger uVispek, but differs from it in certain constructional details. Fig. 5, 7, 20 depicts the actual instrument, and Fig. 5, 7, 21 is a schematic diagram of the optical system. The easily interchangeable light sources are a tungsten-filament lamp for the visible and adjacent spectral region, and a hydrogen-discharge lamp for the ultra-violet. Two large-capacity 6-volt accumulators operate the tungsten lamp and the amplifier circuit (for the photo-cells, etc.), and a mains-operated power pack is used for the hydrogen-discharge lamp. The prism of polished natural quartz is enclosed in the monochromator, the slit aperture of which can be set to 0.01 mm.; the associated wavelength dial (with vernier control) is engraved in millimicrons from 200 to 1020. Two photo-cells are employed—a red-sensitive cell for use above 625 m\(\mu\) but usable to 400 m\(\mu\) (i.e., for the visible and adjacent spectral region) and an ultra-violet-sensitive (or blue) cell for use below 625 m\(\mu\) (i.e., for the ultra-violet range 200–625 m\(\mu\)). The photo cell current is fed to a two-stage amplifier and passes to the indicating meter, which is brought back to zero by means of a
precision potentiometer device. The scale of the potentiometer is calibrated in optical densities and percentage transmission: a sensitivity switch is provided. For transmissions of less than 10 per cent, for example, the switch is set at 0.1, and transmission readings then cover the range 0–10 per cent and optical-density readings infinity to 1.0. A special holder is incorporated which will accommodate fused-quartz or glass cells with a light path up to 40 mm, although 10-mm. cells are normally supplied. Glass cells are, of course, employed for wavelengths above 350 μm, and quartz cells for those below this value. Additional controls are fitted for setting the zero of the instrument (dark current control) and for adjustment to 100 per cent transmission.
Coleman universal spectrophotometer (model 14). This versatile spectrophotometer (compare Hilger Spekker absorptiometer) utilises a replica diffraction-grating monochromator and supplies a monochromatic beam of 35 m\(\mu\) band width over the range 325–800 m\(\mu\).
The monochromator lamp operates at 8·0 volts and consumes about 4·3 amperes; the galvanometer and ventilator motor require 115 volts A.C. A wide variety of matched glass cells (cuvettes), ranging in capacity from 2·5 to 25 ml., is available. The galvanometer scale is calibrated in optical density or percentage transmittance. The photo-cell response may be read directly on the sensitive galvanometer (accuracy ca. 1·0 per cent) or determined (to ca. 0·1 per cent) on a built-in potentiometer calibrated in both density and transmittance, using the galvanometer as a null instrument. A didymium filter is supplied for checking the wavelength calibrations. The instrument is illustrated in Fig. V, 7, 22, whilst Fig. V, 7, 23 is a schematic diagram of the optical and electrical system. It will be noted that adapters are included for use of the instrument for nephelometric and for fluorescence measurements, as well as for acid-base titrations and pH determinations with indicators ("spectro"). A simplified version, the Junior spectrophotometer (model 6A), is marketed for colorimetric analysis only (Fig. V, 7, 24); the cells and scales are interchangeable with those of the larger instrument.

Beckman model B spectrophotometer. This spectrophotometer, which is less costly than the well-known DU quartz model, and is therefore intended to find wide application for routine colorimetric analysis, possesses a number of novel features. It employs a Fery prism (which may be regarded as a combination of a prism and a lens) of borosilicate glass as the dispersive element in the monochromator. The light source is a 6-volt, 32-candle-power tungsten bulb. A special slit system, which permits rapid and smooth variation to the value required, is a valuable feature. It is normally supplied with a blue-sensitive photo-tube for use in the visible spectral region between 320 and 700 mp. A red-sensitive photo-cell is available for use between 400 and 1000 mp. The wavelength mechanism controls the relative position of the Fery prism with respect to the entrance and exit slits. The wavelength dial covers the range 320–1000 mp.; settings are reproducible to about 1 mp., the absolute wavelength accuracy claimed is within 5 mp., and the minimum spectral band width is 5–7 mp. The central scale is calibrated in percentage transmittance and in absorbance (or density), and provision is made by means of a four-position "sensitivity multiplier" for increasing the accuracy of the transmittance (or density) measurements. Controls for the dark current, slit adjustment, and shutter are fitted. The cell carrier accommodates four 10-mm. rectangular plastic cells or two cylindrical cells up to 50 mm. in path length. Power is derived from a 115-volt, 50/60-cycle mains supply. The actual instrument is shown in Fig. V, 27, 25, and a schematic drawing of the optical system in Fig. V, 7, 26. Light from the tungsten light source A falls on the condensing mirror B, and is then reflected by a 45-degree mirror C.
through the entrance slit $D$ of the monochromator to a flat mirror $E$. The light is then reflected to a Féry prism $F$ and back to the flat mirror.

A dispersed image is then formed in the plane of the exit slit $G$. After passing through a focusing lens $H$, the light passes through the sample cell $I$ (housed in the sample compartment) to the photo-cell $K$; $J$ is a shutter control for the light falling on the photo-cell. The output
Colorimetric Analysis

of the photo-cell \( K \) is amplified by a multiple-stage electronic circuit for the operation of the meter, which directly indicates per cent transmittance \((T)\) and absorbance or optical density \((-\log T)\) of the sample being analysed.

Beckman model DU quartz spectrophotometer. This is a precision instrument. Two interchangeable light sources are used: a 6-volt, 25-watt tungsten-filament lamp, operated from a storage battery, for measurements down to 320 \( \mu \)m; a hydrogen-discharge lamp, operated from the 110-volt, 50/60-cycle mains with electronic voltage control, for measurements in the ultra-violet region below 320 \( \mu \)m. It employs a quartz prism of the Littrow type with a concave mirror of 50 cm. focal length for collimation; the relative aperture of the system is about \( F/11 \). The slit mechanism is continuously adjustable to 0.01 mm. The band-spread of the monochromator can, if necessary, be adjusted to less than 1 \( \mu \)m with the appropriate setting of the slit opening over most of the spectral range of the instrument. The wavelength scale is calibrated 200–2000 \( \mu \)m, but the practical limit with present light sources is 200–1000 \( \mu \)m. Two photo-cells are employed: a red-
sensitive photo-tube for use above 625 \( \mu \)m (but usable to 400 \( \mu \)m), and a blue-ultra-violet-sensitive photo-cell for work at 200–625 \( \mu \)m. The photo-tube current is measured by a null method utilising a slide-wire potentiometer and an electronic amplifier. The potentiometer is calibrated in per cent transmission from 0 to 110 and in optical densities from 0 to 2.0; a switch is provided which increases the sensitivity by a factor of 10, thus giving greater accuracy in reading transmission values below 10 per cent and at the same time extending the optical density range from 1.0 to 3.0. Controls are provided inter alia for adjusting the dark current to zero and the percentage transmission to 100. Four standard 10-mm. light-path absorption cells of Corex are supplied in a four-place cell-holder; an interchangeable cell compartment is available to accommodate either Corex or fused-silica cells of 10-, 20-, 50-, and 100-mm. light paths as well as test-tubes of 10–25 mm. diameter.

Schematic diagrams of the optical system and of the electronic wiring systems are given in Figs. \( V, 7, 27 \) and \( V, 7, 28 \) respectively, and the instrument is shown in Fig. \( V, 7, 29 \). An image of the light source \( A \) is focused by the condensing mirror \( B \) and the diagonal mirror \( C \) on the entrance slit at \( D \). The entrance slit is the lower of two slits vertically over each other. Light falling on the collimating mirror \( E \) is rendered parallel, and is reflected towards the quartz

![Diagram](image-url)
prism $F$. The back surface of the prism is aluminised, so that light refracted at the first surface is reflected back through the prism, undergoing further refraction as it emerges from the prism. The collimating mirror focuses the spectrum in the plane of the slits $D$, and light of the wavelength for which the prism is set passes out of

the monochromator through the exit (upper) slit, through the absorption cell $G$ to the photo-cell $H$.

It may be mentioned that accessories are available for the measurement of fluorescence, diffuse reflectance, and flame spectrophotometry, and also for temperature control of the sample compartment.

V, 8. Turbidimetry, nephelometry and fluorimetry.—A coloured substance in true solution may be determined by comparison with a standard—this is one aspect of the true colorimetric method. The transmission of light is measured, and its reflection is zero. With a
colloidal dispersion of a coloured precipitate, however, transmission
and also some reflection of coloured light occurs. If it can be assumed
that the reflection is negligible, then the ordinary colorimetric methods
of determination may be applied; here we have the phenomenon
of turbidimetry, and the instrument is used as a turbidimeter. If the
reflection is appreciable, colorimetric methods are subject to serious
errors; in such cases the reflection (and the accompanying diffraction)
of the light is measured at right angles to a parallel beam of incident
light (the so-called Tyndall light). The
process of measurement is then called
nenphelometry, and the instrument is termed
a nephelometer. A nephelometer therefore
compares scattered light and not trans-
mitt ed light: it measures turbidities by
comparison with a standard. When some
substances in solution are irradiated by
ultra-violet light, fluorescence is produced,
i.e., radiation is emitted which has wave-
lengths characteristic of the light-absorbing
molecules and not only that of the
incident beam. The fluorescence is usually
observed and measured in a direction at
right angles to a parallel beam of incident
light; the process of measurement is then
termed fluorimetry and the instrument a
fluorimeter.* The techniques of nephelo-
metry and fluorimetry are therefore very
similar in practice, although quite different
in theory. Nephelometry is based upon
the scattering of light, without change of
wavelength, of colloidal suspensions, and
makes use of a physical phenomenon largely
independent of the chemical nature of the
dispersed particles. Fluorimetry depends
upon the chemical properties of particular
molecules, and can be used to detect and
to measure quantitatively specific solutes
in filtered homogeneous solutions; the
wavelength of the fluorescent radiation is
usually longer than that of the incident
light. In Fig. 5, 8, 1† the broad differences between colorimetry,
nenphelometry, and fluorimetry are indicated. In A (colorimetry) light
of specific wavelengths is absorbed by the substance in solution, and
the amount of absorption is determined; in B (nephelometry) the
dispersed particles scatter the light by reflection and diffraction, and the
amount of scattered light is measured at right angles to the incident
beam; in C (fluorimetry) light of one wavelength causes some sub-
stances in solution to fluoresce or emit light (usually of a longer wave-
length) and the fluorescent light is measured at right angles to the
incident beam. In all cases the measured quantity is best related to
the concentration by means of a calibration curve.

* U.S.A.: fluorometry and fluorometers.
† Adapted from *The Laboratory*, Volume 18, p. 32 (Fisher Scientific Co.).
The following factors are of importance for the production of suspensions of uniform physical character, upon which the success of nephelometric determinations depends: (i) the concentration of the two ions which combine to produce the precipitate; (ii) the ratio of concentrations in the solutions mixed; (iii) the manner and the rate of mixing; (iv) the amounts of other salts and substances, especially protective colloids, present—i.e., the stability of dispersion; (v) the time required to produce maximum scattering; and (vi) the temperature.

The factors which control the intensity of fluorescence and are therefore of importance in fluorimetry are: (i) concentration of the substance under test, (ii) wavelength of excitation, (iii) pH, (iv) temperature, (v) presence of foreign ions, and (vi) the presence of fluorescing materials other than the test substance.

INSTRUMENTS FOR NEPHELOMETRY AND FOR FLUORIMETRY

Modified Duboscq colorimeter. Since the instrument is to measure scattered light, the light path must be so arranged that the rays enter the side of the cups at right angles to the plungers instead of through the bottom. The usual cups are therefore replaced by clear-glass tubes with opaque bottoms; the glass plungers are accurately fitted with opaque sleeves. For nephelometry a standard suspension is placed in one cup, and the unknown solution is treated in an identical manner and placed in the other cup. The procedure henceforth is identical with that already described under colorimetric analysis (Section V, 6). The lamp and the condensing system should be rigidly attached to the colorimeter base.

Hilger Spekker absorptiometer. For measurements of turbidimetry, a pair of neutral-tint filters are supplied, and readings are taken as in normal absorptiometry. The absorptiometer may be readily converted into a fluorimeter with the aid of special accessories provided by the manufacturers: a Spekker fluorimeter is also available, which may be adapted for absorptiometry. A simplified diagram showing the optical paths and electrical circuit in the fluorimeter constitutes Fig. V, 8, 2. Only the differences from the absorptiometer (Fig. V, 7, 12) will be discussed. The light derived from a mercury-vapour lamp $G$, after passing through the ultra-violet filter $M$, is reflected vertically upwards by the system $S$ into the bottom of one or other
of the two all-glass rectangular cells, containing the comparison substance of known or standard fluorescence and the sample cell, either of which can be placed in the light beam by means of a sliding carriage. The fluorescence produced in the cells by the incident light from below is picked up on either side by a photo-cell, one of which has been omitted in the figure for clarity. The arrangement thereafter is similar to that followed in the absorptiometer with the usual null-indicating circuit and compensating photo-cell, except that a more sensitive galvanometer is employed. The amount of exciting radiation reaching the solution can be varied by the calibrated aperture or measuring disc \( J \), and thus enables the fluorescence of the substance to be specified numerically in terms of the standard. The quantities actually compared are the amount of fluorescence both in the standard substance and the substance to be measured. An important application of the fluorimeter is to the determination of vitamins \( B_1 \) and \( B_2 \) and other substances of biochemical interest. Colour filters may be introduced both in the exciting beam and between the fluorescing substance and the photo-cells to render the tests more specific and to eliminate the effects of impurities in the solutions.

For nephelometry the fluorimeter attachment is employed with the ordinary filament lamp of the absorptiometer.

**Fisher nephro-photometer.** This instrument (Fig. V, 8, 3) has been specifically designed for fluorimetry and nephelometry; colorimetric determinations may also be made. It operates from 115-volt, 50/60-cycle mains. The reading dial is divided into two scales—a log scale and a percentage scale, 0–100 per cent. The dial-control knob varies a built-in polaroid unit reducing the intensity of illumination, i.e., balance is achieved optically. Two multiplier photo-tubes (compare Fisher electrophotometer, Fig. V, 7, 14, which employs barrier-layer photo-cells) constitute the light-sensitive elements. The instrument is provided with the usual filters and light sources required for its various functions.

Many other fluorimeters (e.g., Coleman, Klett, and Lumetron) are
marketed. Mention may be made of the fluorimetric attachments to spectrophotometers for the Beckman, Coleman, and Hilger uvispek instruments.

V, 9. Determination of \( pH \) of solutions by colorimetric methods.—

A. Buffer solution method. An approximate determination of the \( pH \) of the liquid may be made by the use of a multiple-range indicator solution (for example, the B.D.H. universal indicator), or by the systematic use of a number of indicators, or by the use of indicator test papers.* A“ wide range” or “universal” test paper, covering \( pH \) 1–2 to 10, is marketed, as well as a number of narrow-range indicator test papers which cover most of the \( pH \) range in steps of 1·5–2 \( pH \) units. Colour-matching charts are supplied by the manufacturers to show the change in colour at 0·3 \( pH \) intervals. The test papers are best used (and their accuracy is greatest) by dipping the papers into the fluid; if the test solution is “spotted” on the indicator paper, the shade of the spot produced may vary from the centre outwards, and some difficulty may be experienced in deciding which shade to consider as showing the actual \( pH \). The test papers tend to deteriorate upon storage. For the average observer it is doubtful whether test papers permit the determination of \( pH \) closer than to 0·5–1 \( pH \) unit, but this suffices for many purposes.

A series of buffer solutions (Section A, 10) is selected, differing successively in \( pH \) by about 0·2, covering the \( pH \) range of the solutions under investigation; the range of the buffer solutions required will be indicated by the preliminary \( pH \) determination. Equal volumes, say 10 ml., of the buffer solutions differing successively in \( pH \) by about 0·2 are placed in test-tubes of colourless glass and having approximately the same dimensions, and a small equal quantity of a suitable indicator for the particular \( pH \) range is added to each tube. A series of different colours corresponding to the different \( pH \) values is thus obtained. An equal volume (say 10 ml.) of the test solution is treated with an equal volume of indicator to that used for the buffer solutions, and the resulting colour is compared with that of the coloured standard buffer solutions. When a complete match is found, the test solution and the corresponding buffer solution have the same \( pH \). Sometimes a complete match is not obtained, but the colour of the test solution falls between those of two successive standards, then it is known that the \( pH \) value lies between those of the two standards. Further buffer solutions may then be prepared differing by 0·1 \( pH \), if desired, and the \( pH \) value redetermined. As a general rule, colorimetric methods cannot be relied upon to give values of \( pH \) more accurate than to within 0·2 \( pH \) unit. For matching the colours, the buffer solutions may be arranged in the holes of a test-tube stand in order of \( pH \); the test solution is then moved from hole to hole until the best colour match is obtained. Special stands and standards for making the comparison are available commercially. The commercial standards, prepared from buffer solutions, are not permanent, and must be checked every six months.

For turbid or slightly coloured solutions, the direct-comparison method given above can no longer be applied. The interference due to the coloured substance can be eliminated in a simple way by a

device due to H. Walpole (1910). In Fig. V, 9, 1, A, B, C, and D are glass cylinders with plane bottoms standing in a box which is painted dull black on the inside. A contains the coloured solution to be tested (here the test solution + indicator), B contains an equal volume of water, C contains a solution of known strength for comparison (here the standard buffer solution + indicator), whilst D contains the same volume of the solution to be tested as was originally added to A. The colour of the unknown solution is thus compensated for.

For details concerning the preparation of buffer solutions, see Appendix, Section A, 9; compare Section VI, 1.

B. Comparator (or permanent colour standard) method. In this method comparison is made with a series of permanent glass colour standards. Nine glass colour standards are fitted into a disc, and the latter fits into a comparator, which is furnished with four compartments to receive small test-tubes or rectangular cells, and is also provided with an opal glass screen. The disc can revolve in the comparator, and each colour standard passes in turn in front of an aperture through which the solution in the cell (or cells) can be observed. As the disc revolves, the value of the colour standard visible in the aperture appears in a special recess. The Lovibond comparator * is shown in Fig. V, 9, 2; this may be used with 13.5-mm. test-tubes or

* Manufactured by The Tintometer Ltd., Milford, Salisbury, England. The "all-purpose" comparator is similar, but has wider applications.
13·5-mm. rectangular cells. A similar apparatus is marketed by Hellige, Inc.* (Fig. V, 9, 3, a), but this comparator includes a prism attachment by means of which the two colours being compared are brought side by side in the eyepiece (Fig. V, 9, 3, b). A particularly comprehensive range of discs covering a wide variety of pH indicators is available with the Lovibond instrument.

It must be emphasised that the Lovibond comparators utilise specially prepared B.D.H. indicators, whilst the Hellige comparator must be employed with Merck's (U.S.A.) indicators. Neither the discs nor the indicators are interchangeable in the two instruments. A determination of the approximate pH of the solution is first made with a "universal" or "wide-range" indicator or with indicator test papers (see under A), and then a suitable disc is selected. Ten ml. of the unknown solution is placed in the glass test-tube or cell, the appropriate quantity of indicator (usually 0·5 ml.) is added, and the colour produced is matched against the glass disc. Provision is made for the application of the Walpole technique—by the insertion of a "blank" containing the coloured solution. It is claimed that results accurate to 0·2 pH can be obtained.

The colour comparators may be employed for the colorimetric determination of small amounts of certain elements and radicals, as well as for a number of clinical tests, and special colour discs are supplied for this purpose. The B.D.H. Lovibond nesslerimeter (Fig. V, 4, 3) is generally more suitable for the testing of very dilute solutions (yielding paler colours) on account of the greater depth of liquid.

C. With the hydrogen-ion colorimeter. This is a modified form of the Dufuscoq colorimeter which utilises a new principle, due to L. J. Gillespie (1921), and is particularly valuable for use with two colour indicators. It is illustrated diagrammatically in Fig. V, 9, 4. The vessels A, B, C, D, and E are of colourless glass with optically plane

* Hellige, Inc., 3718 Northern Blvd., Long Island City 1, N.Y., U.S.A.
and parallel bottoms. A and C are fixed, whilst B may be moved up and down. The position of B may be read on a scale, the zero graduation of which corresponds to the position of B when B and C are in contact, and the 100 mark of which corresponds to the position of B when B is in contact with A. If a dilute solution of the acid form of an indicator is placed in B and a solution of the same concentration of indicator but transformed completely into the alkaline form be placed in C, then it is clear that the position of B will determine the ratio of the two forms of indicator which are in the field of view. The unknown solution is placed in E, together with the same concentration of indicator as in B and C. The auxiliary cups A and D can be used for compensation by the Walpole technique. B is then moved until the two fields are matched; in this movement the combined depth of the acid and alkaline colours remains the same but their ratio is changed. The pH is then calculated with the aid of a simple formula based upon equation (xiii) in Section 1, 27 or can be read from tables. With a good commercial instrument which embodies the Gillespie principle but carried to a point of refinement, readings may be duplicated to within 0.3 pH unit. If the unknown solution is turbid or coloured, the tube A is filled with the unknown solution and an equal quantity of distilled water is placed in D.

Reference must also be made to the determination of pH with the aid of photo-electric colorimeters, such as the Hilger Spekker absorptiometer. It is doubtful whether such instruments are widely used for this purpose, since results can be obtained more rapidly and conveniently by potentiometric methods and particularly with pH meters.

V. 10. Some general remarks upon colorimetric determinations.—Visual methods are gradually being displaced for many determinations by methods depending upon the use of photo-electric cells (filter photometers or absorptiometers, and spectrophotometers), thus leading to the reduction of the experimental errors of colorimetric determinations. The so-called photo-electric colorimeter is a comparatively inexpensive instrument, and should be available in every laboratory.

The choice of a colorimetric procedure for the determination of a substance will depend upon such considerations as the following:

(i) A colorimetric method will often give more accurate results at low concentrations than the corresponding volumetric or gravimetric procedure. It may also be simpler to carry out.

(ii) A colorimetric method may frequently be applied under conditions where no satisfactory gravimetric or volumetric procedure exists, e.g., for certain biological substances.

(iii) Colorimetric procedures possess advantages for the routine determination of some of the components of a number of similar samples by virtue of the rapidity with which they may be made: there is often no serious sacrifice of accuracy over the corresponding gravimetric or volumetric procedures provided the experimental conditions are rigidly controlled.

The criteria for a satisfactory colorimetric analysis are:
1. Specificity of the colour reaction. Very few reagents are specific for a particular substance, but many give colours for a small group of related substances only, i.e., are selective. By utilising such devices as the introduction of other complex-forming compounds and control of pH, close approximation to specificity may often be obtained. This subject is discussed in detail below.

2. Proportionality between colour and concentration. For visual colorimeters it is important that the colour intensity should increase linearly with the concentration of the substance to be determined. This is not essential for photo-electric instruments, since a calibration curve may be constructed relating the instrument reading of the colour with the concentration of the solution.

3. Stability of the colour. The colour produced should be sufficiently stable to permit an accurate reading to be taken. This applies also to those reactions in which colours tend to reach a maximum after a time: the period of maximum colour must be long enough for precise measurements to be made. In this connexion the influence of other substances and of experimental conditions (temperature, pH, stability in air, etc.) must be known.

4. Reproducibility. The colorimetric procedure must give reproducible results under specific experimental conditions. The reaction need not necessarily represent a stoichiometrically quantitative chemical change.

5. Clarity of the solution. The solution must be free from precipitate if comparison is to be made with a clear standard. Turbidity scatters as well as absorbs the light.

In view of the selective character of many colorimetric reactions, it is important to control the operational procedure so that the colour is specific for the component being determined. This may be achieved by isolating the substance by the ordinary methods of inorganic analysis; double precipitation is frequently necessary to avoid errors due to occlusion and co-precipitation. Such methods of chemical separation may be tedious and lengthy: if minute quantities are under consideration, they may also lead to appreciable loss owing to solubility, supersaturation, and peptisation influences. Use may be made of any of the following processes in order to render colour reactions specific and/or to separate the individual substances:

(a) Suppression of the action of interfering substances by the formation of complex ions or of non-reactive complexes.

(b) Adjustment of the pH; many reactions take place within well-defined limits of pH.

(c) Removal of the interfering substance by extraction with an organic solvent, sometimes after suitable chemical treatment.

(d) Isolation of the substance to be determined by the formation of an organic complex, which is then removed by extraction with an organic solvent. This method may be combined with (a) in which an interfering ion is prevented from forming a soluble organic complex by converting it into a complex ion which remains in the aqueous layer.

(e) Separation by volatilisation. This method is of limited application, but gives good results, e.g., distillation of arsenic as the trichloride in the presence of hydrochloric acid.

(f) Electrolysis with a mercury cathode or with controlled cathode potential.
Oolorimetric Analysis

643

Application of physical methods utilizing selective absorption, chromatographic separation, and base-exchange separations.

11. Determination of ammonia.—Discussion. J. Nessler in 1856 first proposed an alkaline solution of mercuric iodide in potassium iodide as a reagent for the colorimetric determination of ammonia. Various modifications of the reagent have since been made. When Nessler's reagent is added to a dilute ammonium salt solution, the liberated ammonia reacts with the reagent fairly rapidly but not instantaneously to form an orange-brown product, which remains in colloidal solution, but flocculates on long standing. The colorimetric comparison must be made before flocculation occurs. The product has the formula \( \text{NH}_2\text{Hg}_2\text{I}_6 \) (M. L. Nichols and C. O. Willets, 1934).

The reagent is employed for the determination of ammonia in very dilute ammonia solutions and in water. In the presence of interfering substances, it is best to separate the ammonia first by distillation under suitable conditions. The method is also applicable to the determination of nitrates and nitrites: these are reduced in alkaline solution by Devarda's alloy to ammonia, which is removed by distillation. The procedure is applicable to concentrations of ammonia as low as 0.1 mg. per litre.

Nessler's reagent is prepared as follows. Dissolve 35 g. of potassium iodide in 100 ml. of water, and add 4 per cent mercuric chloride solution, with stirring or shaking, until a slight red precipitate remains (about 325 ml. are required). Then introduce, with stirring, a solution of 120 g. of sodium hydroxide in 250 ml. of water, and make up to 1 litre with distilled water. Add a little more mercuric chloride solution until there is a permanent turbidity. Allow the mixture to stand for one day and decant from the sediment. Keep the solution stoppered in a dark-coloured bottle.

Ammonia-free water may be prepared in a conductivity-water still, or by means of a column charged with a mixture of two ion-exchange resins (Section II, 100), or as follows. Redistil 500 ml. of distilled water in a Pyrex apparatus from a solution containing 1 g. of potassium permanganate and 1 g. of anhydrous sodium carbonate; reject the first 100-ml. portion of the distillate and then collect about 300 ml.

Procedure. For practice in this determination, the student may employ either a very dilute ammonium chloride solution or ordinary distilled water which usually contains sufficient ammonia for the exercise.

Prepare a standard ammonium chloride solution as follows. Dissolve 3.141 g. of A.R. ammonium chloride, dried at 100° C., in ammonia-free water and dilute to 1 litre with the same water. This stock solution is too concentrated for most purposes. A standard solution is made by diluting 10 ml. of this solution to 1 litre with ammonia-free water: 1 ml. contains 0.01 mg. of \( \text{NH}_3 \).

If necessary, dilute the sample to give an ammonia concentration of 1 mg. per litre (Hehner cylinders, Fig. V, 6, 1, are useful for this dilution), and fill a 50-ml. Nessler tube to the mark. Prepare a series of Nessler tubes containing the following volumes of standard ammonium chloride solution diluted to 50 ml.: 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 ml. The standards contain 0.01 mg. of \( \text{NH}_3 \) for each ml. of the standard solution. Add 1 ml. of Nessler's reagent to each tube, allow to stand for 10 minutes, and compare the unknown with the
standards in a Nessler stand (Fig. V, 4, 2) or in a B.D.H. nesslerimeter (Fig. V, 4, 3). This will give an approximate figure which will enable another series of standards to be prepared and more accurate results to be obtained.

A photo-electric colorimeter may, of course, be used.

V. 12. Determination of nitrites.—Discussion. When acetic acid solutions of sulphanilic acid and \( \alpha \)-naphthylamine are acted upon by nitrous acid, a red coloration is produced which may be used for the colorimetric determination of nitrites. The sulphanilic acid is converted into the corresponding diazo compound, which couples with the \( \alpha \)-naphthylamine to form \( \alpha \)-naphthylamine-\( \beta \)-azobenzene-\( \beta \)-sulphonic acid, a red azo dye. The full colour does not appear at once; a satisfactory colour comparison can be made after 10–15 minutes, provided the sample and standard are treated in the same way.

The reagent is prepared as follows:

**Solution 1.** Add 1 g. of A.R. sulphanilic acid to 14·7 g. of glacial acetic acid and 15 ml. of water. Warm until solution is complete, dilute with 300 ml. of water, and stir during the addition.

**Solution 2.** Add 0·2 g. of A.R. \( \alpha \)-naphthylamine to 14·7 g. of glacial acetic acid and 25 ml. of water. Warm until solution is complete, dilute with 300 ml. of water, and stir during the dilution.

Mix equal volumes of the solutions immediately before use.

**Standard nitrite solution.** Dissolve 4·93 g. of A.R. sodium nitrite in water and dilute to 1 litre. Dilute 10 ml. of this stock solution to 1 litre with boiled-out water: 1 ml. of this standard solution corresponds to 0·01 mg. of nitrite nitrogen.

**Method 1. Procedure.** For practice in this determination either a very dilute solution of sodium nitrite or ordinary distilled water may be used. If necessary, dilute the sample to give a nitrite concentration of 1 mg. per litre. Prepare a series of Nessler tubes containing the following volumes of the standard nitrite solution diluted to 50 ml.: 0·1, 0·2, 0·4, 0·6, 0·8, and 1·0 ml. Place 50 ml. of the unknown solution in a Nessler tube. To each tube add 2 ml. of the reagent, and stir with a special glass rod with flattened end. After 10 minutes, compare the colours of the tubes. If a closer approximation is required, prepare a fresh series of standards on either side of the first value and repeat the comparison, starting all the tests at the same time.

The following experimental details (Rider and Mellon, 1946) apply to solutions containing 0·03 mg. or less of nitrite. Prepare the following solutions:

- Sulphanilic acid reagent: dissolve 0·60 g. of pure sulphanilic acid in about 70 ml. of hot water, cool the solution, add 20 ml. of concentrated hydrochloric acid, dilute to 100 ml. with water and mix thoroughly.
- \( \alpha \)-Naphthylamine reagent: dissolve 0·60 g. of pure \( \alpha \)-naphthylamine hydrochloride in 100 ml. of water containing 1 ml. of concentrated hydrochloric acid.

Place a quantity of the test solution containing 0·03 mg. or less of nitrite in a 50-ml. volumetric flask, add 1·0 ml. of the sulphanilic acid reagent, mix well, and allow to stand for at least 3, and not more than 10, minutes at room temperature in a diffuse light. Then introduce 1·0 ml. of the \( \alpha \)-naphthylamine reagent and 1·0 ml. of 2N-sodium acetate solution to act as a buffer solution (pH 2·0–2·5). Dilute to
volume and mix well. After 10 minutes, but not later than 30 minutes, measure the intensity of the reddish-purple colour by any suitable means. Use a green filter with a maximum transmission at 520 m\(\mu\) in the appropriate colorimeter. The standard nitrite solution described above may be employed to standardise the colorimeter.

**Method 2 (Shinn, 1941). Procedure.** This is an improvement of the previous method. The nitrous acid is caused to diazotise sulphanilamide (p-aminobenzene-sulphonamide), and the product is coupled with \(N\)-(1-naphthyl)-ethylenediamine dihydrochloride. The resulting azo dye has a much brighter colour, which reaches its maximum intensity more rapidly and remains stable for some hours. Standards may be prepared from freshly made sodium nitrite solution. In view of the fact that sodium nitrite and sulphanilamide react stoichiometrically under suitable conditions, it is better to prepare a series of standard colours from a sulphanilamide solution the strength of which has been determined in terms of nitrite; in this way the use of a highly unstable primary nitrite standard is avoided. A 0·2 per cent sulphanilamide solution is stable for several weeks if stored in a cool place and screened from daylight.

The following reagents are required: 5N-hydrochloric acid, a 0·2 per cent aqueous solution of sulphanilamide (A), a 0·1 per cent solution of \(N\)-(1-naphthyl)-ethylenediamine dihydrochloride and a 0·5 per cent solution of ammonium sulphamate.

To 35 ml. of the neutral nitrite solution, containing not more than 0·05 mg. of nitrite, add 1 ml. of 5N-hydrochloric acid, followed by 5 ml. of solution A. Allow to stand for 3 minutes, add 1 ml. of the ammonium sulphamate solution and, after a further 2 minutes, 1 ml. of solution B. Dilute the mixture to 50 ml. with water, and allow to stand for 3 minutes before comparing with standards.

**V, 13. Determination of iron.**—**Discussion.** Three procedures will be described—the thiocyanate, the thioglycollic acid, and the o-phenanthroline methods.

**A. Thiocyanate method.** Ferric iron reacts with thiocyanate to give an intensely red-coloured compound which remains in true solution, whereas ferrous iron does not react. The colour is usually assumed to be due to ferric thiocyanate:

\[
\text{Fe}^{+++} + 3\text{CNS}^- \rightleftharpoons \text{Fe(CNS)}_3
\]

but recent work has shown that the red solution contains complexes of the type \([\text{Fe(CNS)}_3]^{3-}\) of which the most important with moderate concentration of thiocyanate is \([\text{Fe(CNS)}]^{+++}\):

\[
\text{Fe}^{+++} + \text{CNS}^- \rightleftharpoons [\text{Fe(CNS)}]^{+++}
\]

A large excess of thiocyanate should be used, since this increases the colour intensity. Strong acids (hydrochloric or nitric acid—concentration 0·05–0·5N) should be present to suppress the hydrolysis:

\[
\text{Fe}^{+++} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 \downarrow + 3\text{H}^+
\]

Sulphuric acid is not recommended because sulphate ions have a certain tendency to form complexes with ferric ions. Silver, copper, nickel, cobalt, and large quantities of mercury (> 1 g. per litre), zinc, cadmium, and bismuth (> 0·1 g. per litre) interfere. Mercuroic and stannous salts, if present, should be converted into the mercuric and stannic salts, otherwise
the colour is destroyed. Phosphates, arsenates, fluorides, oxalates, and tartrates interfere, since they form fairly stable complexes with ferric ions; the influence of phosphates and arsenates is reduced by the presence of a comparatively high concentration of acid.

When large quantities of interfering substances are present, it is usually best to proceed in either of the following ways: (i) remove the iron by precipitation with a slight excess of ammonia solution, and dissolve the precipitate in dilute hydrochloric acid; (ii) extract the "ferric thiocyanate" three times either with pure ether or, better, with a mixture of amyl alcohol and pure ether (5:2) and employ the organic layer for the colour comparison.

B. Thioglycollic acid method. Thioglycollic acid, when added to a solution of a ferrous salt and the mixture rendered alkaline with ammonia solution, produces an intense red coloration. Ferric salts in concentrations greater than 1 in 100,000 yield a transient blue coloration; this is immediately reduced to a colourless thioglycollate (I), which then yields the intensely coloured ferrous thioglycollate ion (III) in ammoniacal solution (the thioglycollic acid is oxidised to dithioglycollic acid (II), which gives no colour with either ferrous or ferric iron):

$$2\text{Fe}^{3+} + 2\text{HS} \cdot \text{CH}_2 \cdot \text{COOH} \rightarrow 2\text{Fe}^{2+} + (\text{S} \cdot \text{CH}_2 \cdot \text{COOH})_2 + 2\text{H}^+ \quad \text{(II)}$$

$$\text{Fe}^{2+} + 2\text{HS} \cdot \text{CH}_2 \cdot \text{COOH} \rightarrow \text{Fe(S} \cdot \text{CH}_2 \cdot \text{COOH})_2 \rightarrow \text{Fe(S} \cdot \text{CH}_2 \cdot \text{COO})_2 \quad \text{(II. III. I.)}$$

Strong alkalis slowly discharge the colour. A method is thus available for determining both ferrous and ferric iron colorimetrically. The ferric iron is determined with thiocyanate; the colour is stable in acid solution, and is discharged by alkalis. The total iron is determined with thioglycollic acid, and the ferrous iron by difference.

Fluorides, phosphates, arsenates, sulphates, etc., do not interfere. Chromium, nickel, cobalt, manganese, and uranium interfere, whilst other common metals if present in about the same concentration as the iron have no appreciable effect. Aluminium is rendered innocuous by the addition of excess of citric acid or tartaric acid. Silicates (which have a bleaching effect on the colour), cyanides, and oxidising agents must be absent.

C. o-Phenanthroline method. Ferrous iron reacts with o-phenanthroline to form an orange-red complex \([[(\text{C}_{12}\text{H}_8\text{N}_2\text{S})_2\text{Fe}]]^+\). The colour intensity is independent of the acidity in the pH range 2–9, and is stable for long periods. Ferric iron may be reduced with hydroxylamine hydrochloride or with hydroquinone. Silver, bismuth, copper, nickel, and cobalt interfere seriously, as does perchlorate; other ions interfere to a lesser extent, but not sensibly if their concentrations do not exceed that of iron.

**Procedure (thiocyanate method).** Prepare the following solutions:

**Standard solution of ferric iron.** Use method (a) or (b). (a) Dissolve 0·7022 g. of A.R. ferrous ammonium sulphate in 100 ml. of water, add 5 ml. of 1:5 sulphuric acid, and run in cautiously a dilute solution of potassium permanganate (2 g. per litre) until a slight pink coloration remains after stirring well. Dilute to 1 litre and mix thoroughly. 1 ml. = 0·1 mg. of Fe. (b) Dissolve 0·864 g. of A.R. ferric ammonium sulphate in water, add 10 ml. of concentrated hydrochloric acid and dilute to 1 litre. 1 ml. = 0·1 mg. of Fe.
Potassium thiocyanate solution. Dissolve 40 g. of A.R. potassium thiocyanate in 100 ml. of water; the solution is ca. 4N.

Dissolve a weighed portion of the substance in which the amount of iron is to be determined in a suitable acid, and evaporate nearly to dryness to expel excess of acid. Dilute slightly with water, oxidise the iron to the ferric state with dilute potassium permanganate solution or with a little bromine water, and make up the liquid to 500 ml. or other suitable volume. Place 50 ml. of the solution in a Nessler cylinder, and add 5 ml. of the thiocyanate solution and 2-4 ml. of 4N-nitric or hydrochloric acid. Add the same amounts of the reagents to 50 ml. of water contained in another similar Nessler tube, and run in the standard iron solution from a burette (use a long glass tube with bulb or flattened end for mixing) until the colours are matched; note the exact volume (x ml.) of the standard iron solution added. Repeat the determination using (50 - x) ml. of water. Comparison of the standard and unknown should be made soon after preparation, since the colour fades on standing.

Better results are, of course, obtained with a photo-electric colorimeter. Use a filter showing maximum transmission at or near 480 m\(\mu\), and determine the transmittance of the mixed solution at once. The standard iron solutions employed for the construction of the reference curve should contain the same amount and kind of acids and of the reagent as the unknown.

Procedure (thioglycollic acid method). Prepare the reagent by neutralising a 10 per cent by volume solution of thioglycollic acid (mercaptoacetic acid) with ammonium hydroxide solution. Add 2 ml. of this ammonium thioglycollate solution, then 10 ml. of ca. 3M-ammonium hydroxide solution to the approximately neutral solution of the unknown containing 0·01-0·1 mg. of iron, and dilute to 100 ml. Compare this with standards similarly prepared from a standard solution of ferric iron. Compare the colour intensity soon after it has developed. The maximum absorption is shown by the solution at wavelengths of 530–540 m\(\mu\).

Procedure (o-phenanthroline method). Prepare the following solutions: o-phenanthroline, 0·5 per cent solution of the monohydrate in water; sodium acetate, 0·2M and 2M. Hydroxylamine hydrochloride, 10 per cent aqueous solution or hydroquinone, 1 per cent solution in an acetic acid buffer of pH ca. 4·5 (mix 65 ml. of 0·1M-acetic acid and 35 ml. of 0·1M-sodium acetate solution) is prepared when required.

Take an aliquot portion of the unknown slightly acid solution containing 0·1–0·5 mg. of iron and transfer it to a 50-ml. volumetric flask. Determine by the use of a similar aliquot portion containing a few drops of bromophenol blue, the volume of sodium acetate solution required to bring the pH to 3·5 ± 1·0. Add the same volume of acetate solution to the original aliquot part and then 2 ml. each of the hydroquinone and o-phenanthroline solutions. Make up to the mark with distilled water, mix well, and allow to stand for 1 hour to complete the reduction of the iron. Compare the intensity of the colour produced with standards, similarly prepared, in any convenient way. If a colorimeter is employed, use a filter showing maximum transmission at 480–520 m\(\mu\).

The iron may also be reduced with hydroxylamine hydrochloride. Add 2 ml. of the 10 per cent hydroxylamine solution, adjust the pH
of the slightly acid solution to 3-6 with sodium acetate, then add 2 ml. of the o-phenanthroline solution, dilute to 50 ml., mix, and measure the colour intensity after 5–10 minutes.

V. 14. Manganese.—Discussion. Small quantities of manganese are invariably determined colorimetrically by oxidation to permanganic acid. The oxidising agents which have been employed include lead dioxide and strong nitric acid, sodium bismuthate, potassium or ammonium persulphate in the presence of a little silver nitrate as catalyst, and potassium periodate. The first two are not very suitable, since the excess of the reagent must be removed by filtration. The persulphate method, although widely used, is generally unsatisfactory, for in a number of cases the reaction proceeds incompletely to the permanganate stage. The periodate method is free from these disadvantages. In hot acid solution periodate oxidises manganese quantitatively to permanganic acid:

\[ 2\text{Mn}^{2+} + 5\text{IO}_4^- + 3\text{H}_2\text{O} = 2\text{MnO}_4^- + 5\text{I}^- + 6\text{H}^+ \]

The merits of the periodate method include: (a) the concentration of the acid has little influence, and may be varied within wide limits; (b) the boiling may be prolonged beyond the time necessary to oxidise the manganese without detriment; and (c) the permanganic acid solution will keep for several months unchanged if an excess of periodate is present.

When ready for test the solution should not contain more than 2 mg. of manganese per 100 ml., otherwise the colour will be too dark and colour matching will be difficult. Frequently ferric iron is added to the standard in amount equal to that found independently to be present in the sample. Phosphoric acid must be present to prevent the precipitation of ferric periodate and iodate, and also to decolorise the ferric iron (by complex formation). If chlorides are present it is necessary to evaporate with a mixture of nitric and sulphuric acids until fumes of the latter appear. Chlorides react with the periodate.

Procedure. For practice in this determination, the manganese content of a standard steel sample (Ridsdale or U.S. Bureau of Standards) may be evaluated. Weigh out accurately a suitable quantity of the steel (0·1–0·2 g. for steels containing up to 1 per cent of Mn) into a conical flask, dissolve it in 20–50 ml of 1:3 nitric acid, and boil for 1 or 2 minutes to expel oxides of nitrogen. Remove from the burner, and add 0·5–1·0 g. of A.R. ammonium persulphate; boil for 10–15 minutes to oxidise carbon compounds and to destroy the excess of persulphate. If any permanganate colour develops or oxides of manganese separate, add a few drops of sulphurous acid or sodium sulphite solution to reduce the manganese and render the solution clear, and boil for a few minutes to expel the excess of sulphur dioxide. Dilute the solution to ca. 100 ml., add 5–10 ml. of A.R. syrupy phosphoric acid and 0·5 g. of potassium periodate (1): boil for 1 minute and keep hot for 5–10 minutes. Cool the solution and make up to 250 ml in a volumetric flask and mix thoroughly. Match the colour against standards. Permanganate solutions show maximum absorption at about 525 mμ.

Prepare standard manganese solutions by any of the following methods:

(i) Use a steel of known manganese content, which has been treated like the unknown sample (2).

(ii) Dissolve a known weight of pure electrolytic manganese in
dilute nitric acid, boil out oxides of nitrogen, and dilute to give a 0.01 per cent solution. If pure manganese is not available, reduce standard potassium permanganate solution with a little sulphite after the addition of dilute sulphuric acid, and remove the sulphur dioxide by boiling. Dilute the manganous solution and oxidise it with potassium periodate in the same way as the unknown solution.

(iii) Dilute a mixture of 4.55 ml. of 0.1N-potassium permanganate solution, 5–10 ml. of A.R. syrupy phosphoric acid and 0.1 g. of potassium periodate to 250 ml. (1 ml. = 0.02 of Mn).

Notes. 1. Each 0.1 g. of Mn requires 1 g. of potassium periodate.
2. Such standards, containing excess of periodate, are stable for 2–3 months.

V, 15. titanium.—Discussion. Hydrogen peroxide produces with an acid solution of titanium sulphate a yellow colour, which is said to be due to pertitanic acid. With small amounts of titanium the intensity of the colour is proportional to the amount of the element present, and therefore forms the basis of a colorimetric method for the determination of the element. The method is applicable to solutions containing up to 0.1 mg. of TiO₂ per ml. Comparison is usually made with standard titanic sulphate solutions; a method for their preparation from potassium titanyl oxalate is described below. The hydrogen peroxide solution should be of about 3 per cent strength (10-volume), and the solution should contain at least 5 per cent by volume of sulphuric acid in order to prevent hydrolysis to a basic sulphate and to prevent condensation to metatitanic acid. The colour intensity increases with rise of temperature, hence the solutions to be compared should have the same temperature, preferably 20–25°C.

Elements which interfere are: (a) iron, nickel, chromium, etc., because of the colour of their solutions; (b) vanadium, molybdenum, and, under some conditions, chromium, because they form coloured compounds with hydrogen peroxide; (c) fluorine (even in minute amount) and large quantities of phosphates, sulphates, and alkali salts (the influence of the last two is largely reduced the greater the concentration of sulphuric acid present—up to 10 per cent). The influence of elements of class (a) is overcome, if present in small amount, by matching the colour by the addition of like quantities of the coloured elements to the standard before hydrogen peroxide is added. When large amounts of iron are present, as in the analysis of cast irons and steels, two methods may be adopted: (i) phosphoric acid can be added in like amount to both unknown and standard, after the addition of hydrogen peroxide; (ii) the iron content of the unknown solution is determined, and a quantity of standard ferric alum solution, containing the same amount of iron, is added to the standard solution. Large quantities of nickel, chromium, etc., must be removed. Elements of class (b) must also be removed; vanadium and molybdenum are most easily separated by precipitation of the titanium with sodium hydroxide solution in the presence of a little iron. Fluoride has the most powerful effect in bleaching the colour; it must be removed by repeated evaporation with concentrated sulphuric acid. The bleaching effect of phosphoric acid is overcome by adding a like amount to the standard, or by adding 1 ml. of 0.1 per cent uranyl acetate solution for each 0.1 mg. of Ti present.

Procedure. The sample solution should preferably contain titanium as sulphate in sulphuric acid solution, and be free from the inter-
ferring constituents mentioned in the Discussion above. The final acidity may vary from 1.5 to 3.5N. If iron is present in appreciable amounts, add dilute phosphoric acid from a burette until the yellow colour of the ferric iron is eliminated: the same amount of phosphoric acid must be added to the standards. If alkali sulphates are present in the test solution in appreciable quantity, add a like amount to the standards. Add 10 ml. of 3 per cent hydrogen peroxide solution and dilute the solution to 100 ml. in a volumetric flask: the final concentration of Ti may conveniently be 2–25 parts per million. Compare the colour produced by the unknown solution with that of standards of similar composition by any of the usual methods. A blue filter with maximum transmission at 420–430 mp should be used in the appropriate colorimeter.

For the determination of very small amounts of titanium, the standard series method or the duplication method (Section V, 3) may be used.

Preparation of standard titanium solution. Weigh out 3.68 g. of A.R. potassium titanyl oxalate K₂TiO(C₂O₄)₂.2H₂O into a Kjeldahl flask, add 8 g. of ammonium sulphate and 100 ml. of concentrated sulphuric acid. Gradually heat the mixture to boiling and boil for 10 minutes. Cool, pour the solution into 750 ml. of water, and dilute to 1 litre in a volumetric flask; 1 ml. = 0.50 mg. of Ti.

If there is any doubt concerning the purity of the A.R. salt, standardise the solution by precipitating the titanium with ammonia solution or with cupferron solution, and ignite the precipitate to TiO₂.

V, 16. Vanadium.—Discussion. When hydrogen peroxide is added to a solution containing small quantities of quinquevalent vanadium (up to 0.1 mg. of V per ml.) and 15–20 per cent of its volume of sulphuric acid, a reddish-brown coloration is produced; this is attributed to pervanadic acid, formulated as HVO₄ or as V(O₂)(OH)₃. A large excess of hydrogen peroxide tends to change the colour to yellow and to reduce the intensity.

The colour is unaffected by the presence of phosphate or fluoride. Titanium and molybdenum (VI) (which give colours with hydrogen peroxide) and tungsten interfere. Titanium may be removed by adding fluoride or hydrofluoric acid, which simultaneously remove the yellow colour due to ferric iron. If titanium is absent, phosphate may be used to decolourise any ferric salt present. Oxalic acid eliminates the interference due to tungsten. In the presence of elements which yield coloured solutions, such as chromium or nickel, it is best to add equal amounts of these elements to the standard solution. If steel is being analysed, the most convenient procedure is to use a like steel as standard.

Vanadium may also be determined by making use of the yellow, soluble phosphotungstovanadic acid formed upon adding phosphoric acid and sodium tungstate to an acid vanadate solution. The most intense colour is obtained when the molecular ratio of phosphoric acid to sodium tungstate is in the range 3 : 1 to 20 : 1, and the tungstate concentration in the test solution is 0.01 to 0.1M; the preferred concentrations are 0.5M in phosphoric acid and 0.025M in sodium tungstate.

The following interfere: (a) coloured ions, such as chromate, copper, and cobalt; (b) titanium, zirconium, bismuth, antimony, and tin yield
slightly soluble phosphates or basic salts except in very low concentrations; 
(c) potassium and ammonium ions give sparingly soluble phosphotungstates; 
(d) hexavalent molybdenum in relatively high concentration (> 0·5 mg. per ml.); (e) iodide, thiocyanate, etc., reduces phosphotungstic acid; and 
(f) iron in concentration greater than 1 mg. per ml. (slight interference even in the presence of phosphoric acid).

Procedure (hydrogen peroxide method). Make the solution 1-2N in 
sulphuric acid and add 0·25 ml. of 3 per cent hydrogen peroxide for 
each 10 ml. of test solution. Compare colorimetrically against a 
standard having the same acidity and containing the same volume of 
hydrogen peroxide solution. If titanium is present, add hydrofluoric 
acid (say, 5-10 per cent of the volume); this will decolorise the ferric 
iron also, and suggests the use of the standard series method with 
inexpensive tubes for comparison. If titanium is absent, use phos-
phoric acid for the decolorisation of the iron.

Prepare a standard vanadium solution by dissolving 1·146 g. of A.R. 
ammonium vanadate in water and make up to 1 litre: 1 ml. = 0·5 mg. 
of V. The above solution may be diluted further to give a solution 
containing 0·01 mg. V per ml.

Procedure (phosphotungstate method). Render the solution ca. 0·5N 
in mineral acid, and add 1·0 ml. of 1 : 2 phosphoric acid and 0·5 ml. 
of 0·5-M-sodium tungstate solution (prepared by dissolving 16·5 g. of 
A.R. sodium tungstate Na₂WO₄·2H₂O in 100 ml. of water) for each 
10 ml. of test solution. Heat to boiling, cool, dilute to volume, and 
determine the absorption of the resulting solution or use any conven-
tient colorimetric procedure. A filter with a maximum trans-
mission at 400 mμ may be used. If small amounts of coloured ions 
(nickel, cobalt, dichromate, etc.) are present, these should be incor-
porated in the comparison solution, preferably by employing an aliquot 
portion of the original sample solution.

Vanadium in steel. Dissolve 1 g., accurately weighed, of the steel 
in 50 ml. of 1 : 4 sulphuric acid. When solution is complete, introduce 
10 ml. of concentrated nitric acid, and boil until nitrous fumes are no 
longer evolved. Dilute the solution to 100 ml. with hot water, heat 
to boiling, and add saturated potassium permanganate solution until 
a pink colour persists or a precipitate is formed. Boil for 5 minutes. 
Filter off on asbestos any tungstic oxide or manganese oxide which 
may be precipitated. Add a slight excess of freshly prepared sul-
phurous acid, and boil off the excess. Cool, add 5 ml. of syrupy 
phosphoric acid and 5 ml. of 10-volume hydrogen peroxide.

Simultaneously with the first decomposition prepare in an analogous 
manner a comparison solution from a standard steel which contains no 
vanadium but is otherwise similar; add a standard solution of 
vanadium to the control, followed by hydrogen peroxide, etc., and 
compare this colorimetrically with the solution obtained from the 
unknown steel.

V, 17. Chromium.—Discussion. Small amounts of chromium (up 
to 0·05 per cent) may be determined colorimetrically in alkaline solu-
tion as chromate; uranium and cerium interfere, but vanadium has 
little influence. A more sensitive method is to employ diphenyl-
carbazide CO(NH-NHC₅H₄H₂) (Cazeneuve's reagent, 1900). In acid 
solution (ca. 0·2N) chromates give a soluble violet compound with this 
reagent.
Molybdates (VI), vanadium (V), mercury, and iron interfere; permanganates, if present, may be removed by boiling with a little alcohol. If the ratio of vanadium to chromium does not exceed 10:1, nearly correct results may be obtained by allowing the solution to stand for 10–15 minutes after the addition of the reagent, since the vanadium–diphenylcarbazide colour fades fairly rapidly. Vanadate can be separated from chromate by adding oxine to the solution and extracting at a pH of about 4 with chloroform; chromate remains in the aqueous solution. Vanadium as well as iron can be precipitated in acid solution with cupferron and thus separated from trivalent chromium.

Procedure. Prepare a 0·25 per cent solution of diphenylcarbazide in 50 per cent acetone as required. The test solution may contain from 0·2 to 0·5 part per million of chromate. To about 15 ml. of this solution add sufficient 6N-sulphuric acid to make the concentration about 0·2N when subsequently diluted to 25 ml., add 1 ml. of the diphenylcarbazide reagent and make up to 25 ml. with water. Match the colour produced against standards prepared from 0·001N-potassium dichromate solution. A green filter having the transmission maximum at about 640 μμ may be used.

Chromium in steel.—Discussion. The chromium in the steel is oxidised by perchloric acid to the dichromate ion, the colour of which is intensified by ferric perchlorate which is itself colourless. The coloured solution is compared with a blank in which the perchlorate is reduced with ferrous ammonium sulphate. The method is not subject to interference by iron or by moderate amounts of alloying elements usually present in steel.

Procedure. Place a 1·000 g. sample of the steel (Cr content <0·1 per cent) in a 100 ml. beaker and dissolve it in 10 ml. of dilute nitric acid (1:1) and 20 ml. of A.R. perchloric acid (sp. gr. 1·70; 70–72 per cent). [If the Cr content is 0·1–1 per cent, dissolve a 0·5000 g. sample in 10 ml. of dilute nitric acid (1:1) and 15 ml. of perchloric acid (sp. gr. 1·70).] Evaporate to dense fumes of perchloric acid and boil gently for 5 minutes to oxidise the chromium. Cool the beaker and contents rapidly, dissolve soluble salts by adding 20 ml. of water, transfer the solution quantitatively to a glass-stoppered 50 ml. volumetric flask, and dilute to the mark. Remove an aliquot portion to an absorption cell, reduce it with a little (ca. 20 mg.) A.R. ferrous ammonium sulphate, and adjust the photoelectric colorimeter so that the reading with this solution is zero. A violet filter having a maximum transmission between 410 and 480 μμ may be used. Discard the solution in the absorption cell, and refill it with an equal volume of the oxidised solution: the reading is a measure of the colour due to the dichromate.

Standardisation may be carried out by the use of solutions prepared from a chromium-free standard steel and standard potassium dichromate solution: after the dissolution of the standard steel, the chromium is oxidised by boiling with perchloric acid, the resulting solution is diluted to volume, and measurements are carried out as above. The chromium content of any unknown steel may then be deduced from the colorimeter reading.

V, 18. Aluminium.—Discussion. Aluminium salts give a bright-red lake when treated with ammonium aurintricarboxylate, known as aluminon, in the presence of an acetic acid–acetate buffer. If the concentration of the aluminium is small (up to 0·1 mg. in 100 ml.),
Colorimetric Analysis

a coloured liquid (faint pink to deep red according to the concentration of the aluminium) is obtained, which is suitable for the colorimetric determination of aluminium. Excellent results are obtained with non-ferrous alloys (such as solders, bearing metals, etc.) after the removal of the other metals by electrolysis with a mercury cathode.

The chief interfering element is iron—even minute amounts give a purplish-red tint and must be entirely removed; this may be effected by extraction as ferric thiocyanate with ether-amyl alcohol or with amyl alcohol alone. Beryllium also gives a red lake and must be removed. Bismuth, lead, antimony, stannic tin, mercuric mercury, titanium, and silicic acid give white precipitates. Large amounts of alkaline or rare earths, of basic acetates or hydroxides of chromium, cerium, thorium, and zirconium give red lakes, and phosphates also interfere; these are either dissolved or decolorised by the addition of ammonium carbonate solution. Reducing agents must be absent.

**Procedure.** Prepare the aluminon reagent by dissolving 0·2 g. of a good sample of ammonium aurintricarboxylate in 100 ml. of water. Prepare also the standard aluminium solution by dissolving 1·759 g. of A.R. potassium aluminium sulphate in water and diluting to 1 litre: 1 ml. contains 0·1 mg. of Al, and may be diluted as required.

The almost neutral test solution (say, 30 ml.) should contain 0·01–0·1 mg. of aluminium and be free from iron, beryllium, and other interfering substances. Add 4 ml. of 1 : 9 hydrochloric acid and 4 ml. of the aluminon reagent. Dilute to 50–60 ml. and add 20 ml. of 10 per cent ammonium acetate solution. Make up to 100 ml. with water. Compare the colour produced with standards by any convenient method. A green filter (ca. 520 mp.) may be used with a photo-electric colorimeter.

**V. 19. Molybdenum.—Discussion.** If a molybdate in acid solution is treated with a solution of stannous chloride and a thiocyanate, a reddish-brown coloration, said to be due to $\text{H}_2\text{MoO}_3(\text{CNS})_3$, is produced. The coloured compound can be extracted from the solution by such solvents as diethyl ether, di-n-butyl ether, or cyclohexanol. The best results are obtained when the solution contains 5 per cent hydrochloric acid, the potassium thiocyanate concentration exceeds 0·6 per cent, and the stannous chloride concentration is 0·6–0·8 per cent. If the molybdenum complex is extracted by an organic solvent, the determination may be made in the presence of most elements with the exception of gold, platinum, rhodium, rhenium, selenium, and tellurium. Copper when present in more than small amounts gives a precipitate of cuprous thiocyanate, which must be removed by filtration.

**Procedure.** Prepare the following reagents as required:

(a) Stannous chloride solution: dissolve 10 g. of stannous chloride crystals in 100 ml. of ca. 2N-hydrochloric acid.

(b) Diethyl ether: shake A.R. ether with one-tenth of its volume of equal amounts of stannous chloride solution and of 5 per cent A.R. potassium thiocyanate solution on the same date as it is to be used.

(c) Standard molybdenum solution: dissolve 1·500 g. of A.R. molybdenum trioxide in a few millilitres of dilute sodium hydroxide solution, dilute with water, render slightly acid with hydrochloric acid, and make up to 1 litre with water. The solution contains 1 mg. of Mo per ml., and may be diluted further if required.
To the neutralised test solution, containing up to 0.5 mg. of Mo, add 4 ml. of concentrated hydrochloric acid and dilute with water to 50 ml. in a separatory funnel with a short stem. Cool the solution to 15°C., add 6–7 ml. of 5 per cent potassium thiocyanate solution, followed by 2 ml. (or more, if required) of the stannous chloride solution. Shake the solution for 1 minute, and then add 15 ml. of the purified ether. Shake with the usual precautions for 30 seconds, and allow the two liquids to separate. Run off the lower aqueous phase into a beaker; dry the stem of the funnel with a rolled-up filter-paper, and run off the ether layer into a dry 25-ml. volumetric flask. Return the aqueous solution to the separatory funnel and extract with a further 10 ml. of purified ether. Combine this extract with the first, and make up to the 25-ml. mark with ether. Determine the molybdenum content of the ethereal extract by comparison with standards similarly prepared. A blue filter (450–500 μm) may be used.

Molybdenum in steel. Dissolve 0.20 g. (accurately weighed) of the sample (Mo < 0.2 per cent) in 10 ml. of 1: 4 sulphuric acid and warm to about 60°C. When the reaction has ceased, add 1 ml. of 30 per cent hydrogen peroxide and boil for 5 minutes. If any insoluble material (e.g., carbon) remains, filter it off and wash with hot water. Concentrate the filtrate and washings to 5 ml. in order to destroy the excess of hydrogen peroxide. If tungstic acid has separated, add 0.5 g. of tartaric or citric acid, followed by ca. 3N-sodium hydroxide solution until the solution is just alkaline, and then 15 ml. of 1: 4-sulphuric acid. Transfer to a separatory funnel and dilute the mixture to 40 ml. with water. Cool the resulting solution if necessary, add 5 ml. of 5 per cent potassium thiocyanate solution, mix, and add 5 ml. of a solution containing 30 per cent stannous chloride in ca. N-hydrochloric acid. Cool the solution to room temperature, add 30 ml. of purified ether, and shake well for 30 seconds. Allow the layers to separate, run off the aqueous solution, and transfer the ether layer to a 100-ml. volumetric flask. Extract the aqueous layer with two 20-ml. portions of ether as above, combine the extracts with the first ethereal layer, and make up to 100 ml. with ether. Determine the molybdenum content by any convenient colorimetric method. Prepare the comparison solutions using 14 per cent ferric ammonium sulphate solution in 5N-sulphuric acid containing the equivalent of 0.20 g. of iron and various amounts of molybdenum, and which have been treated in the same manner as the test solution.

V, 20. Nickel.—Discussion. When dimethylglyoxime is added to an alkaline solution of a nickel salt which has been treated with an oxidising agent (such as bromine), a red coloration is obtained. This reaction is a very sensitive one, being approximately equal in sensitivity to that between iron and thiocyanate. The red, soluble complex contains nickel in the quadrivalent state, and is formulated as nickelic (IV) dimethylglyoxime (Feigl, 1924). It will be recalled that for the gravimetric determination of the element, divalent nickel forms, e.g., in ammoniacal solution, the sparingly soluble nickelous (II) dimethylglyoxime.

Cobaltous, auric, and dichromate ions interfere under the conditions of the test. Metals which precipitate in ammoniacal solution can be removed by double precipitation, or by taking advantage of the solubility of nickolous
Colorimetric Analysis

(II) dimethylglyoxime in chloroform (the nickelic complex is insoluble, as is also the brown cobalt dimethylglyoxime). Copper may accompany the nickel in the extraction; most of the copper is removed from the chloroform extract when it is shaken with dilute ammonia solution, whereas the nickel remains in the organic solvent. The nickelous dimethylglyoxime in the chloroform layer may be decomposed by shaking with dilute hydrochloric acid; most of the dimethylglyoxime remains in the chloroform, the nickel is transferred to the aqueous phase and may be determined colorimetrically. Citrate or tartrate may be added to prevent the precipitation of iron, aluminium, etc. Much manganese may interfere, but this is prevented by adding hydroxylamine hydrochloride, which maintains the element in the divalent state.

Procedure (nickel in steel). Dissolve 0·50 g., accurately weighed,* of the steel in 10 ml. of warm 1 : 1 nitric acid, boil to expel oxides of nitrogen, cool, and make up to 250 ml. with water in a volumetric flask. Mix well, and transfer 5 ml. of the solution to a 50-ml. volumetric flask. Add, with mixing after each addition, 5 ml. of 10 per cent citric acid solution, 2 ml. of saturated bromine water, 2 ml. of 1 : 1 ammonium hydroxide solution, and finally 1 ml. of a 1 per cent solution of dimethylglyoxime in rectified spirit. Dilute to the mark with water, mix well, and measure by any suitable means. A green filter (maximum transmission at 520–530 mµ) is recommended for filter photometers. It must be emphasised that the measurements should be completed within 20 minutes of the formation of the colour, since the solution is unstable; the intensity of the colour then increases (about 10 per cent in the following hour) slowly on standing and finally fades. Attention is directed to the important fact that the standard nickel solution for the construction of the reference curve must contain approximately the same concentration of nickel-free iron as the sample solution.

Prepare the standard nickel solution by dissolving 0·673 g. of pure nickel ammonium sulphate in water and diluting to 1 litre: 1 ml. contains 0·1 mg. of Ni. The solution may be further diluted to a basis of 0·01 mg. of Ni per ml., if necessary. Pure nickel metal may also be employed for the preparation of the standard solution.

V, 21. Cobalt.—Discussion. An excellent method for the colorimetric determination of minute amounts of cobalt is based upon the soluble red complex salt formed when cobalt ions react with an aqueous solution of nitroso-R-salt (sodium 1-nitroso-2-hydroxynaphthalene-3:6-disulphonate).

The cobalt complex is usually formed in a hot acetate-acetic acid medium. After the formation of the cobalt colour, hydrochloric or nitric acid is added to decompose the complexes of most of the other heavy metals, if present. Iron, copper, cyanide, peroxide, persulphate, and reducing agents interfere; small quantities of nickel, manganese, chromium, titanium, and vanadium are without effect. Appreciable amounts of iron may be largely removed by extracting as ferric chloride from a 1 : 1 hydrochloric acid solution with peroxide-free ether. Copper may be removed from the diluted solution by precipitation with hydrogen sulphide.

* The weight of steel to be taken will naturally depend upon the nickel content. The final nickel concentration should not exceed 0·6 mg. per 100 ml. because a precipitate may form above this concentration.
**Quantitative Inorganic Analysis**

**Procedure.** The test solution, free from the interfering elements referred to above, should contain between 0.001 and 0.02 mg. of cobalt. Evaporate almost to dryness, dissolve the residue in 10 ml. of water containing 0.5 ml. each of 1:1 hydrochloric acid and 1:10 nitric acid. Boil for a few minutes to dissolve any solid material. Add 2 ml. of a 0.1 per cent aqueous solution of nitroso-R-salt and 2 g. of A.R. crystallised sodium acetate. The pH of the solution should be close to 5.5; check with bromocresol green or with a pH meter. Boil for 1 minute, add 1.5 ml. of concentrated hydrochloric acid, and boil for a further 1 minute. Cool the solution, dilute to 50 ml. with water, and compare the colour with standards by any convenient method. A ca. 510-μ filter is recommended for filter photometers.

**Arsenic.**

**Discussion.** Very small amounts of arsenic (0.001-0.1 mg.) may be determined by volatilising the element as arsine AsH₃, and comparing its reaction under certain experimental conditions with that obtained by the use of known amounts of arsenic. Various reactions have been proposed: that due to Marsh utilises the formation of the mirror of arsenic produced by the action of heat, whilst that due to Gutzeit compares the colorations formed upon discs of dry paper impregnated with mercuric chloride. A modification of the original Gutzeit method will be described.

The reduction to arsine is best effected electrolytically in an apparatus incorporating a mercury cathode or, more simply, by the older process with arsenic-free zinc and hydrochloric acid. Both procedures are given below.

An alternative method, due essentially to C.R. Sanger and O.F. Black (1907), replaces the disc by a thin strip of mercuric bromide paper: the arsenic content is given both by the depth of the tint and also by the length of the paper bearing the stain.

The arsenic must be in the tervalent state. Nitric acid, the halogens, and compounds that yield sulphur dioxide, hydrogen sulphide, or phosphine must be absent. The last-named are readily eliminated by boiling with nitric acid; the excess of the latter is removed by evaporation with sulphuric acid to fumes of sulphur trioxide. In such treatment the arsenic becomes quinquevalent and must be reduced, e.g., with ferrous sulphate, hydrazine sulphate, or by heating with potassium iodide and stannous chloride solution. The following metals and their salts are undesirable: silver, mercury, platinum, palladium, nickel, cobalt, and copper. In the presence of interfering substances, it is usually best to separate the arsenic first as the trichloride by distillation in an all-glass apparatus from a solution containing hydrochloric acid and a reducing agent, such as hydrazine sulphate.

The molybdenum-blue method is widely used. When arsenic, as arsenate, is treated with ammonium molybdate solution and the resulting heteropoly molybdic-arsenate (arseno-molybdate) is reduced with stannous chloride or with hydrazine sulphate, a blue, soluble complex "molybdenum blue" is formed. The constitution is uncertain, but it is evident that the molybdenum is present in a lower valency state. Various experimental techniques for carrying out the determination have been described, but only one can be given here.

**Procedure.** Prepare a standard arsenic solution by dissolving 1.320 g. of A.R. arsenious oxide in the minimum volume of pure sodium hydroxide solution, acidify with dilute hydrochloric or sulphuric acid,
and make up to 1 litre: 1 mL contains 1 mg of As. A solution containing 0.001 mg. As per mL is prepared by dilution.

Prepare the sensitised mercuric chloride papers by immersing Whatman arsenic test strips or strips cut from Whatman No. 20 paper in a 5 per cent solution of A.R. mercuric chloride in 95 per cent alcohol, and dry them on a horizontal rack of glass rods at the laboratory temperature; do not expose to direct sunlight. Keep them in a desiccator over calcium chloride in the dark until required.

Prepare the lead acetate papers by soaking filter-papers (10 cm. by 5 cm.) in a 10 per cent solution of lead acetate in recently boiled water; dry the papers and keep them in a closed tube. (These will serve to retain any hydrogen sulphide which may be evolved in the apparatus.)

A. Zinc and acid method. Fit up the apparatus shown in Fig. V, 22, 1, a. A is a wide-mouthed bottle of about 100 mL capacity fitted with a two-holed rubber bung. A small tap funnel B is inserted into one of the holes, and a glass tube C, 20 cm. in length and 5–7 mm. internal diameter and drawn out at the lower end to an aperture of about 2 mm., is passed through the other hole: a hole of about 2 mm. diameter is made in C (below the cork) to allow of the free escape of the gases. The upper end of C is ground smooth (e.g., on a fine carborundum stone) at right angles to the tube, and is fitted with a device whereby the mercuric chloride paper is held firmly in position over the opening of the tube, thus ensuring that all the arsine evolved passes through the paper and a uniform circular stain is produced. The simplest of these is to fit a wide tube (about ½ in. long and ca. 1 in. internal diameter) round the upper part of C by means of a cork and also to provide another cork, bored with a hole equal in diameter to the external bore of the tube, which fits tightly on to the flat end of C. A circle of mercuric chloride paper (about 10 mm. in diameter) is cut out by means of a cork borer and placed on top of the tube; the paper is held firmly in position by inserting the other bored cork (see Fig. V, 22, 1 b). A. J. Lindsey (1930) has developed an all-glass apparatus* (Fig. V, 22, 1, c) which serves the same purpose; the tube is 20 cm. long, with internal bore 5 mm. or 6–5 mm., and is provided with a flange and two ears at the upper end. The

paper is placed on this flange and is held securely in position by means of a cap with an identical flange, the upper part of which is worked into a double-lipped shape; the cap and tube are held together by means of a pair of rubber bands.

Roll one of the prepared lead acetate papers in the form of a cylinder 10 cm. in length and place it so that the upper end is not less than 2·5 cm. below the upper end of the tube; alternatively, the tube may be packed with strips of the lead acetate paper about 10 cm. in length.

Prepare a series of standard stains, covering a range of, say, 0·001–0·05 mg. of As, as follows. Place 5–10 g. of arsenic-free zinc (e.g., A.R.) in the bottle, together with about 0·5 g. of stannous chloride. Fit the apparatus together, and place one of the prepared discs of mercuric chloride paper into position as described above. Introduce 2 ml. of the arsenic solution (0·001 mg. per ml.) into the flask, and then run in 50–55 ml. of 2·5N-sulphuric or hydrochloric acid (prepared from the A.R. acids), and close the tap. Immerse the bottle in a large beaker of water containing water at room temperature. Allow the reaction to proceed for 1 hour, then remove the mercuric chloride paper disc and dry it in the dark on a sheet of filter-paper. Repeat the procedure with fresh discs, using increasing amounts of arsenic solution. Mark each disc clearly with the exact arsenic content.

If the standards are likely to be used frequently, a fair degree of permanence may be secured by any of the following procedures: (i) dry the discs between filter-paper, and (a) dip them into cellulose varnish, mount on a sheet of white paper, and preserve over calcium chloride in a desiccator in the dark or (b) dip the discs into molten paraffin wax, and preserve them over phosphoric oxide in a closed tube which is kept in the dark; (ii) immerse the discs in a 10 per cent solution of potassium iodide until the red colour of mercuric iodide at first produced disappears, leaving a brown stain, and then dry in the dark on a sheet of filter-paper. Prepared papers, which are claimed to preserve their permanence for 1 year, are available commercially.

If the arsenic content of the solution is approximately known, the solution is added to zinc and stannous chloride contained in the bottle, dilute sulphuric or hydrochloric acid introduced, and the determination carried out exactly as in the preparation of the standards. If the arsenic content is entirely unknown and interfering substances are absent, a preliminary test should be carried out as follows. Set up the apparatus, add the acid to the zinc, and then run in the arsenic solution in suitable quantities at a time, commencing with 1 ml. and waiting 15 minutes after each addition until a stain is produced within the range of standards. The procedure is then repeated in the manner used in preparing the standards, taking the appropriate amount of the arsenic solution. The reagents should first be tested for the presence of arsenic by running a blank with distilled water.

B. Electrolytic (mercury cathode) method. A mercury-cathode cell, due to T. Callan and Jones (1930), suitable for the determination of small quantities of arsenic, is shown in Fig. V, 22, 2, a.

It consists of a flat-bottomed tube, 5 in. long and 1½ in. in diameter, having an aperture of 1 in. diameter blown on the side about ½ in. from
the bottom of the tube. The aperture is covered by a piece of parchmentised paper,* which acts as an efficient diaphragm of very low electrical resistance between the catholyte and anolyte. The aperture is flanged so that the parchment paper may be held in position by means of a rubber band. Purified mercury is placed in the bottom of the tube so that its surface is just below the level of the aperture. Electrical connexion is made with the mercury by means of a narrow glass tube, into the lower closed end of which is sealed a short platinum wire. The whole of the exposed platinum wire dips into the mercury; a little mercury is placed inside the tube, and a copper wire dipping into this forms the negative terminal of the cell. The narrow tube, carrying the cathode lead, passes through a three-holed rubber stopper which closes the cell. The rubber stopper also carries a tap funnel of 20 ml. capacity, through which the electrolyte or test solution may be introduced, and also an exit tube having a small hole near the bottom and which is connected directly with the purifying tube of the Gutzeit apparatus (not shown). The cathode cell is immersed in the electrolyte of the anode cell (1 : 8 sulphuric acid), which is itself immersed in a cooling-bath maintained at room temperature. The anode is a sheet of platinum foil (2 in. by 1 in.) welded to a short length of thick platinum wire.

Fig. V, 22, 2, b shows the essential parts of the same apparatus, but with the rubber stopper replaced by a ground-glass joint.†

In use a current of 2 amps. is passed for 15 minutes, followed by 4 amps. for 15 minutes. In other respects the procedure for the determination is similar to that given in A.

C. Modified Sanger-Black-Gutzeit method. Prepare the sensitised mercuric bromide paper as follows. Dry some Whatman arsenic test strips No. 130 (120 X 2·5 mm. or 150 X 5 mm.) or strips prepared from Whatman No. 20 paper in an electric oven at 105° C. for 1 hour, and store in a desiccator over calcium chloride until required. Saturate

* Parchmentised paper is prepared by rapidly immersing Whatman No. 1 filter paper in pure 80 per cent sulphuric acid for a few seconds, and then washing with water. The paper is stored under water until required.
† Both forms of apparatus are obtainable from Baird and Tatlock (London) Ltd., Freshwater Road, Chadwell Heath, Essex, England.
the strips with a 0.35 per cent solution of pure mercuric bromide in 95 per cent ethyl alcohol, allow them to drain, and dry in a desiccator for 10 minutes. The strips are then ready for use: no treated strips should be stored for longer than 2 hours before use.

Prepare a ferric ammonium sulphate solution by dissolving 8.4 g. of A.R. iron alum with 1 ml. of 1:4 A.R. sulphuric acid in 100 ml. of water. 10 ml. of this solution contains the equivalent of ca. 0.5 g. Fe₂O₃.

Prepare a stannous chloride solution by dissolving 16 g. of A.R. stannous chloride in 20 ml. of water containing 1 ml. of A.R. hydrochloric acid (sp. gr. 1.2).

The apparatus used is shown in Fig. V, 22, 3. It consists of a 60-ml., wide-mouthed bottle in the mouth of which is fitted by means of a rubber stopper a tube 12 cm. long and 1.25 cm. in diameter and constricted 5 cm. from the top. The lower part of the tube contains a roll or strips of heavy filter-paper soaked in 10 per cent lead acetate solution and dried (this filter-paper is held in position by a plug of purified glass wool, which also serves to remove acid spray); the upper portion contains purified glass wool soaked in the same solution. This tube is connected by a rubber stopper to a glass tube 10 cm. long and 4 mm. internal diameter which is constricted 4 cm. from the lower end; the strip of test paper is placed in this tube. In order to obtain uniform results which are independent of the temperature of the laboratory, a small water-condenser, through which water below 20° C. is circulated, surrounds the tube containing the test-strip.

Place the solution under test (containing not more than 0.02 mg. of As₂O₃) in the generating bottle, add sufficient acid so that the acid content is equivalent to 4.2-6.3 g. of sulphuric acid, then introduce 2 ml. of the ferric solution and 0.5 ml. of the stannous chloride solution: dilute to 50 ml. Introduce about 15 g. of arsenic-free zinc (preferably in the form of shot, 1/4-in. mesh). Immediately insert the connecting tubes, and place the mercuric bromide strip (120 × 2.5 mm.) in position; shake the bottle gently and allow to stand for 60 minutes. The temperature should be maintained at 20° ± 1° C. (or, less satisfactorily, at 25° ± 1° C.) by immersing the bottle in a water-bath or a large beaker containing water at this temperature. Remove the strip, dry it between sheets of filter-paper, dip it into either cellulose varnish or into molten paraffin wax (free from water).

* Formerly more concentrated solutions (up to 5 per cent) of mercuric bromide were employed. The weaker the solution, the longer and the less intense will be the stain.

† Ferrous iron prevents polarisation between the zinc and acid, and hence accelerates the liberation of the arsine.
and mount it on a sheet of white paper. Compare the stain produced with stains obtained in the same manner by known amounts of arsenic, using portions of a standard solution containing 0·001, 0·002, 0·004, 0·006, 0·01, 0·015, and 0·02 mg. of As₂O₃ and adding water, acid, etc., so as to have the same volume and concentration as the final unknown solution. The strips bearing the standard stains should be mounted on a sheet of white paper, folded back to form a cylinder and preserved in the dark in a closed test-tube containing phosphoric oxide. A blank determination must, of course, be carried out with the reagents; this should show not more than 0·001 mg. of As₂O₃. Instead of direct comparison with standards, the lengths of the stains by a given procedure may be plotted on a graph and values interpolated; results accurate to 5 per cent are obtained.

**Procedure (molybdenum-blue method).** The arsenic must be in the trivalent state; this may be secured by first distilling in an all-glass apparatus with concentrated hydrochloric acid and hydrazine sulphate, preferably in a stream of carbon dioxide or nitrogen. Another method consists in reducing the arsenate (obtained by the wet oxidation of a sample) with potassium iodide and stannous chloride: the acid concentration of the solution diluted to 100 ml. must be diluted below 5 per cent; 1 ml. of 50 per cent potassium iodide solution and 1 ml. of a 40 per cent solution of stannous chloride in concentrated hydrochloric acid are added, and the mixture heated to boiling.

Transfer an aliquot portion of the arsenate solution, containing not more than 0·1 mg. of arsenic, to the 50-ml. evolution vessel A shown in Fig. V, 22, 4: add 2 ml. of concentrated sulphuric acid, 10 ml. of concentrated hydrochloric acid, 1 ml. of a 40 per cent solution of stannous chloride in concentrated hydrochloric acid, sufficient water to bring the total volume of the mixture to about 50 ml., and finally 5 g. of zinc shot. Insert the rubber stopper rapidly; the evolved gas passes through the tube B, loosely packed with glass-wool soaked in lead acetate solution (to remove hydrogen sulphide and to trap acid spray), and then through a capillary tube (4 mm. external and 0·5 mm. internal diameter) into a narrow absorption tube D charged with 5 ml. of 0·02N-i iodine solution and 1 ml. of 7N-sodium bicarbonate solution. After 30 minutes all the arsine will have been evolved and converted into arsenate by the iodine solution. Meanwhile, prepare the sulphuric acid–molybdate solution by mixing equal volumes of 13N-sulphuric acid and a 9·5 per cent aqueous solution of sodium molybdate (Na₃MoO₄·2H₂O). Remove tube D and introduce 2·0 ml. of the acid molybdate solution, and then 1·0 ml. of a 0·5 per cent aqueous solution of sodium metabisulphite (to destroy the excess of iodine). To the resulting colourless solution add 1·0 ml. of 0·2 per cent stannous chloride solution, which has been prepared by diluting 1 part of the 40 per cent solution with 200 parts of water. The blue coloration is fully developed in 5 minutes. Measure the intensity of the colour by any convenient method, e.g., with a Spekker absorptio-
Qu,antitative Inorganic Analysis

Prepare standards by treating solutions containing 0-005–0-10 mg. of As in exactly the same manner as the unknown.

V. 23. Antimony.—Discussion. A satisfactory method for the colorimetric determination of small amounts (up to 0-5 mg.) of antimony is the potassium iodide–pyridine method (S. G. Clark, 1928), and is particularly well adapted to the determination of antimony in tin. The preliminary separation is effected by deposition on copper foil (Reinsch’s reaction). The deposit is dissolved in sodium peroxyde solution, and any dissolved copper is precipitated by hydrogen sulphide in the alkaline solution and the copper sulphide removed by filtration. The solution is acidified with sulphuric acid and evaporated to fuming; the residue is diluted with water, and to it are added aqueous solutions of pyridine, sulphur dioxide, potassium iodide, and gum arabic or "starch glycerite".* The yellow coloration is then compared against standards similarly prepared.

Tin and arsenic when present in moderate amounts (several centigrams) do not interfere. Bismuth and several other heavy metals give a coloured precipitate, whilst zinc yields a white crystalline precipitate: these metals should therefore be absent. The best acid to employ is sulphuric acid. Hydrochloric acid, and particularly chlorides, bleach the colour. Excessive amounts of sulphurous acid cause liberation of iodine, whilst a large excess of pyridine produces colour fading.

Procedure. Full details for the determination of small amounts of antimony (0-001–0-05 per cent) in tin are given below.

Prepare a standard solution of antimony by dissolving 0-2668 g. of A.R. potassium antimonyl tartrate in 1000 ml. of 10 per cent sulphuric acid; 1 ml. contains 0-1 mg. of Sb.

Weigh out accurately a suitable quantity of tin (1–5 g. according to the antimony content, which should be ca. 0-5 mg.) into a 750-ml. conical flask; add 60 ml. of concentrated hydrochloric acid and sufficient bromine to ensure an excess while the tin is dissolving. When the tin has dissolved, add 2–10 g. of oxalic acid (according to the amount of antimony), followed by about 350 ml. of water. Boil the liquid gently; the oxalic acid will dissolve and yield a solution tinged with bromine. Add about 0-5 g. of sodium hypophosphite to reduce all the free bromine, to separate completely any arsenic which may be present, and to render the solution colourless. Introduce a flat, open spiral of copper (made from a strip of clean copper foil, 15 × 2 cm.) into the solution; it should stand upright on the bottom of the flask. Boil for 2 hours, remove the copper coil by means of a hooked glass rod, and wash it successively with a gentle stream of 5 per cent hydrochloric acid and of water. Place the coil in a small beaker, cover it with water, add 1–2 g. of pure sodium peroxyde, and warm until the deposit is dissolved and the copper is well darkened by oxidation. Pour off the solution from the coil, and then rinse it with water. Pass hydrogen sulphide into the solution and washings for 15 seconds, allow the small precipitate of copper sulphide to coagulate on the

* This is prepared by heating starch with glycerine and diluting with water. This (and also gum arabic) is added as a protective colloid to stabilise the suspension of the yellow complex. It also gives a bluish-green coloration with free iodine, and then will indicate whether the solution is completely reduced by the sulphur dioxide added.
water-bath (15 minutes) and filter; wash with a dilute solution of ammonium nitrate. Add 5 ml. of concentrated sulphuric acid and a few drops of concentrated nitric acid to the filtrate and washings, evaporate just to fuming, cool, and add 15 ml. of water. The antimony in the resultant solution (ca. 20 ml.) is determined colorimetrically as follows.

Introduce the reagents in the order given into a 100-ml. Nessler cylinder: 10 ml. of 1 per cent gum-arabic solution, 5 ml. of 20 per cent potassium iodide solution, 1 ml. of 10 per cent aqueous pyridine, 1 ml. of sulphur dioxide solution prepared by 10-fold dilution of a saturated aqueous solution, and 60 ml. of cold 1:3 sulphuric acid. The antimony solution prepared as above is then added, the beaker being rinsed with not more than 5 ml. of water, and the whole stirred with a glass stirrer of which the lower end is flattened. Run the standard antimony solution from a burette into another Nessler tube containing similar quantities of the reagents (except that 80 ml. of 1:3 sulphuric acid are used instead of 60 ml.) until the colours match after the solution has been well stirred. The final adjustment is made by adding a small quantity of water to make the volumes in the two Nessler tubes equal. Not more than 10 ml. of the standard antimony solution should be required, for otherwise the colour will be too deep for accurate comparison. A blank determination should be made on the reagents.

V, 24. Tin.—Discussion. 4-Methyl-1:2-dimercaptobenzene (dithiol) forms a red compound when warmed with stannous salts. Stannic tin also reacts, but more slowly than stannous; thioglycollic acid may be employed to reduce stannic tin to the divalent form. A useful application is to the determination of small amounts of tin in foodstuffs (derived from contact with tin cans) or in organic materials. A protective colloid, such as agar, is generally added, although this is not essential if the tin content of the solution is less than 30 parts per million. The reagent solution is not stable, being easily oxidised, and hence it should be prepared as required.

Many heavy metals react with dithiol to give coloured precipitates. Of these only arsenic distils over with the tin when a mixture is distilled from a medium of concentrated sulphuric acid and concentrated hydrobromic acid in a current of carbon dioxide. If arsenic is present in quantities larger than that of the tin, it should be removed.

Procedure (tin in foodstuffs or organic material). Ignite the sample at a dull red heat in a silica crucible. (Alternatively, digest, say, 10 g. of the food sample with 30 ml. of concentrated sulphuric acid and 10 g. of potassium sulphate.) Transfer the residue quantitatively with the aid of 30 ml. of concentrated sulphuric acid to an all-glass distillation apparatus.* The distillation flask is provided with two necks, one carrying a dropping funnel, and the other an inlet tube for passing carbon dioxide through the apparatus; three small receivers, connected in series and each containing 5 ml. of water, are used. Charge the dropping funnel with A.R. constant-boiling-point hydrobromic acid. Heat the flask in an oil-bath maintained at 220°. Allow the hydrobromic acid to flow into the flask at a rate of about

* Obtainable from Quickfit and Quartz Ltd., King's Norton, Birmingham.
1 drop per second, and at the same time bubble a steady stream of carbon dioxide through the solution. After distillation has continued for 1 hour rinse the condenser with a little water. Combine the rinsings and the distillates, and dilute to a known volume (say, 50 or 100 ml.). Take an aliquot part (expected to contain about 0.020 mg. of tin) and add a 25 per cent solution of A.R. phenol in A.R. glacial acetic acid dropwise until the free bromine is destroyed. Determine the strong acid concentration in an aliquot part by titration with N-sodium hydroxide solution to a methyl orange end point. Decolorise a further aliquot part by means of phenol as before and add 7.5N-sodium hydroxide solution (with due regard to the previous titration) until the residual concentration of free hydrobromic acid is equivalent to 0.5 ml. of constant-boiling-point hydrobromic acid (48% HBr). Then add 0.2 ml. of a freshly prepared 0.4 per cent aqueous solution of thioglycollic acid, 4 drops of fairly stiff agar mucilage, and 1 ml. of the dithiol reagent (a 0.1 per cent solution in 1 per cent sodium hydroxide, freshly prepared). Dilute the mixture to 10 ml. and heat in a boiling water-bath for 1 minute. After cooling, compare the colour against standard solutions similarly prepared in a colorimeter or a Spekker absorptiometer.

Prepare the standard tin solution by dissolving 1.000 g. of A.R. tin in 100 ml. of 1:1 hydrochloric acid and diluting with the same acid to 1 litre: 1 ml. contains 1 mg. of Sn. Prepare more dilute standards as required (e.g., 0.02 mg. of Sn per ml.) by dilution with 1:1 hydrochloric acid.

V. 25. Lead.—Discussion. For the determination of minute quantities of lead (0.005-0.25 mg.) advantage is taken of the fact that when a sulphide is added to a solution containing lead a brown colour, due to the formation of colloidal lead sulphide, is produced.

Interference is produced by the presence of: (a) neutral salts, such as ammonium chloride and particularly tartrates and citrates, and (b) other metals, such as copper, bismuth, iron, and aluminium. Errors due to (a) may be allowed for by ensuring that the standards for comparison contain amounts of salts approximately equal to those in the solution under test, whilst those produced by (b) are eliminated by the usual analytical procedure or by the use of diphenylthiocarbazone (see below). The disturbing effect due to copper and iron if present in small amount may be overcome by the addition of a few drops of a 10 per cent aqueous solution of potassium cyanide; aluminium may be retained in ammoniacal solution by the addition of ammonium citrate solution, a corresponding amount of the latter being added to the standards.

In case of doubt as to the presence of other metals it is best to isolate the lead quantitatively by means of sym.-diphenylthiocarbazone C₆H₅NH-NH-CS-N═NC₆H₅ (dithizone). The reagent consists of an approximately 0.1 per cent solution in carbon tetrachloride or, preferably, chloroform in which it is more soluble, and yields a red coloration with minute quantities of lead salts. A number of metals interfere, but the reaction of most of these, with the exception of bismuth, is inhibited by the addition of aqueous potassium cyanide solution. The lead complex is removed by extraction with chloroform, but the resulting coloured lead compound is not well adapted for simple colorimetric technique unless strictly comparable standards.
are used; the organic lead complex may be oxidised, and the lead determined by the colloidal sulphide method.

**Procedure (sulphide method).** Prepare a standard lead solution by dissolving either 0·183 g. of A.R. lead acetate crystals or 0·160 g. of A.R. lead nitrate in 100 ml. of water; 10 ml. of this are diluted to 100 ml. for a working solution: the latter contains 0·1 mg. of Pb per ml.

As an illustration of the simple lead sulphide procedure, the determination of lead in commercial tartaric acid will be described. Dissolve 10 g. of the tartaric acid in about 40 ml. of hot water, add 5 to 6 drops of 10 per cent potassium cyanide solution, then 25 ml. of 1:2 ammonia solution (which should make the solution ammoniacal), and finally 2 to 3 drops of ammonium sulphide solution (prepared by saturating 1:4 ammonia solution with well-washed hydrogen sulphide). Make up to 100 ml. Match the solution thus prepared against a standard solution made by treating 10 g. of lead-free tartaric acid in exactly the same way and adding to it 2 ml. of the standard lead solution. If the acid being tested yields an appreciably darker colour than the standard, a smaller quantity of it should be taken and subjected to a similar treatment. A darker standard should not be used.

**Procedure (dithizone method).** Prepare the following solutions:

(i) Dithizone solution: dissolve 6 mg. of A.R. dithizone in 100 ml. of redistilled carbon tetrachloride.

(ii) Ammonium hydroxide solution: pass ammonia gas from a cylinder into cold redistilled water until saturated.

If any of the other reagents, e.g., ammonium citrate and potassium cyanide, are suspected to contain traces of lead, treat the basic solutions (adding ammonia solution, if necessary) with successive small quantities of the dithizone reagent (prepared with pure chloroform) until all the lead has been removed as indicated by the green colour in the final extract; extract the dithizone in the aqueous layer with chloroform. A.R. reagents are used throughout, and are usually satisfactory.

If metals precipitated by ammonia solution are present, treat the test solution with sufficient 50 per cent ammonium citrate solution to inhibit precipitation, and render basic (litmus paper) with ammonia solution. Add sufficient 5 per cent potassium cyanide solution (say, 5 ml. per 10 ml. of sample solution) to convert foreign heavy metals into their complex cyanides, followed by 1 ml. of 5 per cent hydroxylamine hydrochloride solution in order to prevent the interference of oxidising agents such as ferrie iron. Heat the solution to boiling, cool to room temperature, and transfer to a small separatory funnel. Extract with 4-ml. portions of the dithizone reagent until the carbon tetrachloride is no longer coloured red; separate the layers after each extraction. Shake the combined carbon tetrachloride extracts with 3 ml. of 0·5 per cent potassium cyanide solution, run off the organic layer, wash the latter again with cyanide solution, and finally with a little water. The carbon tetrachloride extract should now be free from dithizone, and the aqueous phase should be practically colourless. Make up the carbon tetrachloride solution to a definite volume and determine the lead dithizonate content in any convenient manner with the aid of standards; the latter are obtained from known amounts.
of lead which have been treated in exactly the same way as the sample. A filter giving a maximum transmission at 520–530 μm may be used with a filter photometer.

V. 26. Copper.—Discussion. The sodium diethylthiocarbamate and the dithizone methods are employed for the determination of small quantities of copper; the latter method is said to be the more sensitive.

The addition of an aqueous solution of sodium diethylthiocarbamate \((C_2H_5)_2N\overset{\cdots}{C}S\overset{\cdots}{S}Na\) to a slightly acid or an ammoniacal solution of a copper salt produces a brown precipitate of a sparingly soluble copper derivative; with minute amounts of copper a golden-brown coloration is obtained. The copper derivative is soluble in organic solvents, such as carbon tetrachloride, and the resulting yellow-brown solution is compared against a similar standard solution.

The reaction is not specific for copper. Many of the heavy metals give slightly soluble products with the reagent, most of which dissolve in carbon tetrachloride. Those of zinc, cadmium, mercury (II), silver, lead, tin, etc., are white, that of ferric iron is brown-black in an acid or neutral medium, although it does not react in an ammonium acetate solution if the pH is 9 or above. The chief interfering elements are nickel, cobalt, and bismuth, and, to a lesser extent, manganese. Cobalt and nickel may be removed by adding 1 ml. of 0·5 per cent dimethylglyoxime solution to the sample solution and separating the precipitate by centrifugation.

Copper reacts with dithizone (compare Section V, 25) in dilute \((0·1N)\) mineral acid solution to form a red-violet complex, which is soluble in chloroform or in carbon tetrachloride. The removal of the excess of dithizone from the organic extract by dilute ammonia or other alkaline solution is accompanied by appreciable quantities of copper dithizonate (compare lead, in which the loss is proportionately lower), hence this mono-colour technique yields only approximate results. A modified (mixed-colour) method gives satisfactory results.

Palladium, gold, silver, mercury, and bismuth react in acid solution and must be absent; moderate amounts of lead, zinc, cadmium, nickel, etc., have no influence. The isolation of the copper dithizonate in acid solution by a preliminary extraction with chloroform or carbon tetrachloride usually removes most other interfering elements.

**Procedure** (sodium diethylthiocarbamate method). Prepare a standard copper solution by dissolving 0·3928 g. of A.R. crystallised copper sulphate in water, add enough hydrochloric (or sulphuric) acid to make the final acidity about 0·1N, and dilute to 1 litre; 1 ml. contains 0·1 mg. of Cu. This solution may be diluted 10- or 50-fold with 0·1N-hydrochloric acid. Alternatively, dissolve 0·1000 g. of A.R. copper in a slight excess of 1:1 nitric acid, boil to expel all oxides of nitrogen, and then dilute to 1 litre as before.

The neutral copper solution should be free from large quantities of interfering elements; thus for a sample solution having a volume of 10–20 ml. and containing up to 0·05 mg. of copper, not more than 50 mg. of iron and 0·5 mg. of manganese should be present. To the sample solution contained in a small separatory funnel, add 5 ml. of 20 per cent ammonium citrate solution, and adjust the pH to 9·0–9·2 by the addition of ammonium hydroxide solution (use a pH
meter or indicator test papers). Add 10 ml. of a freshly prepared 0·1 per cent aqueous solution of sodium diethyldithiocarbamate, mix, and immediately extract with 2·5 ml. of A.R. carbon tetrachloride. Run the lower layer into a dry 10- or 20-ml. measuring-vessel. Repeat the extraction with three further successive 2·5-ml. portions of carbon tetrachloride, and combine the extracts. The final extract should be colourless; if not, repeat the operation until all the complex is removed. Dilute the combined extracts to 20 ml., and clarify by adding about 1 g. of anhydrous sodium sulphate. Measure the colour intensity by any convenient method by comparison with standard solutions of copper similarly treated. A blue filter may be used with a filter photometer.

Procedure (dithizone method). The solution may conveniently have a volume of 10–20 ml. and contain not more than 0·01 mg. of copper. Render the test solution 0·05–0·1N in hydrochloric (or sulphuric) acid, transfer to a separatory funnel, and shake with 5 ml. of a 0·0025 per cent solution of A.R. dithizone in A.R. carbon tetrachloride. If the colour of the carbon tetrachloride solution is red-violet, an excess of dithizone may not be present; repeat the extraction with a further 5 ml. of the dithizone solution. Measure the colour of the carbon tetrachloride extract by any convenient means; the comparison solution should have approximately the same volume and acidity as the sample solution. A filter with maximum transmittance at about 510 mμ may be used with a filter photometer.

It may be noted that when dealing with such small concentrations of copper, it is important that the reagents be copper-free. Thus the distilled water must be redistilled from an all-Pyrex glass apparatus, as should also the A.R. hydrochloric acid.

V. 27. Bismuth.—Discussion. When potassium iodide solution is added to a dilute sulphuric or nitric acid solution containing a small amount of bismuth, a yellow coloration, due to the formation of a complex iodide, is produced. This is suitable for the colorimetric determination of quantities up to about 1 mg. of bismuth.

The solution must be free from large amounts of lead, copper, tin, arsenic, antimony, thallium, gold, silver, and from elements in sufficient quantity to colour the solution, e.g., nickel. Substances which liberate iodine from potassium iodide interfere, for example, ferric iron; the latter should be reduced either by sulphurous acid and the slight excess of gas boiled off or by a 30 per cent solution of hypophosphorous acid. Separation of bismuth from copper is best effected by extraction of the bismuth as the dithizonate by treatment in ammoniacal potassium cyanide solution with a 0·1 per cent chloroform solution of dithizone. The bismuth complex is soluble in an amyl alcohol–ethyl acetate mixture, and this fact may be utilised for the determination in the presence of coloured ions, such as nickel, cobalt, chromium, and uranium.

Procedure. Prepare a standard solution of bismuth by dissolving 0·105 g. of A.R. bismuth * in 20 ml. of concentrated sulphuric acid, and dilute to 1 litre with water; 1 ml. contains 0·1 mg. of Bi.

Treat the colourless solution (20–30 ml.), containing not more than 0·5–1 mg. of bismuth and free from interfering substances but acid with sulphuric acid, with 1 ml. of a saturated solution of sulphur

* Obtainable, for example, from the Mallinckrodt Chemical Works, New York, U.S.A.
dioxide, 10 ml. of a 30 per cent solution of potassium iodide, and dilute to 50 ml. Match the yellow colour produced against standards containing the same concentration of sulphuric and sulphurous acids. After the determination add starch solution to make sure that the colours are not partially due to free iodine.

Procedure (bismuth in lead). Dissolve 20 g. of the sample of lead in a mixture of 25 ml. of concentrated nitric acid and 50 ml. of water, add 30 ml. of concentrated hydrochloric acid, cool to at least 20°, filter and wash the lead chloride with cold 1:1 hydrochloric acid. Treat the combined filtrate and washings with 5 ml. of a solution containing 1 mg. of ferric iron per ml., followed by 20 ml. of 20 per cent ammonium acetate solution. Add sodium hydroxide pellets gradually, while stirring the solution, until a small amount of lead hydroxide is precipitated; then add strong hydrochloric acid drop-wise and with efficient stirring until the lead hydroxide precipitate just dissolves, and finally add a further 1 ml. of the acid. Filter off the precipitated ferric hydroxide (upon which the bismuth hydroxide is co-precipitated) immediately on a small asbestos mat with the aid of suction, wash three times with cold water and discard the filtrate. Dissolve the precipitate in a solution of 3 g. of tartaric acid in a mixture of 45 ml. of water and 5 ml. of 1:1 sulphuric acid by allowing the warm solution (ca. 80° C.) to flow slowly through the filter: wash the filter twice with a little water. Treat the combined filtrate and washings with 5 ml. of hypophosphorous acid (sp. gr. 1-135) and dilute to 100 ml. with water. Pour this solution into a dry flask containing 1.5 g. of A.R. potassium iodide: heat to 70° C., cool to 20° C., and determine the colour intensity by any convenient method.

V, 28. Magnesium.—Discussion. When magnesium hydroxide is precipitated with sodium hydroxide in the presence of the organic dyestuff titan yellow (the sodium salt of dehydrothio-p-toluidine sulphonic acid) a red lake is formed (pH > 12). Fairly stable colloidal suspensions of the lake can be obtained if the magnesium concentration is below 3-4 parts per million, and the fading of the colour is prevented by the presence of hydroxylamine hydrochloride. The reagent alone gives a yellow-brown colour in sodium hydroxide solution.

Many metals interfere, particularly those which give insoluble hydroxides in alkali hydroxide solution (e.g., cadmium) or those of which the hydroxides are soluble in an excess of sodium hydroxide, such as aluminium and tin. Appreciable amounts of phosphate destroy the colour. Calcium tends to deepen the colour given by magnesium, and its influence may be minimised by the addition of sucrose.

Procedure. Remove all interfering elements, for example, iron, aluminium, and phosphate by double precipitation with ammonium hydroxide solution; also calcium (if present in quantity) with ammonium oxalate solution, and other metals by appropriate methods. Evaporate the filtrate to dryness to expel ammonium salts, moisten the residue with a few drops of dilute hydrochloric acid, and dilute to volume in a volumetric flask of suitable size. Transfer into a 50-ml. volumetric flask a quantity of the sample solution (say, 25 ml.) containing 0.3 mg. or less of magnesium. Add 1 ml. of 5 per cent aqueous hydroxylamine hydrochloride solution, 5 ml. of 1 per cent gelatin solution, and 1-0 ml. of a 0-05 per cent
aqueous solution of titan yellow (special quality for analytical use). Dilute to 30–40 ml., add 5 ml. of \( N \)-sodium hydroxide solution while swirling the contents of the flask, and then make up to the mark. Measure the intensity of the colour in the colloidal suspension by suitable means. Use a green filter having a maximum transmission in the vicinity of 550 m\( \mu \) with a filter photometer. Employ as reference solution a standard magnesium solution (0·01 per cent: from pure magnesium metal dissolved in a slight excess of dilute hydrochloric acid and appropriately diluted) which has been treated in a similar manner to the sample solution.

**V. 29. Silicate.—Discussion.** Small quantities of dissolved silicic acid react with a solution of a molybdate in an acid medium to give an intense yellow coloration, due probably to the complex silicomolybdic acid \( H_4[SiMo_{12}O_{40}] \). The latter may be employed as a basis for the colorimetric determination of silicate. It is usually better to reduce the complex acid to molybdenum blue (the composition is uncertain): a solution of hydroquinone in aqueous sodium sulphite is a satisfactory reducing agent.

Phosphates and arsenates give similar colorations, and should best be absent: minute amounts of phosphates do not interfere seriously, but larger amounts should be removed as magnesium ammonium phosphate in acetic acid solution or rendered innocuous by the addition of ammonium citrate. Reducing substances, such as ferrous iron and hydrogen sulphide, must, of course, be absent. Water used for dilution must be freshly distilled in an all-Pyrex glass apparatus, for it dissolves significant traces of silica on standing in glass.

**Procedure.** The sample solution, free from interfering elements and radicals, may conveniently occupy a volume of about 10 ml. and contain between 0·05 and 0·8 mg. of silica. Add 3 ml. of 10 per cent acetic acid, 2·0 ml. of a 0·5 per cent solution of hydroquinone in 20 per cent sodium sulphite solution: make up the volume of the mixture to 25 ml. with water. Allow to stand at room temperature for 30 minutes, and measure the colour intensity in any suitable manner with the aid of standard solutions of silica which have been treated similarly. A filter with a transmittance maximum between 600 and 700 m\( \mu \) may be used with filter photometers.

Prepare a standard solution of silica by fusing pure precipitated silica with A.R. anhydrous sodium carbonate, leaching the melt with water, filtering, and diluting to a suitable volume. Determine gravimetrically the exact silica content in an aliquot part of the solution. Dilute the remainder, after neutralisation with dilute sulphuric acid, to a convenient volume.

**V. 30. Sulphate.—Discussion.** The sulphate in the sample is precipitated as benzidine sulphate and separated centrifugally: the precipitate is dissolved in 0·2N hydrochloric acid, diazotised and coupled (after destroying the excess of nitrous acid with ammonium sulphamate) with \( N \)-(1-naphthyl)ethylenediamine dihydrochloride. The resulting intense purple colour is measured with the aid of a photoelectric colorimeter.

Phosphates and chlorides should be absent, since these cause incomplete precipitation of the benzidine sulphate.
Quantitative Inorganic Analysis

Procedure. Prepare the following aqueous solutions:

Sodium nitrite: 0·1 per cent. A fresh solution is prepared as required.

Ammonium sulphamate: 0·5 per cent.

N-(1-naphthyl)ethylenediamine dihydrochloride: 0·1 per cent. Keep in a dark bottle, preferably in a refrigerator.

Benzidine hydrochloride reagent: dissolve 4·0 g. of pure benzidine hydrochloride in a little distilled water and dilute to 250 ml. with 0·2N hydrochloric acid.

Acetone-ethanol: 1 volume of 95 per cent ethanol and 1 volume of A.R. acetone.

Standard sulphate solutions: dissolve 0·5437 g. of dry A.R. potassium sulphate in a litre of water; 1·0 ml. of this solution contains 0·3 mg. of sulphate. By diluting 10·0 ml. of the standard solution to 100 ml. with 0·2N hydrochloric acid, 1·0 ml. of the resulting solution will contain 0·03 mg. of sulphate.

Standard benzidine hydrochloride solutions: dissolve 0·4014 g. of pure benzidine hydrochloride in a little 0·2N hydrochloric acid and dilute to 100 ml. with the same solvent; 1·0 ml. is equivalent to 1·5 mg. of sulphate. Upon dilution of 2·00 ml. of this standard solution to 100 ml. with 0·2N hydrochloric acid, 1·0 ml. of the resulting solution is equivalent to 0·03 mg. of sulphate.

To a 15 ml. centrifuge tube with a narrowed conical bottom containing 1·0 ml. of glacial acetic acid and 1·0 ml. of the benzidine hydrochloride reagent, add an amount of the sample containing between 0·015 and 0·15 mg. of sulphate. Mix the solutions, add 2·0 ml. of acetone-ethanol, mix the contents thoroughly and place the tube in an ice-water bath to complete the precipitation. At the end of this period, centrifuge the tube at 2,500 r.p.m. for 10 minutes, and pour off the supernatant liquor with one rapid motion. Whilst still inverted, carefully touch the mouth of the tube with a pad of clean filter paper to remove any remaining liquid, and allow to drain in the inverted position on the filter pad for 5 minutes.

Wash the walls of the centrifuge tube with 2·0 ml. of acetone-alcohol without disturbing the tightly packed precipitate. Centrifuge the tube for 5 minutes, pour off the supernatant liquid, and permit to drain for 5 minutes on the filter paper pad. Repeat the washing and draining procedure once more.

Introduce 2·0 ml. of 0·2N hydrochloric acid into the centrifuge tube; the precipitate will dissolve rapidly. Place the tube in an ice-water bath, add 1·0 ml. of freshly prepared sodium nitrite solution, shake the tube to mix the contents, and set aside for 3 minutes. Then add 1·0 ml. of ammonium sulphamate solution, shake the tube, and allow to stand for 2 minutes. Finally, add 1·0 ml. of the N-(1-naphthyl)-ethylenediamine dihydrochloride solution, mix, and, after 20 minutes, transfer the violet solution quantitatively with a teat pipette to a 50 ml. volumetric flask, and dilute to the mark with distilled water.

Measure the absorption in a photoelectric colorimeter, using a green filter.

Standardise the instrument with either a solution of benzidine hydrochloride or a standard sulphate solution equivalent to 0·03 mg. of sulphate. The former solution need only be diazotised and coupled; the latter must be subjected to the full procedure detailed above. It
is advisable to carry out a blank determination with 2·0 ml. of 0·2N hydrochloric acid in order to secure a zero reading of the instrument.

V, 31. Determination of other elements and radicals.—Space does not permit of the inclusion of a detailed account of the determination of small quantities of other elements and radicals. The reader is referred, for example, to references 1, 2, 3, 4, 5, 6, 7, 8, and 9 in the selected bibliography given in the following Section. It is hoped that this Chapter has provided an adequate introduction to this important subject.
SELECTED BIBLIOGRAPHY

CHAPTER VI

POTENTIOMETRIC TITRATION METHODS

VI. 1. General considerations.—The various visual methods, dependent largely upon the use of indicators, for the detection of the end point in titrations have already been discussed in Sections I, 27, I, 41, and I, 50. We shall now deal with a physico-chemical method which may be applied to those cases where no suitable colorimetric indicators are available, and also to those in which the visual method fails or is of limited accuracy, e.g., for coloured or very dilute solutions. This method may often be employed for the determination of two or more constituents in a single operation. Thus a mixture of iodide and chloride may be titrated with silver nitrate solution; the first point of inflexion is the equivalence point of the iodide reaction, and the second inflexion point is that for the chloride reaction (compare Fig. I, 39, 1).

The theory of potentiometric titration is very similar to that already given for ordinary titrations. It has been shown (Section I, 43) that the potential of a metal electrode and a solution of its own ions at 25° C. is given by the expression:

\[ E_{25°} = E^o + \frac{0.0591}{n} \log c_+ \quad \ldots \ldots \quad (1) \]

where \( E^o \) is the standard potential of the metal, \( n \) the valency of the ions, and \( c_+ \) is the ionic concentration (strictly, this should be the ionic activity). If we write \( c_+ \) in the exponential form, i.e., \(-\log [Me^{n+}] = pMe^{n+}\), the equation becomes:

\[ E_{25°} = E^o - \frac{0.0591}{n} pMe^{n+} \quad \ldots \ldots \quad (1') \]

The expression for a hydrogen electrode at 25° C. is:

\[ E_{25°} = E_{H^o}^o - 0.0591 \, pH \quad \ldots \ldots \quad (2) \]

where \( E_{H^o}^o \) is the standard potential of the normal hydrogen electrode.

For an oxidation-reduction electrode, the expression is:

\[ E_{25°} = E^o + \frac{0.0591}{n} \log \frac{[Ox]}{[Red]} \quad \ldots \ldots \quad (3) \]

where \( E^o \) is the standard oxidation potential, \( n \) the number of electrons gained by the oxidant in being converted into the reductant, and \([Ox]\) and \([Red]\) are the concentrations (strictly, the activities) of the oxidant and reductant respectively.

The determination of \( E \) is the essence of potentiometric titration: this may be used either to measure the ionic (or \([Ox]/[Red]\)) concentration of a solution, or, what is more important for our present purpose, to follow the changes in ionic concentration or of the ratio \([Ox]/[Red]\) during the course of a titration.

Since \( E_{H^o}^o \), the normal potential for hydrogen, viz., the potential of
the hydrogen electrode immersed in a solution of hydrogen ions of unit activity at one atmosphere pressure, is taken arbitrarily as zero at all temperatures, expression (2) reduces to:

\[ E = -0.0591 \, \text{pH} \, (\text{at } 25^\circ \text{C}.* ) \]

on this scale. On theoretical grounds, therefore, the determination of the hydrogen-ion concentration is the simplest case to deal with, and it is proposed to discuss this first.

It is now generally realised that expression (2) does not possess a sound theoretical basis, and that pH defined as \(-\log a_{H^+}\) (this may be written \(p\text{H} \)) cannot be determined exactly. Sörensen and Linderström–Lang (1924) put forward a new pH scale, viz., \(p\text{H} = -\log a_{H^+}\), where \(a\) is the activity; this quantity, as defined, is also not capable of precise measurement. It can be shown that the \(p\text{H} \) value is nearly equal to \(-\log 1.1a_{H^+}\), hence:

\[ p\text{H} = p\text{H} + 0.04. \]

This equation is a useful practical formula for converting tables of \(p\text{H}\) (based upon concentrations, i.e., \(p\text{H} \)) to the activity basis.

In view of the importance of accurate \(p\text{H}\) measurements in research and in industry and also in order to ensure that a given solution may be assigned the same value in different laboratories when measured with \(p\text{H}\) meters, etc., it is important to have a universally accepted definition of \(p\text{H}\). The British Standards Institution (1950) have adopted the following definition, which is an operational, and to some extent an arbitrary, one. The difference in \(p\text{H}\) between two solutions \(A\) and \(B\) at the same temperature is given by:

\[ p\text{H} (A) - p\text{H} (B) = \frac{E_A - E_B}{2.3026 \, RT/F} \]

where \(E_A\) is the e.m.f. of the cell

Pt, \(H_2\)/Solution \(A\)/3M KCl/Reference electrode,

\(E_B\) is the e.m.f. of the cell

Pt, \(H_2\)/Solution \(B\)/3M KCl/Reference electrode,

\(R\) is the gas constant, \(T\) the absolute temperature, and \(F\) the Faraday. (At 25° C. the quantity 2.3026 \(RT/F\) is 0.05916.) The \(p\text{H}\) difference is thus a pure number. The primary standard selected is a \(0.05\text{M}\) solution of pure potassium hydrogen phthalate, the \(p\text{H}\) of which is 4.000 at 15° C. At any other temperature \(t\)° C. between 0° and 60° C., the \(p\text{H}\) is given by:

\[ p\text{H} = 4.000 + \frac{1}{2} \left( \frac{t - 15}{100} \right)^2 \]

The \(p\text{H}\) at 25° C. of the following solutions are known with an accuracy of at least 0.01, and have been determined in accordance with the above definition: 0.1M-KH \(_2\)PO \(_4\), 0.1M-H \(_2\)PO \(_4\), 2H \(_2\)O, 1.48; 0.01M-HCl + 0.09M-KCl, 2.07; 0.1M-CH \(_3\)COOH + 0.1M-CH \(_3\)COONa (prepared from pure acetic acid, diluted, and half-neutralised), 4.64; 0.025M-KH \(_2\)PO \(_4\) + 0.025M-Na \(_2\)HPO \(_4\), 6.85; 0.05M-Na \(_2\)B \(_4\)O \(_7\), 10H \(_2\)O, 9.18. These solutions may

* At any other temperature \(T\), the expression becomes:

\[ E = -0.0001982T \, p\text{H} \]

where \(T\) is the absolute temperature.

† \(p\text{H}\) Scale (British Standard 1647: 1950). For a comprehensive review see R. G. Bates, “Definitions of \(p\text{H}\) Scales” (Chemical Reviews, 1946, 42, 1).
be employed for the calibration of the glass electrode when an accuracy of ±0.01 pH unit is desired. If an accuracy of ±0.03 pH is acceptable, a wide choice of solutions is available (see Appendix; Section A, 10).

VI, 2. Determination of pH.—A. The hydrogen electrode. A typical hydrogen electrode has already been described (Section I, 43). For routine work, the most convenient source of hydrogen is the compressed gas, sold in cylinders; a steady stream of hydrogen gas may be readily obtained by means of a reducing valve. The gas may be passed through all-glass wash bottles containing respectively 0.2N-potassium permanganate solution, alkaline pyrogallol solution (1–2 g. of pyrogallol in ca. 35 ml. of 4N-sodium hydroxide solution), dilute sulphuric acid (ca. 0.1N; to neutralise alkali which might splash over), and distilled water, before reaching the electrode. If a hydrogen electrode is immersed in a solution the pH of which is to be determined, and the half-cell is coupled with a normal hydrogen electrode by means of a saturated potassium chloride bridge (Fig. VI, 2, 1) in order to eliminate the liquid-junction potential,1 the e.m.f. of the resulting cell:

\[ \text{Pt} | H_2, H^+ || H_2, H^+ | \text{Pt} \]

\[ a = 1 \quad a = x \]

may be measured by means of a potentiometer (see below). The e.m.f. of this concentration cell at 25° C. (see Section I, 44) is given by:

\[ E = \frac{0.0591}{n} \log \frac{c_2}{c_1} = \frac{0.0591}{1} \log \frac{1}{[H^+]} = 0.0591 \text{ pH} ; \]

or

\[ \text{pH} = \frac{E}{0.0591}. \]

The following notes on the preparation and the use of the hydrogen electrode may be useful. The hydrogen ions of the solution are brought into equilibrium with the gaseous hydrogen by means of platinum black; the latter absorbs the hydrogen and acts catalytically. The platinum black may be supported on platinum foil of about 1 sq. cm. total area; a platinum wire, 1 cm. long and 0.3 mm. diameter, is often satisfactory. The platinum electrode is first carefully cleaned with hot chromic acid mixture and thoroughly washed with distilled water.

1 The open ends of the bridge are plugged tightly with pure filter-paper or fitted with sintered-glass plates in order to minimise diffusion effects. In practice, it is usually more convenient to employ a gel formed from 3 per cent agar in saturated potassium chloride solution, the so-called agar-potassium chloride bridge. This gel is prepared by heating 3 g. of agar, 30 g. of A.R. potassium chloride, and 100 ml. of water gently until all has dissolved and the solution is clear. The narrow, U-shaped tubes are filled by suction with the warm solution: upon cooling, the solution sets to a gel. The siphons can be kept for prolonged periods if their open ends are placed, when not in use, in a saturated solution of potassium chloride.
Then it is plated from a solution containing 3.0 g. of chloroplatinic acid and 25 mg. of lead acetate per 100 ml. with platinum foil as an anode. The current may be obtained from two accumulators connected to a suitable sliding resistance; the current is adjusted to produce a moderate evolution of hydrogen, and the process is complete in about 2 minutes. It is important that only a thin, jet-black deposit be made; thick deposits lead to unsatisfactory hydrogen electrodes. After platinising, the electrode must be freed from traces of chlorine; it is washed thoroughly with water, electrolysed in ca. 0.5 N-sulphuric acid as cathode for about 30 minutes, and again well washed with water. Hydrogen electrodes should be stored in distilled water; they should never be touched with the fingers. It is advisable to have two hydrogen electrodes so that the readings obtained with one can be periodically checked against the other.

The electrode depicted in Fig. VI, 2, 1 is the Hildebrand bell-type. The platinum electrode proper is surrounded by an outer tube or bell into which hydrogen enters through a side inlet, escaping at the bottom through the test solution. There are four small holes near the bottom of the bell; when the speed of the gas is suitably adjusted, the hydrogen escapes at the bottom only, whilst the test solution running through the side holes gives the former an oscillatory motion—a process which promotes rapid saturation of the electrode. The Lindsay hydrogen electrode, illustrated in Fig. VI, 2, 2 has many valuable features and utilises 5-7 ml. of the test solution. The introduction and the removal of the test solution is simple, and rapid saturation of the platinum is readily attained. The hydrogen-outlet trap is at right angles to the plane of the paper; and not in the same plane as indicated in the figure. The funnel limb serves for filling and washing out the vessel, and also supplies the connexion to the reference electrode. The hydrogen stream is adjusted to produce a pulsating movement up and down the platinum electrode.

The use of the normal (or molar or standard) hydrogen electrode as a standard electrode or half-cell presents certain practical difficulties. It is usual to employ a reference electrode as a secondary standard half-cell; the potential of the reference electrode relative to the normal hydrogen electrode is known with accuracy. The most widely used reference electrode, due to its ease of preparation and constancy of potential, is the calomel electrode. A calomel half-cell is one in which mercury and calomel are covered with potassium chloride solution of definite concentration; this may be 0.1N, 1.0N, 3.5N, or saturated. The potassium chloride solution must be saturated with the calomel. The potential of, say, the saturated calomel electrode (i.e., that prepared with saturated potassium chloride solution) must first be determined with reference to the normal hydrogen electrode. Let this value
be designated $E_{\text{cal.sat.}}$. For the measurement of the hydrogen-ion concentration, we then employ the cell:

$$\text{Hg} | \text{Hg}_2\text{Cl}_2, \text{KCl (satd.)} || \text{H}^+, \text{H}_2 | \text{Pt}$$

Let the resultant e.m.f. be $E_{\text{obs}}$. Then, at 25° C.:

$$E_{\text{obs}} = E_{\text{cal.sat.}} - 0.0591 \log [\text{H}^+]$$

$$p\text{H} = \frac{E_{\text{obs}} - E_{\text{cal.sat.}}}{0.0591}$$

The potentials of the 0·1N, 1·0N, and saturated calomel electrodes at 25° C. relative to the normal hydrogen electrode are 0·3371, 0·2846, and 0·2458 volt respectively.

Various forms of the calomel electrode are illustrated in Fig. VI, 2, 3; 0·1N, N, or saturated potassium chloride may be used, but the last-named is generally preferred for routine work. One of these, (a), will

![Diagram](image-url)

be described in detail; the others will then be self-evident. It consists of a glass vessel provided with a bent side tube $A$ and another side tube $B$, over the end of which a piece of rubber tubing is placed which can be closed by a spring or screw clip. Electrical connexion with the electrode is made by means of a platinum wire, sealed through a glass tube $C$; the latter contains a little pure mercury into which an amalgamated copper wire dips. To set up the electrode, a saturated solution of analytically pure potassium chloride containing some of the solid salt is first prepared. Pure mercury to a depth of 0·5–1 em. is placed in the bottom of the dry electrode vessel; the mercury is then covered with a layer of calomel paste $D$. The latter is prepared by rubbing pure calomel, mercury, and saturated potassium chloride solution together in a glass mortar; the supernatant liquid is poured off and the rubbing process repeated twice with fresh quantities of saturated potassium chloride solution. The rubber bung carrying the glass tube and platinum wire is then inserted, care being taken that the platinum wire dips into the mercury. The vessel is then filled with a saturated solution of potassium chloride (previously saturated with calomel by shaking with the solid salt) by drawing in the solution through the bent tube $A$, and then closing the rubber tube $B$ with a clip. The electrode is then ready for use. In electrode (b), the siphon
tube or salt bridge may be filled with a jelly of 3 per cent agar in saturated potassium chloride solution. The electrode (c) is suitable for precision work; it has a three-way stop-cock for flushing away the contaminated potassium chloride after it has been employed in a titration.

The silver-silver chloride electrode is perhaps next in importance to the calomel electrode as a reference half-cell, but it is more difficult to prepare. It consists of a silver wire or a silver-plated platinum wire, coated electrolytically with a thin layer of silver chloride, dipping into a potassium chloride solution of known concentration. The potentials of the 0.1N, 1.0N, and saturated silver-silver chloride electrodes at 25° with respect to the normal hydrogen electrode are 0.290, 0.236, and 0.203 volt respectively.

The most satisfactory method for the measurement of the e.m.f. of a cell is that known as Poggendorff's compensation method, an outline of which is given below. The principle of the method is to balance the unknown e.m.f. against a known e.m.f., which can easily be varied. When these two e.m.f.s are exactly equal, no current will flow through a galvanometer placed in the circuit; the galvanometer is therefore employed as a null instrument. The essential details are shown in Fig. VI, 2, 4.

A 2- or 4-volt accumulator furnishes the opposing e.m.f.; this is connected in series with a rheostat and with the terminals of a slide wire AB. The latter is a thin wire of uniform cross-section, and is often termed the "potentiometer wire." The cell, the e.m.f. of which is to be determined, is connected to one end A of the slide wire, and through a galvanometer G and a key S₂ to a sliding contact C, which can be moved along AB. A special double-throw switch S₁ may be provided to permit the standard cell to be placed in the circuit. In connecting the accumulator and the cell to the bridge, it is essential that the positive poles should be connected to the same end of the bridge wire; the unknown cell will then send a current through the circuit in a direction opposite to that furnished by the accumulator.

If we assume that the potentiometer wire has uniform cross-section and resistance, then the fall of potential along the slide wire will be uniform. The difference of potential between A and any point C will be proportional to the length AC, and will be equal to the fraction AC/AB of the total fall of potential along the wire. If the unknown cell is now placed in circuit and the position of C is so adjusted that when the switch S₂ is depressed, no current passes through the galvanometer G, then the e.m.f. of the cell is equal to that of the accumulator multiplied by AC/AB. For most potentiometric work, only changes of potential are required, so that variations of the length AC are all that are required during a titration.

In general, however, the e.m.f. of the accumulator is not quite
Potentiometric Titration Methods

A standard cell is employed. This is usually a Weston cell which has an e.m.f. of 1.0183 volts at 20° C, or

\[ 1.0183 - 0.0000406 (t - 20°) \]

at any other temperature \( t \)° C. If the standard cell is placed in circuit by means of the switch \( S_1 \) and the point of balance \( C' \) on the bridge is determined, then the unknown e.m.f. may be calculated from the expression:

\[
\frac{AC}{AC'} = \text{e.m.f. of unknown cell} \quad \text{e.m.f. of standard cell}
\]

For approximate work, the slide wire \( AB \) may consist of a simple meter bridge, and the indicating instrument may be a milliammeter. It is preferable, however, to employ a commercial type of potentiometer which utilizes the more compact spiral type of bridge wire. The author has found the potentiometers manufactured by H. Tinsley and Co., of Werndee Hall, South Norwood, London, S.E.25, by the Cambridge Instrument Co., of Grosvenor Place, London, S.W.1, and by the Leeds and Northrup Co., of Philadelphia, U.S.A., very satisfactory. The most convenient type of indicating instrument is the direct-vision type of mirror galvanometer; the galvanometer, lamp, and scale are incorporated in a blackened wooden (or plastic) box or compartment, and the "spot" is clearly visible in daylight. Such galvanometers are manufactured by the firms referred to above; those supplied by the Cambridge Instrument Co. are preferred by the writer. The rheostat in the commercial potentiometer provides for the requisite drop of potential along the slide wire. If the bridge is divided into, say, 2000 equal parts, then the rheostat may be adjusted with the standard cell in circuit and with the sliding contact \( C \) at a position corresponding to 1018.3 divisions so that no current flows through the galvanometer. The position of the sliding contact will then give the e.m.f. of any unknown cell directly in milli-volts. It is usual for the rheostat to contain both coarse and fine adjustments: the fine adjustment may be used to compensate for the slight variations of the accumulator during the measurements.

The Tinsley general-utility potentiometer (type 3387B) is shown in Fig. VI, 2, 5, and a schematic diagram of the circuit in Fig. VI, 2, 6. The writer has found this to be an excellent commercial potentiometer. Balancing is effected upon a main dial having eighteen steps of 0.1 volt and a calibrated circular slide wire 6 in. in diameter, range 0.005 to +0.105 volt, which can be read to 0.0001 volt by estimation, the smallest division being 0.0005 volt. The instrument has three range multipliers of \( \times 1, \times 0.1, \) and \( \times 0.01 \), giving the following ranges of direct calibration for the respective multipliers: 1.9 volts to 1 millivolt, 0.19 volt to 100 microvolts, and 0.019 volt to 10 microvolts respectively. There is an independent standardizing circuit, adjusted to 20° C, so that standardisation may be effected with a Weston cell independently of the dial setting. The selector switch has three positions, one for the standardizing circuit, and two for external test circuits.

The measurement of potential may be simplified by the use of a thermionic valve voltmeter (see below, under pH meters); the great advantage of these instruments is that so little current is drawn from
Quantitative Inorganic Analysis

Fig. VI, 2, 5.
the cell under measurement that it may be connected directly to the
two electrodes.

The hydrogen electrode cannot be used in solutions containing oxidizing agents, e.g., permanganate, nitrate, ceric and ferric ions, or of other substances capable of reduction, such as unsaturated organic compounds, or in the presence of sulphides, compounds of arsenic, etc. (catalytic poisons) which destroy the catalytic property of platinum black. It is also unsatisfactory in the presence of salts of the noble metals, e.g., copper, silver, and gold, and also in solutions containing lead, cadmium, and thallous salts. There are many other electrodes which are more convenient to use in the range in which they are applicable. Some of these will be described below.

Mention must, however, be made of the advantages of the hydrogen electrode: (1) it is a fundamental electrode to which all measurements of pH are ultimately referred; (2) it can be applied over the entire pH range; and (3) it exhibits no salt error.

B. The quinhydrone electrode. The preparation of reproducible hydrogen electrodes is a comparatively tedious process and, moreover, the electrode has certain limitations (see previous paragraph). E. Bilmann (1921) has introduced the quinhydrone electrode: this renders the determination of pH a rapid and simple process, and does not require the use of hydrogen gas. Quinhydrone is a compound of quinone and hydroquinone, and in solution is decomposed into equimolecular quantities of these substances:

\[ \text{C}_6\text{H}_4\text{O}_2\cdot\text{C}_6\text{H}_4(\text{OH})_2 \Rightarrow \text{C}_6\text{H}_4\text{O}_2 + \text{C}_6\text{H}_4(\text{OH})_2 \]

Quinone and hydroquinone form a reversible oxidation-reduction system which may be represented as:

\[ \text{C}_6\text{H}_4\text{O}_2 + 2\text{H}^+ + 2e \Rightarrow \text{C}_6\text{H}_4(\text{OH})_2 \]

If an inert electrode, such as platinum, is immersed in the system, the potential is given by (Section I, 47):

\[
E = E^0 + \frac{RT}{2F} \log a_{Q^+} + a_{Q^-} a_{H^+} + a_{H_2Q} a_{\text{H}^+}
\]

where \(a_Q\), \(a_{Q^+}\), and \(a_{H_2Q}\) are the activities of the quinone, hydrogen ions, and hydroquinone respectively, and \(E^0\) is the standard potential referred to the molar hydrogen electrode. Now under those conditions, in which quinhydrone dissociates to give equimolecular quantities of quinone and hydroquinone, the ratio of the activities may be regarded as constant, hence:

\[
E = E^0 + \frac{RT}{F} \log a_{\text{H}^+} \quad \quad \quad (1)
\]

\(E^0\) has been determined in the usual manner by direct reference to the molar hydrogen electrode, and has a value of 0·7044 volt at 18° C. and 0·6991 volt at 25° C. By making the usual substitution for the values of the constants in equation (1), we have, at 25° C.:

\[
E = 0·6991 + 0·0591 \log a_{\text{H}^+} \quad \quad \quad (1')
\]
Thus the potential of the quinhydrone electrode changes with the hydrogen-ion activity in a manner which is exactly similar to that of the hydrogen electrode.

For convenience, a calomel electrode often replaces the molar hydrogen electrode as the other half-cell. The complete cell is then:

\[ \text{Hg} | \text{Hg}_2\text{Cl}_2, \text{KCl} \text{ (satd.)} \ | \text{Solution, quinhydrone} | \text{Pt} \]

The potential of the saturated calomel electrode, \( E_{\text{cal. sat.}} \), against the molar hydrogen electrode, is 0.2458 volt at 25°C.

Hence \( E_{\text{obs.}} = E_{\text{quinhydrone}} - E_{\text{cal. sat.}} \)

\[ = 0.6991 + 0.0591 \log [H^+] + 0.2458 \]

\[ = 0.9483 + 0.0591 \log [H^+] \]

\[ pH = - \log [H^+] = \frac{0.4533 - E_{\text{obs.}}}{0.0591} \quad \ldots \quad (2) \]

To carry out a determination of the hydrogen-ion concentration of a solution, about 0.15 g. of quinhydrone * per 100 ml. of solution is added, and the solution stirred. A bright platinum electrode is immersed in the solution and the quinhydrone electrode combined in a cell with a saturated calomel electrode; a saturated solution of potassium chloride or, less accurately but perhaps more conveniently, a jelly of 3 per cent agar in saturated potassium chloride solution may be used as the salt bridge. The \( pH \) is then calculated by equation (2). It may be mentioned that the platinum electrode should be highly polished and clean; it is best cleaned by treatment with hot chromic acid mixture, then thoroughly washed with distilled water, and ignited in an alcohol flame.

An alternative method is to use a solution of known \( pH \) as standard and to combine the two quinhydrone electrodes into a concentration cell:

\[ \text{Pt} | \text{Solution of unknown} \quad | \text{Solution of known} \quad | \text{Pt} \]

\[ pH, \text{ quinhydrone} \quad | \quad pH, \text{ quinhydrone} \]

Then \( E_{\text{obs.}} = \frac{0.0591}{1} \log c_2 \text{ at } 25^\circ \text{C.} \)

where \( c_2 \) and \( c_1 \) are the respective hydrogen-ion concentrations:

\[ pH_2 = \frac{pH_1 - E_{\text{obs.}}}{0.0591} \]

where \( pH_2 \) refers to \( c_2 \) and \( pH_1 \) to \( c_1 \). If \( pH_2 \) is known, \( pH_1 \) can be readily calculated.

The advantages of the quinhydrone electrode are: (i) it attains equilibrium rapidly; (ii) it may be used in many solutions in which the hydrogen electrode is inapplicable, e.g., in solutions of zinc, cadmium, tin, lead, copper, and nickel salts, dilute nitric acid, and in solutions of unsaturated organic acids, of amino acids and of alkaloids; (iii) it is not so readily incapacitated as the hydrogen electrode. Its disadvantages are: (i) it cannot be used in solutions of \( pH \) greater

* Pure quinhydrone (analytical reagent quality) is available commercially. It can also be readily prepared by oxidation of hydroquinone with ferric ammonium sulphate at 65°C.
than about $\text{pH} \ 8$ (this is because hydroquinone behaves as a weak dibasic acid and then begins to have an effect on the $\text{pH}$ of the solution; moreover, this will also effect the molecular ratio of quinone to hydroquinone, since the concentration of the undissociated hydroquinone becomes reduced); (ii) the potential may be slightly affected by large concentrations of neutral salts—the "salt error"; this error, however, is negligible under the conditions that the electrode is normally used.

C. The antimony electrode. An electrode consisting of a metal and its oxide, or of an inert metal (e.g., platinum) in contact with a higher and lower oxide, may be regarded as an oxygen electrode with the gas at a pressure equal to the dissociation pressure of the oxide. It can be shown* that the potential of any oxygen (or oxide) electrode is given by the equation:

$$E = \text{Constant} + \frac{RT}{F} \ln a_{\text{H}^+}$$

which reduces to the form, at $25^\circ$ C., of:

$$E = E^0 + 0.0591 \ \text{pH}$$

Such electrodes may theoretically be used for the measurement of $\text{pH}$; the value of the constant $E^0$ for the particular electrode may be determined by measurement in solutions of known $\text{pH}$. The oxide electrode can be used for $\text{pH}$ measurements only if the oxide is sparingly soluble in solutions of all hydrogen-ion concentrations and the metal does not displace hydrogen from solution. The most satisfactory electrode of this type is one consisting of antimony and antimony trioxide, the antimony-antimonious oxide electrode. There is generally sufficient oxide on the surface of cast antimony for its addition not to be necessary. The antimony electrode may be used over the $\text{pH}$ range 3–8; if the electrode is soaked in a buffer solution for several hours prior to use, or if the solution is saturated with oxide (in order to ensure the presence of antimony ions at the electrode interface—$\text{Sb}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{SbO}^+ + 2\text{OH}^-$), the effective range may be extended on the alkaline side to a $\text{pH}$ of 12.

The electrode reaction has been stated to be:

$$\text{Sb} + \text{H}_2\text{O} \rightleftharpoons \text{SbO}^+ + 2\text{H}^+ + 3\text{e}$$

In practice it is found that the potential does not change in an exactly linear manner with the $\text{pH}$ of the solution and also that different samples of antimony may give different potentials. Hence the electrode should be calibrated with several standard buffer solutions before use and also under the same experimental conditions to which it will be subjected in use, for example, in the presence or absence of oxygen, etc.

The antimony electrode cannot be applied: (a) in the presence of strong oxidising agents or of complexing reagents (such as tartrates and organic hydroxy acids); (b) in solutions with a $\text{pH}$ lower than 3, since the oxide then becomes appreciably soluble; and (c) in the presence of metals more noble than antimony. The electrode is not readily poisoned, is simple to use (no reagents are usually required), and is rugged; it has therefore found application for the continuous recording or control of $\text{pH}$ in conditions where it is applicable.

D. The glass electrode. F. Haber and Z. Klemensiewicz (1909) found that the potential difference between a thin glass surface and the solution in which it was immersed varied in a regular manner with the pH of the solution. This remarkable fact has been utilised in recent years as the basis of a valuable method for measuring the pH of solutions. Ordinary soft glass has too great a resistance to be of any great value. A suitable glass has the composition 6 per cent CaO, 22 per cent Na₂O, and 72 per cent SiO₂; this is the lowest-melting-point glass which can be prepared using these three ingredients. The glass made by the Corning Company of America, known as Corning No. 015 glass, is also suitable. Two types of electrode are employed. In the first type (a in Fig. VI, 2, 7), a tube A of the special glass is blown out at the lower end into an extremely thin bulb B. In the second type (b in Fig. VI, 2, 7), due to McInnes and Dole, a very thin membrane of the special glass is sealed on to the end of a glass tube, which is smooth and square. This is accomplished by first blowing a large, thin bubble on the end of the special glass tubing; the end of A is heated to redness and then pressed against the thin bulb. The heat in the tube A is sufficient to fuse the thin membrane into place. Considerable experience is required to prepare satisfactory electrodes of type (b); in general, particularly for routine work, the bulb type is to be preferred. Both types are available commercially. Considerable progress has been made in recent years by commercial firms (e.g., by National Technical Laboratories, South Pasadena, California, the manufacturers of the Beckman instruments) in producing more robust glass electrodes. The following description of a typical commercial glass electrode may be given. A small bulb of special low-resistance glass, about 0.05 mm. in thickness, is sealed to a stem made from glass exhibiting a much greater resistance to ion transfer, thus eliminating errors due to variable depth of immersion. The stem incorporates an auxiliary bulb (Fig. VI, 2, 8A), just above the membrane proper and of larger diameter, in order to afford protection against mechanical damage. Electrical contact with the membrane is established by means of a chloride or buffer solution sealed within the bulb, an internal electrode of the silver-silver chloride type immersed in this solution providing connexion with the external screened lead, which emerges through a moulded cap at the top of the stem. It may be mentioned that some other types of glass electrode employ a platinum wire dipping into dilute hydrochloric acid saturated with quinhydrone for electrical contact with the membrane.

The Muirhead "JipHy"* glass electrode cell is an improved version

* Supplied by Muirhead and Co., Ltd., Elmers End, Beckenham, Kent, England, for use with their pH meters.
of the Morton cell, and is illustrated in Fig. VI, 2, 8B. It may be used with 2.5 ml. of solution. The assembly includes a glass electrode incorporating a silver-silver chloride half-cell supported in a reservoir of saturated potassium chloride solution. The reservoir is connected to the solution under test through a tube of plastic material containing a partial obstruction (thus rendering the renewal of the junction a facile process) and a glass tube terminating in a capillary which is held close to the electrode.

To carry out a determination the glass electrode is immersed in the solution of which the pH is to be determined; a calomel (or other convenient) electrode completes the cell. Owing to the high resistance of the glass electrode (5–50 megohms), special methods must be adopted for measuring the e.m.f. of the cell. The development of thermionic valve circuits has rendered the measurement of the e.m.f. of high-resistance cells a comparatively easy determination, and a typical circuit is given in the description of the Cambridge pH meter below.

The potential of the glass electrode at 25°C can be shown to be given by the equation:

$$E = K + 0.0591 \cdot \text{pH}$$

where $K$ is a constant. This expression holds over the range of pH of 1–10. The value of $K$ is most simply evaluated by immersing the glass electrode in buffer solutions, coupling with a reference (e.g., a calomel) electrode, and measuring the e.m.f. This standardisation must be carried out at least once a day, since $K$ varies slightly. The variation of $K$ has its origin in the following properties of the electrode. All glass electrodes are known to have a small residual e.m.f. across the glass membrane when identical solutions are brought in contact with the inside and outside surfaces. The exact cause of this asymmetry potential is not known, but is usually less with thin than with thick electrodes. This potential may change slightly from day to day, and may also be influenced temporarily by exposure of the electrode to very strong alkali or acid. These facts emphasise the importance of calibrating the electrode frequently against standard buffer solutions.

For solutions of pH greater than 10 the usual glass electrode gives low values, owing to the fact that the membrane transfer may include other (particularly sodium) ions in addition to hydrogen ions. The use of special lithium-glass electrodes in the strongly alkaline range will decrease the errors appreciably and extend the useful range of the glass electrode to a pH approaching 14. The Cambridge “Alki” and the Beckman Type E glass electrodes are examples of electrodes which may be employed in the alkaline range above pH 9–10. In solutions of high acid concentration, below pH 1, the electrode exhibits a slight error; corrections must therefore be applied, or special electrodes
Quantitative Inorganic Analysis

used. A robust glass electrode (Beckman), which is claimed to cover the entire pH scale (0–14) and to possess only 0.2 pH deviation in sodium hydroxide solution, is also marketed.

Numerous pH meters are marketed;* three typical instruments will be described. The Cambridge pH meter is shown in Fig. VI, 2, 9,

the electrical circuit in Fig. VI, 2, 10, and the dip-type of calomel electrode in Fig. VI, 2, 11; the glass electrode calls for no further comment. This instrument is designed mainly for use with the glass electrode, and is calibrated directly for the pH range 0–14 in 0.02 units.

* For example by:
- Muirhead and Co., Ltd., Elmers End, Beckenham, Kent.
- Electronic Instruments, Ltd., Richmond, Surrey.
- Pye and Co. Ltd., Newmarket Road, Cambridge.
- National Technical Laboratories, 820 Mission Street, South Pasadena, California, U.S.A. (manufacturers of Beckman pH meters).
The galvanometer acts as a null-point detector; compensation is provided \textit{inter alia} for the temperature of the test solution. In some forms of the instrument a standard cell is incorporated, and can be brought into circuit for standardising purposes at any time. The instrument may be used, by throwing a switch, also as a millivolt potentiometer; each division represents 2 millivolts, and the total range is 0–1400 millivolts.

The Cambridge direct-reading pH indicator (Fig. \textit{VI, 2, 12}) is a robust instrument, also designed for use with the glass electrode, covering the range 0–14 pH, and directly readable to 0·1 and by estimation to 0·05 pH. Standardisation against a standard buffer solution is carried out daily; temperature compensation for the solution in the electrode system is provided for by a dial in the front of the apparatus.

The Beckman pH meter (model G) is presented in Fig. \textit{VI, 2, 13}. The dial covers the pH range 0–13, and is graduated in 0·1 pH units; readings may be made by estimation to 0·02 pH unit. A temperature-compensation device is incorporated. A switch enables the instrument to be used for millivolt readings on the meter scale, the scale then becomes 0–1300 millivolts instead of
0–13 pH; the switch also permits the polarity to be reversed, thus giving a total range of −1300 to +1300 millivolts.

The pH meters may be standardised with any suitable buffer solutions; 0·05 M-potassium hydrogen phthalate (pH 4·00 at 20°) or 0·05 M-sodium borate (pH 9·18 at 20°) are frequently used (see Section VI, 1). The standard acetate buffer, i.e., an aqueous solution which is 0·1 M with respect to acetic acid and also sodium acetate, has a pH of 4·64 at 20° and is an excellent standard; it is prepared by mixing 200 ml. of M-acetic acid with 100 ml. of M-sodium hydroxide and diluting to 1 litre with distilled water.

VI, 3. Potentiometric titrations.—Classical method. In the previous section the determination of the hydrogen-ion concentration of a solution was described; this involved the measurement of the e.m.f. between two electrodes, one an indicator electrode, the potential of which was a function of the pH of the solution, and the other a reference electrode of constant potential. In potentiometric titrations absolute potentials or potentials with respect to a standard half-cell are not usually required, and measurements are made whilst the titration is in progress. The equivalence point of the reaction will be revealed by a sudden change in potential in the plot of e.m.f. readings against the volume of the titrating solution; any method which will detect this abrupt change of potential may be used. One electrode must maintain a constant, but not necessarily known, potential; the other electrode must serve as an indicator of the changes in ion concentration, and
must respond rapidly. The solution must, of course, be stirred during the titration. A simple arrangement for potentiometric titration is given in Fig. VI, 3, 1. A is a reference electrode (e.g., a calomel half-cell), B is the indicator electrode, and C is a mechanical stirrer; the
solution to be titrated is contained in the beaker. The e.m.f. of the cell incorporating the initial solution is determined, and the measurement is repeated at intervals of 1 ml. addition from the burette. When the e.m.f. changes somewhat more rapidly as the end point is approached, the e.m.f. readings are taken at more frequent intervals, and eventually after each drop. After the first rough titration, the exact procedure will be apparent. Draw a curve with the e.m.f. readings as ordinates and the burette readings as abscissae; the point of inflexion (or the middle of the steepest portion of the curve) is regarded as the end point of the titration. A more satisfactory determination of the end point is obtained by the differential method, in which the change of e.m.f. per unit volume of titrant is the ordinate. If we plot the change of potential in millivolts caused by 0·1-ml. increments of the reagent \(\frac{\Delta E}{\Delta V}\) against the middle of the titration interval, a curve of the type shown in Fig. VI, 3, 2 is obtained. The abscissa corresponding to the maximum gives the end point of the reaction with sufficient accuracy for all ordinary purposes.

A commercial form of the simple potentiometric-titration apparatus is available from the Cambridge Instrument Company, and is illustrated in Fig. VI, 3, 3. The apparatus comprises an electrode system (platinum; calomel electrode; antimony electrode, etc.) with a stirring motor, a potentiometer, and a robust, sensitive “spot” galvanometer of high resistance. A coarse and a fine adjustment and also a sensitivity control are provided on the high-resistance galvanometer. In use the electrodes are connected to two terminals at the rear of the galvanometer. The approach of the end point of the titration is indicated by temporary deflections of the galvanometer “spot” of increasing magnitude, and the end point is shown by a sudden large and permanent deflection; the sensitivity control renders it easy to avoid over-running the end point.

It is possible by means of the differential method of potentiometric titration to obtain values of \(\frac{\Delta E}{\Delta V}\) directly, and thus to increase considerably the accuracy of the determination of the end point. The procedure depends upon the concentration polarisation of one of two similar electrodes by some mechanical device which prevents mixing of a small portion of liquid surrounding one electrode with the remainder of the solution being titrated. A simple device for this purpose is depicted in Fig. VI, 3, 4. A small portion of the solution is withdrawn into a medicine dropper provided with platinum-wire electrodes as shown in the figure. The potential difference between the two electrodes is determined before and after the addition of each increment of reagent. After each reading near the end point the sheltered solution is forced into the main volume of solution and the e.m.f. measured. The graph of e.m.f. readings against volume resembles Fig. VI, 3, 2.

A. Neutralisation reactions.—The indicator electrode may be a hydrogen, glass, antimony, or quinhydrone electrode (in the last case the acid is placed in the beaker and the base in the burette); a calomel electrode is generally employed as the reference electrode.

The accuracy with which the end point can be found potentiometrically depends upon the magnitude of the change in e.m.f. in the neighbourhood of the equivalence point, and this depends upon the
Potentiometric Titration Methods

concentration and the strength of the acid and alkali (compare Sections I, 33-36). Satisfactory results are obtained in all cases except: (a) those in which either the acid or the base is very weak \((K < 10^{-8})\) and the solutions are dilute, and (b) those in which both the acid and the base are weak. In the latter case an accuracy of about 1 per cent may be obtained in 0.1N solution.

The method may be used to titrate a mixture of acids which differ greatly in their strengths, e.g., acetic and hydrochloric acids; the first break in the titration curve occurs when the stronger of the two acids is neutralised, and the second when neutralisation is complete. For this method to be successful, the two acids or bases should differ in strength by at least \(10^5\) to 1.

B. Oxidation-reduction reactions.—The theory of oxidation-reduction reactions is given in Sections I, 48-49. The determining factor is the ratio of the concentrations of the oxidised and reduced forms of certain ion species. For the reaction:

\[
\text{Oxidised form} + n \text{ electrons} \Rightarrow \text{Reduced form}
\]

the potential \(E\) acquired by the indicator electrode at 25° C. is given by:

\[
E = E^* + \frac{0.0591}{n} \log \frac{[\text{Ox}]}{[\text{Red}]}
\]

where \(E^*\) is the standard oxidation potential of the system. The potential of the immersed electrode is thus controlled by the ratio of these concentrations. During the oxidation of a reducing agent or the reduction of an oxidising agent the ratio, and therefore the potential, changes more rapidly in the vicinity of the end point of the reaction. Thus titrations involving such reactions (e.g., ferrous iron with potassium permanganate or potassium dichromate or ceric sulphate) may be followed potentiometrically and afford titration curves characterised by a sudden change of potential at the equivalence point. The indicator electrode is usually a bright platinum wire or foil, and the oxidising agent is generally placed in the burette.

C. Precipitation reactions.—The theory of precipitation reactions is given in Sections I, 39-41. The ion concentration at the equivalence point is determined by the solubility product of the sparingly soluble material formed during the titration. In the precipitation of an ion \(I\) from solution by the addition of a suitable reagent, the concentration of \(I\) in the solution will clearly change most rapidly in the region of the end point. The potential of an indicator electrode responsive to the concentration of \(I\) will undergo a like change, and hence the change can be followed potentiometrically. Here one electrode may be a saturated calomel or, less conveniently, a hydrogen electrode, and the other must consist of one which will readily come into equilibrium with one of the ions of the precipitate. For example, in the titration of silver ions with a halogen (chloride, bromide, or iodide) this must be a silver electrode. It may consist of a silver wire, or of a platinum wire or gauze plated with silver and sealed into a glass tube. Since a halide is to be determined, the salt bridge must be a saturated solution of potassium nitrate. Excellent results are obtained by titrating silver nitrate solution with thiocyanate ions.
VI. 4. Potentiometric titrations.—Simplified electrode systems and methods. The elimination of the troublesome standard reference electrode of the calomel or metal-salt type and the provision of a continuous-reading instrument to replace the slide-wire potentiometer would clearly render the determination of end points (the main purpose of potentiometric titrations) a more facile procedure than with the classical set-up. The polarised mono-metallic system and the bi-metallic self-polarising system have been developed, particularly for oxidation-reduction work. The former consists of two identical pure platinum wires, one polarised anodically and the other cathodically with a polarising current of the order of microamperes; these appear to behave as two dissimilar metals, and their single electrode potentials respond in a different manner. At all events a sharp polarisation phenomenon is apparent at the equivalence point, and if the potential difference between the electrodes is plotted against the volume of reagent added, the usual differential type of curve is obtained. The potential difference developed at the end point may be of the order of 100-200 millivolts.

Foulk and Bowden (1926) introduced the dead-stop technique with polarised metallic electrodes, and thus rendered the system continuous reading. The following discussion should assist the reader in appreciating the underlying principles. When a small e.m.f. is applied to a pair of identical platinum electrodes dipping into a solution containing no depolarising substances, little or no current flows. This may be due to the formation of adsorbed layers of hydrogen and oxygen upon the cathode and anode respectively. The electrodes are thus polarised, and current cannot flow unless the depolarisation of both is effected.

The fundamental requirement of the dead-stop technique (as opposed to other methods employing bimetallic systems) is the small potential difference between the electrodes. This low potential is balanced by the back e.m.f. of polarisation, hence no current flows, and a galvanometer in the circuit remains undeflected. Under these conditions the dead-stop end-point method of titration is applicable to all systems in which a sharp transition from the polarisation (or depolarisation) of at least one electrode to the complete depolarisation (or polarisation) of both coincides with the end point of the reaction. Thus in the determination of sodium thiosulphate by titration with iodine solution, the thiosulphate acts as an anode depolariser:

\[ 2\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} + \text{O} = \text{S}_4\text{O}_6^{2-} + 2\text{OH}^- \]

Upon the addition of iodine solution, iodide is formed which can also act as an anode depolariser. Immediately the equivalence point is reached, the free iodine will act as a cathode depolariser:

\[ \text{I}_2 + 2\text{H} = 2\text{I}^- + 2\text{H}^+ \]

current will now commence to flow, and the end point is thus indicated by the sudden commencement of flow of current (and therefore galvanometer deflection) through the solution. Thus no current flows through the galvanometer until the end point is reached, which is indicated by a permanent deflection of the galvanometer index. Owing to the momentary production of high local concentrations, each addition of the reagent near the end point may cause the galvanometer index to move temporarily from its zero position. This effect, which depends
upon the rate of titration and the efficiency of stirring, is due to partial depolarisation of the cathode, and its magnitude often provides a useful warning of the approach of the end point. In the reverse titration, i.e., when a solution of iodine (which contains iodide) is titrated with a solution of thiosulphate or arsenite, the character of the end point is reversed. Both electrodes are depolarised, and consequently until almost to the end point, the galvanometer index will be deflected off the scale. When the equivalence point is reached, all the iodine will have been removed and the cathode becomes polarised; the galvanometer index returns to zero, and remains so even after an excess of titrant has been added. The dead-stop technique may be carried out with the simple apparatus shown in Fig. VI, 4, 1. G is a galvanometer of sensitivity of 50–200 mm. per microampere, B is a 2-volt accumulator or a single dry cell, $R_1$ is a high resistance, usually 100,000 ohms, and $R_2$ is a resistance or potentiometer of value between 1 and 2 per cent of $R_1$. The latter should preferably be a radio potentiometer, which can be adjusted so that the galvanometer is brought to zero when at least one electrode is polarised, e.g., by dipping it into a solution of sodium thiosulphate.* The mechanical stirrer, which is essential, is not shown in the figure.

The essential feature is the adjustment of the two resistances so that the potential difference between the two electrodes is 10–15 millivolts, just sufficient to balance the back e.m.f. It is advisable to provide the galvanometer with an adjustable shunt, thus enabling the sensitivity to be reduced when conditions likely to cause a large flow of current are encountered. The Cambridge titration apparatus (potentiometric pattern), Fig. VI, 3, 3, includes a pair of platinum electrodes, and is particularly suitable for determinations depending upon the dead-stop end point. The galvanometer may be replaced by a valve system (compare Mullard-B.T.L. apparatus, Fig. VI, 4, 2) which supplies the polarising e.m.f. and serves to detect the end point.

The mode of action of the bimetallic system will be apparent from the following considerations. Noble metals, like platinum or gold, behave as indicator electrodes in oxidation-reduction reactions in solution. If an electrode material could be found (e.g., tungsten) which would not respond to a change of electron activity in solution, it could be employed as a reference electrode in potentiometric titrations. If the indicator electrode and the “inert” electrode are placed in the same

* The following were used by the author and gave satisfactory results: $G$ a Tinsley galvanometer, type SS1, of 49 ohms resistance and a sensitivity of 52 mm./microampere; $R_1$ a 100,000 ohms carbon resistance (Erie Resister, Ltd., Carlyle Road, The Hyde, London, N.W.3); and $R_2$ a 2500 ohms wire-wound variable resistance (Colvern, Ltd., Mawneys Road, Romford, Essex) or a 2200 ohms carbon variable resistance (Centralab). A 20 ohms variable resistance $R_3$ (A. F. Bulgin and Co., Ltd., Bury Park Road, Barking, Essex) should be placed in parallel with the galvanometer to act as a sensitivity control during the initial stages of the titration.

The components (excluding the galvanometer) are conveniently mounted in a small box; the latter is provided with a panel to house the controls for $R_2$ and $R_3$, and terminals for the electrolytic cell, 2-volt accumulator, and galvanometer.
solution, then the change of the e.m.f. of such a cell would be the same as the variation in potential of the indicator electrode during the titration. Such a system is termed a bimetallic electrode system. With these systems the e.m.f. is quite small initially, and does not increase considerably until the titration is within 0–2–0–3 ml. of the equivalence point. A slight rise in e.m.f. gives warning of the approaching end point, and at the equivalence point there is a very sharp change of e.m.f. which may be of the order of 0–1–0–2 volt. The most satisfactory combination for oxidation–reduction titrations is platinum–tungsten. For a number of acid–base titrations the combination of tungsten with natural graphite, copper, nickel, cobalt, silicon, or silver are frequently applicable; it is necessary, however, to test the bimetallic pair with each type of acid and base used, and consequently, the procedure has not become popular for neutralisation reactions.

It may be mentioned that the glass electrode is employed as a reference electrode either in conjunction with a platinum indicator electrode for oxidation–reduction reactions or with a suitable indicator electrode, such as silver for argentometric titrations, for precipitation reactions. Apart from the condition that the $pH$ of the solution must remain practically constant throughout the titration, it may be employed in solutions containing excess of acid or base, or sufficient amount of an effective buffer. The advantages of the use of a glass electrode as a reference electrode in potentiometric titrations are: (i) it is chemically inert, and will therefore not contaminate the solution; (ii) it is readily available for use, and requires little preparation; and (iii) it rapidly establishes a reproducible potential. The only apparent disadvantage of the glass–metal system is that a special instrument, which functions accurately with high resistances, is required to measure the potential of the electrode system. This is readily overcome by the use of $pH$ meters (see Section VI, 2) or suitable electronic voltmeters (see below).

The slide-wire potentiometer may be replaced by circuits incorporating an electronic voltmeter, thereby providing a more or less continuous-reading instrument. A number of inexpensive commercial instruments are available. The Mullard–B.T.L. titration apparatus * is shown in

* Supplied by Baird and Tatlock (London), Ltd., Freshwater Road, Chadwell Heath, Essex, England.
Potentiometric Titration Methods

Fig. VI, 4, 2, and the essential features of the circuit are presented in Fig. VI, 4, 3. An electron-beam tuning indicator (magic eye) replaces the usual galvanometer. The apparatus, which is operated from the 50-cycle supply mains, consists of a titration unit and a potentiometer unit. In the latter the potential difference between the two electrodes in the solution is compared with a standard e.m.f. derived from the power pack built in the unit, equality being indicated by the closing of the magic eye. The large calibration dial is continuously variable from 0 to 400 millivolts, whilst a switch below extends the range to 2000 millivolts in steps of 400 millivolts. During the course of a titration the rate of change of potential between the electrodes per unit volume of titrant is very small until the end point is reached, and then the rate of change is rapid. Thus the equivalence point of a titration may be detected either by measurement of the actual potential or by reducing the sensitivity of the apparatus (by means of the sensitivity control provided) so that only large changes of potential are detected. At maximum sensitivity a potential difference of 1–2 millivolts can be detected. The titration unit is provided with two burette holders, electrode holders, an enclosed motor-driven stirrer, a hot plate, and magic eye located at a convenient angle and provided with a tubular light shield for facile observation. Five electrodes are normally supplied: a calomel electrode, a hydrogen electrode with sealed-in platinum spiral, a tungsten electrode with sealed-in tungsten spiral, and two platinum electrodes of similar construction to the tungsten...
electrode. The calomel electrode is depicted in Fig. VI, 4, 4. Particular attention is directed to the brass holder or sleeve, which engages in a spring clip in the titration stand and provides both mechanical location and electrical connexion to the potentiometer circuit; a similar brass sleeve is fitted on all the electrodes. For neutralisation reactions the calomel and hydrogen electrodes or the calomel and bright platinum electrodes (solution saturated with quinhydrone) are used; quinhydrone cannot, of course, be employed if the pH of the solution rises above pH 8–9. For oxidation–reduction titrations any of the following three pairs of electrodes may be used, viz., calomel–platinum, tungsten–platinum or platinum–platinum (the last-named with polarising current). A special switch is provided for applying polarising current to the platinum electrodes; this current may be left on during the titration, but must be switched off at all other times. Throughout the course of an oxidation–reduction titration with calomel–platinum electrodes, there is a gradual change of potential per unit volume of reagent added, and this value rises to a maximum at the end point. With tungsten–platinum and with polarised platinum electrodes, the potential does not change appreciably until the end point is approached; a slight rise occurs with the former pair just before the end point, so that some warning of the equivalence point is given; no such warning of the approach of the approaching end point is usually given with polarised platinum electrodes, and care must be taken that the sharply defined end point is not overstepped. The tungsten electrode tends to become dull, due to oxide formation, and this may result in loss of sensitivity. The oxide film may be removed by immersion of the tungsten in just-molten sodium nitrite for 5 seconds or by immersion in a 1:1 mixture of 10-volume hydrogen peroxide and 5 per cent ammonium hydroxide solution; the electrode is then thoroughly washed with distilled water.

The Fisher electrometric titrimer * is similar in purpose to the B.T.L.–Müllard apparatus, and is supplied for operation on 110-volt, 60-cycle mains. It is depicted in Fig. VI, 4, 5; a schematic circuit diagram is given in Fig. VI, 4, 6. The apparatus consists of a titration stand (upon which the magic eye is located centrally) and a control unit. The response of the instrument is such that a potential difference of only 20 millivolts at the electrodes completely opens or closes the magic eye. The following electrodes are available: glass electrodes (several types), platinum, tungsten, antimony, silver, calomel, and silver–

Potentiometric Titration Methods

silver chloride. These are employed in conjunction with a special motor-driven glass stirrer. In addition, a platinum–tungsten electrode stirrer is employed with the electrode wires emerging from the blades of the stirrer. The apparatus, when operated with a glass electrode calibrated with a standard buffer, may be employed for pH determinations with an accuracy of 0.1 pH unit. All the usual potentiometric determinations (neutralisation, oxidation-reduction, moisture, etc.)
may be conveniently and rapidly made. The manufacturers issue with each apparatus an instructional manual which contains valuable experimental details for numerous determinations.

VI. 5. Titrations with the Karl Fischer reagent.—Karl Fischer (1935) described a reagent containing iodine, sulphur dioxide, anhydrous methanol, and anhydrous pyridine; this was developed primarily for the determination of water in sulphur dioxide, and was subsequently found to be applicable to the determination of water in general. Fischer suggested that the reaction proceeded as follows:

$$I_2 + 2H_2O + (C_5H_5N)_2SO_2 + 2C_5H_5N \rightarrow (C_5H_5N)_2H_2SO_4 + 2C_5H_5N\cdot HI$$

A relatively sharp and reproducible end point was obtained by adding the reagent until the first appearance of unused iodine. The specific nature of the reagent and its simplicity of use were soon recognised by chemists; the reagent has been termed the Karl Fischer reagent, and the process of water measurement has been called aquametry. Smith, Bryant, and Mitchell (1939) showed that Fischer's conception of the reaction which requires the removal of two molecules of water by each molecule of iodine is incorrect; the reaction in methanol solution appears to take place in two stages:

$$I_2 + SO_2 + 3C_5H_5N + H_2O \rightarrow 2C_5H_5N\cdot HI + C_5H_5N\cdot SO_2$$

$$C_5H_5N\cdot SO_2 + CH_3OH \rightarrow C_5H_5N\cdot SO_2CH_3$$

The intermediate compound (A) (pyridine-sulphur trioxide, which is the "inner salt" of pyridinium hydroxide-N-sulphonic acid) can be readily isolated by omitting the methyl alcohol from the reagent.

Preparation of the Karl Fischer reagent. Method 1. It is usual to prepare 3 litres of the "stock" reagent and store it in a Pyrex glass-stoppered bottle of the same capacity. Place 254 g. of A.R. resublimed iodine in the bottle and add 800 ml. of pure dry pyridine. Shake the mixture until the iodine has dissolved (about 10 minutes) and add 2 litres of pure dry methyl alcohol. (This solution may be kept indefinitely, since little, if any, loss of strength occurs before the addition of sulphur dioxide). The homogeneous "stock" solution is stored until a few days before use, at which time a quantity, say 1 litre, is transferred to a, say, 2-litre, storage bottle for the Karl Fischer reagent. Cool the bottle in crushed ice; transfer 135 ml. (192 g.) of liquid sulphur dioxide to a narrow-mouthed, graduated vessel cooled in a bath of dry ice-methanol (the liquid may, if desired, be obtained by condensing the gas). Add the liquid sulphur dioxide rapidly, but cautiously, with shaking to the cold iodine solution. Stopper the storage vessel, and allow the contents to attain the laboratory temperature. Momentarily loosen the glass stopper (to release the pressure), and set the solution aside for a day or two before actual use.

Method 2. The above procedure takes advantage of the greater solubility of iodine in pyridine than in methyl alcohol. The order of
addition of the components has no effect upon the strength of the final reagent. It is convenient to have two "stock" solutions—a solution of sulphur dioxide in pyridine and a solution of iodine in methanol.\* The former may be prepared by dissolving 135 ml. (192 g.) of liquid sulphur dioxide in 800 ml. of pure dry pyridine (experimental details as in Method I), and the latter by dissolving 254 g. of pure dry iodine in 2 litres of pure dry methanol. For use the second solution is added to an equal volume of the first and the mixture is allowed to stand for about 24 hours.

For some purposes, e.g., when dealing with small water contents, the above reagent is too concentrated; it may be diluted with an equal volume of anhydrous methyl alcohol.

It is important that the various reagents are perfectly dry. Synthetic methanol containing less than 0.1 per cent of water can be purchased † and is satisfactory; it, and also specimens with a higher water content, may be rendered anhydrous by fractionation through an efficient column.‡ Pyridine may be dried by allowing it to stand over anhydrous barium oxide for at least a week, pouring off, and fractionating. Another method is to make use of the benzene–water azeotrope, which contains 8.9 per cent of water. If the approximate water content of the pyridine is known, a slight excess (say, 10 per cent) of benzene over that required to remove the water initially present is added and the mixture fractionated: the benzene–water azeotrope passes over at 69.3°C, followed successively by benzene at 80.1°C, the pyridine–water azeotrope (47 per cent of water) at 92.3°C, and anhydrous pyridine at 115–116°C.

**Standardisation of the Karl Fischer reagent.** Although side reactions slowly decrease the effective strength of the reagent, it is so easily standardised that the lack of stability is only a minor disadvantage in its application in analysis. A methanol solution of known water content is generally employed for standardisation: 10-ml. portions of a solution containing about 150 mg. of water usually give a titre of 40–80 ml. of the Fischer reagent.

Place about 900 ml. of dry methanol (<0.1 per cent water) in a dry 1-litre, glass-stoppered volumetric flask. Add about 15 g. of water, accurately weighed, to the contents of the flask, and then make up to the mark with dry methanol. It has been recommended that the volumetric flask and the small flask containing about 150 ml. of methyl alcohol be placed in a water-bath at 25°C. before making up to the mark.

For the standardisation, 10-ml. portions of the standard water-in-methanol solution are titrated with the Karl Fischer reagent until the colour of iodine just persists; an electrometric method for determining the end point may also be used, and possesses many advantages. Precautions must, of course, be taken to exclude atmospheric moisture. Full experimental details are given below.

\* These solutions may be purchased from suppliers of laboratory chemicals, for example, British Drug Houses, Ltd.

† For example, from James Burroughs, Ltd., Cale Distillery, Hutton Road, Lambeth, London, S.E.11 (a Customs and Excise licence is required for the duty-free product); or from Carbide and Carbon Chemicals Corporation, 30 East 42nd Street, New York 17, N.Y.

Note. Mitchell and Smith (1948) state that flasks which have been dried at 110-130° C. and then immediately stored in a desiccator contained a negligible quantity of water (<0·2 mg.); those which were allowed to cool in the laboratory contained 0·6 mg. (100 ml.), 1·2-1·8 mg. (250 ml.), 4·5 mg. (500 ml.), and 15·6 mg. (1000 ml.) respectively. A correction for the small amount of moisture within the flask in equilibrium with the atmosphere may be made by titrating in similar flasks 25 ml. of dry methanol and also 10 ml. of the reagent to which 25 ml. of the dry methanol had been added.

A more dilute standard water solution, containing 1-5 g. of water per litre of anhydrous methanol, is often used. A mixture of equal volumes of anhydrous methanol and anhydrous dioxan has been recommended (Bonner, 1946) as the solvent for the water. Anhydrous dioxan is less hygroscopic than methyl alcohol, and either alone or diluted with dry methyl alcohol is a better solvent for the extraction of water from many solids. Pure dioxan is non-conducting under the conditions required for the electrometric determination of the end point, but is rendered sufficiently conducting by the addition of about 25 per cent of its volume of dry methanol; the latter may be derived from the Karl Fischer reagent introduced during the titration. Anhydrous dioxan of adequate purity for this work may be prepared by allowing it to stand for 3-4 days over freshly ignited calcium oxide and filtering the supernatant diethylene dioxide through a sintered-glass funnel with atmospheric moisture excluded: distillation is usually unnecessary.

Standardisation of the "standard water" solution. The water content of the "standard water" solution can, of course, be calculated from the known weight of water added to the methanol or other solvent; the solvent is assumed to be anhydrous. A more trustworthy figure, particularly for more dilute solutions (1-5 g. of water per litre), may be obtained by the following procedure (Bonner, 1948; the titration apparatus is described below) which utilises a solution of water (about 1·5 g. per litre) in equal volumes of dry methanol and dry dioxan, but may, of course, be applied to solutions in methanol alone.

By means of a pipette attached to an air- or water-suction pump with a tower charged with calcium chloride or silica gel inserted between the pipette and the pump, transfer 50 ml. of "dry" dioxan into each of two glass-stoppered measuring-cylinders: stopper the vessels immediately. Introduce 0·1-0·2 g. of water, accurately weighed, by means of a weight pipette into one of the measuring-cylinders and mix well. Titrate each of the two solutions in turn by withdrawing a 5-ml. portion in a pipette, introduced into the titration vessel through the side arm (Fig. VI, 5, 1); add a measured excess (about 25 per cent) of the Karl Fischer reagent and titrate back the excess of Fischer reagent with the "standard water" solution. Repeat until two successive values do not differ by more than 0·01 ml. A further check may be obtained by preparing another solution of a weighed amount of water in 50 ml. of "dry" dioxan and titrating again. The results of a typical experiment by Bonner, using the Fischer reagent prepared as above but diluted with an equal volume of anhydrous methanol, will make the method of calculation clear.

(i) Titration of Fischer reagent (F.R.) against "standard water" solution (S.W.S.):

\[ 1·00 \text{ ml. of F.R.} = 1·33 \text{ ml. of S.W.S.} \quad \ldots \quad (a) \]
(ii) Titration of 5·00 ml. of "dry" dioxan:
F.R. added, 3·00 ml.; S.W.S. required for back titration, 2·90 ml.
From (a) 3·00 ml. of F.R. = 3·99 ml. of S.W.S.
Back titration = 2·90 ml. of S.W.S.
:. Water in 5·00 ml. of "dry" dioxan = 1·09 ml. of S.W.S. (b)

(iii) Titration of 5·00 ml. of dioxan containing 0·01396 g. of added water:
F.R. added, 8·50 ml.; S.W.S. required for back titration, 1·12 ml.
From (a) 8·50 ml. of F.R. = 11·30 ml. of S.W.S.
Back titration = 1·12 ml. of S.W.S.
:. Total water in dioxan solution = 10·18 ml. of S.W.S.
From (b), water in "dry" dioxan = 1·09 ml. of S.W.S.
:. The added water, 0·01396 g. = 9·09 ml. of S.W.S.
Hence 1 ml. of S.W.S. = 0·01396/9·09 = 0·00154 g. of water.
A similar titration to (iii) but with 0·0151 g. of added water, gave 1 ml. of S.W.S. = 0·00155 g. of water.

If at any stage during the standardisation it is found necessary to detach the Fischer titration vessel (e.g., through blockage of a burette), it is essential upon replacing the vessel to titrate again 4-5 ml. portions of the Fischer reagent with the "standard water" solution, and the standardisation is then resumed. The Fischer reagent gradually decreases in strength; it should be standardised against the "standard water" solution (which may be a standard water-in-methanol solution) daily; the latter should be standardised weekly by the procedure described above.

**Apparatus and experimental details for Karl Fischer titrations.** The Karl Fischer reagent is extremely sensitive to, and must therefore be protected from, atmospheric moisture. The burette and the reservoir containing the reagent must accordingly be provided with guard tubes containing such desiccants as anhydrous calcium chloride, anhydrous calcium sulphate, or silica gel. The "standard water" solution must be similarly protected.

Titrations must be carried out with minimum exposure to the atmosphere, preferably in volumetric flasks or flasks with elongated narrow necks or, best, in virtually closed systems. The sample is weighed or pipetted into the titration flask. A known volume of a dry solvent (methanol or dioxan or dioxan–methanol) is added, and the mixture is titrated directly with the Karl Fischer reagent delivered from the protected burette. As the end point is approached, as shown by a decrease in the rate of discharge of the brown colour, the reagent is added in very small increments until the brownish colour of iodine persists. The end-point change from chromate yellow to the red-brown of iodine is usually sharp and reproducible. After correction for water present in the solvent, the net titre is equivalent to the moisture in the sample. When only small quantities of water are involved, it is advisable to titrate first an equal volume of the solvent. Some workers prefer to add an excess of Fischer reagent to the sample, after which the solution is back-titrated with a standard water-in-methanol solution, equivalent to about 2·5 mg. of water per ml., to the chromate.
yellow colour of the spent reagent: this technique requires an additional burette to deliver the standard water-in-methanol solution. The visual end point possesses the advantage of permitting rapid titrations requiring only simple apparatus, but its limitations concerning the rigid exclusion of water vapour must be borne in mind. Karl Fischer (1935) stated: "The reaction is so sensitive that a sample which has been titrated to a distinct brown end point changes immediately to yellow if one breathes gently towards the flask. Therefore, a better indicator is unnecessary."

Notwithstanding what has already been stated, the determination of the end point by a potentiometric method is widely used. Furthermore, the electrometric method is usually more sensitive, and can be applied to coloured solutions and suspensions. The platinum–tungsten electrode pair can be used for the determination of the back titration of excess of Karl Fischer reagent with standard water-in-methanol; the change in potential at the end point is of the order of 20–25 millivolts, and at least 10 seconds is required for the full potential to develop (this short time lag is characteristic of all Fischer titrations). The glass electrode (reference)–platinum wire electrode pair have also been employed in conjunction with a pH meter: the end point is equally sharp (and remains stationary for 10–15 seconds) whether the solution is titrated directly with the Fischer reagent or by the back-titration procedure. The most widely used method employs a pair of platinum electrodes and the dead-stop end point (Section VI, 4). In the back-titration method (addition of excess of Fischer reagent, followed by standard water-in-methanol), the potential difference between the platinum electrodes immersed in the solution containing the Fischer reagent is adjusted to a value between 10 and 80 millivolts; sufficient current will flow through the solution to deflect the galvanometer off the scale. During the addition of the standard water-in-methanol the indicator remains displaced until the end point is approached; near the end point the galvanometer spot returns to the scale, and at the actual end point it comes to rest at the zero position. Here both electrodes remain depolarised during the titration, since active Fischer reagent (which always contains iodide ions) provides the iodine–iodide couple of oxidising and reducing agents; at the end point, when all the iodine has been reduced, the iodide ion polarises the cathode, after which current ceases to flow. The direct titration with the Fischer reagent may be carried out by employing a greatly increased potential between the platinum electrodes. This will vary during a titration, since the resistance of the solution decreases to a considerable extent; thus in methanol solution the potential may vary from 1 to 2 volts at the beginning of a titration to about 0.15 volt at its completion. The galvanometer action in this direct titration is reversed, the current increasing suddenly at the first appearance of unused iodine. The explanation of this is that only one electrode (cathode) is polarised; the anode is depolarised by the iodide ions. At the end point the free iodine depolarises the cathode, resulting in a sudden flow of current.

The apparatus employed by Bonner (1946) is illustrated in Fig. VI, 5, 1. The Fischer reagent and the "standard water” solution are separately contained in dark-coloured bottles; both solutions are pumped into the respective burettes by a hand-bellows, the air passing
Potentiometric Titration Methods

into the bottles being dried by a calcium chloride tower. The burettes are of 10 ml. capacity, graduated in 0.02 ml., and are closed by small calcium chloride tubes having a short length at the top of the tube filled with silica gel or cotton wool to prevent "caking" of the calcium chloride: this involves no danger of loss of water from the "standard water" solution, which is very dilute (1-2 g. per litre). The titration vessel has a ground-glass B34 neck and a capacity of about 60 ml. It carries a well-fitting Bakelite stopper drilled with holes to take the two burettes, the two glass tubes with sealed-in platinum wires, the stirrer and an inlet tube attached to a drying train through which nitrogen from a cylinder of the compressed gas is passed continuously into the vessel; the drying train consists of a calcium chloride tower, two wash-bottles containing concentrated sulphuric acid, and a silica gel or anhydrous calcium sulphate tube. All the tubes passing through the stopper are treated with sealing-wax to give an air-tight seal; the stirrer and stopper are thickly coated with a suitable inert grease. A
tap is provided to allow titrated solutions to be run off and replaced by dry nitrogen, thus avoiding the necessity of removing the titration vessel after each titration and the exposure of the dry, hygroscopic solvent on the interior surface of the vessel to atmospheric moisture. The solution to be titrated is introduced through the narrow side arm, which at all other times is closed with a small drying tube, the end of which is ground to fit the B7 ground-glass neck of the side arm. The bottles, the burettes, the electric motor for driving the stirrer, and the titration vessel are mounted on a wooden stand and baseboard. A self-contained portable potentiometer (Cambridge, calibrated to 2 millivolts) was used to apply an e.m.f. of 80 millivolts to the platinum electrodes; the Cambridge titration apparatus (potentiometric pattern), Fig. VI, 3, 3, is to be preferred, since inter alia a sensitivity control for the galvanometer is provided.

The dead-stop method of titration is employed. Thus the titration of the Fischer reagent against the "standard water" solution is carried out as follows with the above apparatus. Pass dry nitrogen through the dry titration vessel for 15 minutes, deliver 4.00 or 5.00 ml. of the Fischer reagent into the titration vessel, and apply an e.m.f. of 80 millivolts to the platinum electrodes. The galvanometer needle (of the portable potentiometer) will be deflected off the scale. Stir the solution slowly and add the "standard water" solution until the
colour approaches a yellow-brown. Then continue the addition drop-wise until the galvanometer index is on the scale and eventually returns to the zero position. Run out the solution, deliver another 4.00 or 5.00 ml. of the Fischer reagent into the vessel and titrate as before. Repeat until two successive titrations do not differ by more than 0.01 ml.

The Cambridge titration apparatus (potentiometric pattern), Fig. VI, 3, 3, is well adapted for Karl Fischer determinations using the dead-stop end point. The auxiliary apparatus is shown in Fig. VI, 5, 2. It comprises: two 250-ml. reservoir burettes, one for the Fischer reagent and the other for the standard water-in-methanol solution; a coned stopper with ground joint to accommodate the two burette tips, the double platinum electrodes and the stirrer; 150-ml. flask with B34 ground joint, and supporting ring with spring suspension. Each burette is graduated to 20 ml. in 0.05 ml.; the reservoir is closed by a drying-tube charged with silica gel to prevent absorption of atmospheric moisture.

The Mullard-B.T.L. Karl Fischer apparatus* utilises their potentiometric titration apparatus with magic-eye indicator (Fig. VI, 4, 2) for the determination of the end point and the usual pair of platinum electrodes. The essential features of the apparatus will be evident from

* Supplied by Baird and Tatlock (London), Ltd., Freshwater Road, Chadwell Heath, Essex, England.
Fig. VI, 5, 3; the complete apparatus is shown in Fig. VI, 5, 4. The two 25-ml. burettes may be filled from the respective reservoirs holding 1 litre of the Fischer reagent and the standard water-in-methanol solution. Magnetic stirring is provided for the titration cell, and the speed of stirring by means of the iron core sealed in glass is controlled by a rheostat; difficulties arising with stirrers operated through the neck of the titration cell are thus avoided.

VI, 6. Some applications of the Karl Fischer reagent.—It is usual to add an inert solvent, such as dry methanol, in which both the sample and the reaction products are soluble in order to secure satisfactory end points; for some compounds the finely powdered solid must be suspended in the inert solvent and the suspension kept well stirred during the titration. Generally macro samples should contain 25–250 mg. of water, and the volume of solvent, when employed, is 25–50 ml. The determination may be checked by adding a known weight of water and carrying out a duplicate titration.

The following types of organic compounds, as well as many others which will not be described, have been studied.

Organic acids. These include oxalic acid dihydrate, malonic, citric, and tartaric acids. Esterification due to the presence of methanol is not appreciable for acetic and formic acids if the titration is carried out rapidly; for these acids it is best to use a mixture of equal volumes of dry methanol and dry pyridine as solvent.

Alcohols. The Karl Fischer titration is generally applicable, and is superior to density measurements for methanol, ethanol, and glycerol.

Esters. These include methyl formate, methyl and ethyl acetates, and methyl and ethyl sulphates; the alkyl sulphates must be dissolved in 5–10 volumes of anhydrous methyl alcohol for satisfactory end points.

Lactones, acetals, and others.

Hydrocarbons. These include benzene and cyclohexane. When the water content is very low, as in n-hexane, it is best to extract with pure ethylene glycol, which is usually immiscible with the hydrocarbon. In this manner it is possible to determine the equilibrium moisture in hexane after treatment with various desiccants; the results are collected in the following table:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂, fused</td>
<td>1·97</td>
<td>Al₂O₃</td>
<td>0·02</td>
</tr>
<tr>
<td>CaCl₂, granular</td>
<td>0·8</td>
<td>KOH, fused</td>
<td>0·01</td>
</tr>
<tr>
<td>NaOH, fused</td>
<td>0·0</td>
<td>P₂O₅</td>
<td>0·0001</td>
</tr>
</tbody>
</table>

Anhydrides and acyl halides. Interesting results have been obtained in the study of the dehydration of glacial acetic acid with acetic anhydride. An acid containing 0·5 per cent of water was mixed with slightly more than the calculated amount of acetic anhydride required to produce the anhydrous acid. The mixture was allowed to stand at room temperature, and was analysed at intervals by the Karl Fischer procedure. The results were:
Basic, neutral, or slightly acidic nitrogen compounds. The procedure is generally applicable except for amines (e.g., n-butylamine) stronger than benzylamine \( (K = 2.4 \times 10^{-5}) \), which must first be treated with an excess of glacial acetic acid before titration.

Neutral halogen compounds. These include chloroform and carbon tetrachloride.

Neutral sulphur compounds. These include carbon disulphide, sulphides, disulphides, and thiophene.

Carbonyl compounds. These represent one of the few classes of organic compounds which, in general, interfere in the Fischer titration. This is due to their tendency to form acetals or ketals by reaction with the methanol of the standard reagent and the consequent production of additional water:

\[
\begin{align*}
RCHO + 2CH_3OH & \rightleftharpoons RCH(OCH_3)_2 + H_2O \\
R_2CO + 2CH_3OH & \rightleftharpoons R_2C(OCH_3)_2 + H_2O
\end{align*}
\]

The presence of carbonyl compounds is characterised by the rapidly fading end points and the apparently high water contents. Moderately satisfactory results can be obtained by employing pyridine as solvent. The best procedure, applicable to all types of carbonyl compounds, consists in converting them into the cyanohydrins by the addition of a hydrogen cyanide reagent; the resulting cyanohydrin does not interfere with the titration. The reagent consists of a 5 per cent solution of liquid hydrogen cyanide in dry dioxan or dry pyridine, together with a little sodium or potassium cyanide dissolved in methyl alcohol as catalyst. Those ketones which do not readily form cyanohydrins behave normally.

Water of hydration in organic compounds. The titration in methyl alcohol solution or suspension may be applied inter alia to oxalic acid, citric acid, sulphanilic acid, p-toluene sulphonic acid, chloral, o-phenanthroline, brucine, and brucine sulphate.

Water in inorganic compounds. The reagent may be used for determining water present in hydrated salts or which is absorbed on the surface of solids. The procedure, where applicable, is more rapid and direct than the commonly used drying process. A sample of the powdered compound, equivalent to 5–10 millimols (90–180 mg.) of water is dissolved or suspended in 25 ml. of dry methanol in a 250-ml. glass-stoppered volumetric flask, and the mixture is titrated with the standard Karl Fischer reagent to the usual light brown end point. The water content of the methanol solution is determined by a separate titration of an equal volume, and the titre of the sample is reduced by this amount. The corrected titre is equivalent to the available water in the sample. It need hardly be added that the electrometric dead-stop end-point procedure may also be used.

The Karl Fischer titration has been successfully applied inter alia...
to the following: barium, cadmium, cobalt, lead, magnesium, nickel, sodium, zinc, and uranyl acetates; calcium lactate, malonate, and propionate; sodium citrate, naphthionate, succinate, formaldehyde sulphoxylate, bisulphate, nitroprusside, and phosphate; potassium and ammonium oxalates; barium, strontium, cadmium, and stannic chlorides; chromic, cobalt, and mercurous nitrates; aluminium, cobalt, ferrous, ferrous ammonium, magnesium, manganese, nickel, and zinc sulphates.

An interesting application has been to the determination of water in desiccants. The percentages by weight found for a number of desiccants were: activated alumina 7·02, silica gel 5·48, calcium chloride 11·28, and anhydrous calcium sulphate (drierite) 5·31.

For further applications, including the quantitative determination of organic functional groups and miscellaneous inorganic analyses, the reader is referred to Mitchell and Smith's monograph on Aquametry.

VI. 7. Some experimental details for potentiometric titrations.—A few typical experiments will be briefly described in order to enable the student to obtain experience of the technique involved by both the classical and modern instrumental methods.

EXPERIMENT I. Neutralisation reactions. Prepare 0·1000N solutions of acetic acid and of sodium hydroxide. To avoid repetition, the following general instructions will be given which are applicable to most potentiometric titrations by the classical method.

(a) Fit up the apparatus shown in Fig. VI, 3, 1. The beaker has a capacity of about 400 ml., and contains the solution to be titrated (here 50 ml. of 0·1000N-acetic acid). The reference electrode may be a calomel half-cell; the side arm of the calomel electrode may dip into a small vessel containing saturated potassium chloride solution, and the latter is connected to the beaker by an agar-potassium chloride bridge. The indicator electrode is a bright platinum wire or foil, and about 0·1 g. of quinhydrone is added to the solution in the beaker (quinhydrone electrode).

(b) Stir the solution in the beaker gently. Read the potential difference between the electrodes with the aid of the slide-wire potentiometer. Record the reading and also the volume of alkali in the burette.

(c) Add 2–3 ml. of solution from the burette, stir for about 30 seconds, and, after waiting for a further half minute, measure the e.m.f. of the cell.

(d) Repeat the addition of 1-ml. portions of the base, stirring and measuring the e.m.f. after each addition until a point is reached within about 1 ml. of the expected end point. Henceforth, add the solution in portions of 0·1 ml. or less, and record the potentiometer readings after each addition. Continue the additions until the equivalence point has been passed by 0·5–1·0 ml.

(e) Plot potentials as ordinates and volumes of reagent added as abscissae; draw a smooth curve through the points. The equivalence point is the volume corresponding to the steepest portion of the curve. In some cases the curve is practically vertical, one drop of solution causing a change of 100–200 millivolts in the e.m.f. of the cell; in other cases the slope is more gradual.

(f) Compute $\Delta E/\Delta V$ in the vicinity (say, within 5 ml.; $\Delta V = 0·1$ ml.) of the end point, and plot $\Delta E/\Delta V$ (ordinates) against the average
Potentiometric Titration Methods

The volume of reagent added (abscissa). The end point is the volume of titrating reagent at which the curve reaches a maximum.

<table>
<thead>
<tr>
<th>Total Volume Added (ml.)</th>
<th>$E$ (mV).</th>
<th>$\Delta E/0.1$ ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>41.0</td>
<td>435</td>
<td>1.0</td>
</tr>
<tr>
<td>42.0</td>
<td>445</td>
<td>1.2</td>
</tr>
<tr>
<td>43.0</td>
<td>457</td>
<td>1.5</td>
</tr>
<tr>
<td>44.0</td>
<td>472</td>
<td>2.4</td>
</tr>
<tr>
<td>44.5</td>
<td>484</td>
<td>15</td>
</tr>
<tr>
<td>44.6</td>
<td>499</td>
<td>50</td>
</tr>
<tr>
<td>44.7</td>
<td>588</td>
<td>15</td>
</tr>
<tr>
<td>44.9</td>
<td>618</td>
<td>1.8</td>
</tr>
<tr>
<td>46.0</td>
<td>638</td>
<td>1.0</td>
</tr>
<tr>
<td>47.0</td>
<td>648</td>
<td></td>
</tr>
</tbody>
</table>

The nature of the results which may be expected will be evident from the data presented in the accompanying table. The maximum change per 0.1 ml. of the reagent added occurs after the addition of 44.7 ml. of the solution, and this is accordingly the end point of the titration.

**EXPERIMENT 2. Oxidation-reduction reactions.** A typical exercise is the titration of an iodide solution with standard potassium permanganate solution:

$$2\text{MnO}_4^- + 16\text{H}^+ + 10\text{I}^- \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{I}_2$$

If A.R. potassium iodide is employed, the reaction may be utilised for the standardisation of potassium permanganate solution.

Prepare a ca. 0.1N-potassium permanganate solution. Place 0.3320 g. (0.002 mol.) of dry A.R. potassium iodide and 100 ml. of 0.2–0.3N-sulphuric acid in the beaker (Fig. VI, 3, 1). Use a saturated calomel electrode as reference electrode and a bright platinum wire as the indicator electrode. Determine the end point as in Experiment 1, but allow about 1 minute to elapse, when near the equivalence point, after each addition of the reagent before measuring the e.m.f. Calculate the normality of the potassium permanganate solution.

**EXPERIMENT 3. Precipitation reactions.** The indicator electrode must be reversible to one or the other of the ions which is being precipitated. Thus in the titration of a potassium iodide solution with standard silver nitrate solution, the electrode must be either a silver electrode or a platinum electrode in the presence of a little iodine (best introduced by adding a little of a freshly prepared alcoholic solution of iodine), i.e., an iodine electrode (reversible to I$^-$). The exercise recommended is the standardisation of silver nitrate solution with pure sodium chloride.

Prepare an approximately 0.1N-silver nitrate solution. Place 0.1169 g. of dry A.R. sodium chloride in the beaker, add 100 ml. of water, and stir until dissolved. Use a silver-wire electrode (or a silver-plated platinum wire), and a silver–silver chloride or a saturated calomel reference electrode separated from the solution by a saturated ammonium nitrate or potassium nitrate–agar bridge. Titrate the sodium chloride solution with the silver nitrate solution following the general procedure described in Experiment 1; it is important to have efficient stirring. Continue the titration to 5 ml. beyond the end point.
mine the end point and thence the normality of the silver nitrate solution.

**Experiment 4.** Dead-stop end-point method of titration. Fit up the apparatus depicted in Fig. VI, 4, 1,* using clean platinum wire electrodes and a suitable sensitive galvanometer (e.g., of the Cambridge spot type). Prepare a 0-1N-sodium thiosulphate solution and also a 0-1N-iodine solution containing potassium iodide in 0-1N concentration. Place 50 ml. of the thiosulphate solution in a 250- or 400-ml. beaker in which the electrodes † are supported and also provided with a mechanical stirrer. Adjust the galvanometer spot to zero with the aid of the $R_2$ potentiometer. Add the iodine solution slowly and with stirring. The galvanometer spot will remain at zero during most of the titration; the equivalence point is indicated by the first permanent displacement of the galvanometer index. The galvanometer deflection will be increased by further addition of the iodine solution. Note the volume of the iodine solution added, and compare it with the value obtained by direct titration with starch indicator. Repeat the experiment with iodine solution in the beaker and the thiosulphate solution in the burette. The galvanometer spot must first be adjusted to zero with both electrodes dipping into sodium thiosulphate solution. It will be noted that at the commencement of the titration the galvanometer spot will be off the scale (it is advisable to use a galvanometer shunt to bring it just on the scale). Near the end point the displacement will gradually decrease in magnitude (if a shunt is employed it should be cut out of circuit at this stage). With successive drops of the thiosulphate solution, the rest point of the galvanometer spot will approach the zero position, and may make temporary excursions towards the zero of the scale, until, at the end point, it will come to rest at or near the zero. Further addition of the thiosulphate solution has no effect upon the position of the galvanometer spot.

The thiosulphate solution may be replaced by 0-1N-sodium arsenite solution, and thus provide an alternative exercise.

**Experiment 5.** Use of a commercial thermionic valve titrimeter. The experimental details to be given below refer to the Mullard-B.T.L. potentiometric-titration apparatus (Fig. VI, 4, 2), but can be readily adapted to any other commercial titrimeter (e.g., the Fisher electro­metric titrimeter, Fig. VI, 4, 5). The e.m.f. may be measured with the aid of the magic-eye balance-point indicator. Excellent practice may be obtained by determining the ferrous-ion concentration of a solution by titration with standard potassium dichromate solution.

Prepare 250 ml. of 0-1N-potassium dichromate solution (using the dry A.R. solid) and an equal volume of ca. 0-1N-ferrous ammonium sulphate solution; the latter must contain sufficient dilute sulphuric acid to produce a clear solution, and the exact weight of A.R. ferrous ammonium sulphate employed should be noted. Place 25 ml. of the ferrous ammonium sulphate solution in the beaker, add 25 ml. of ca. 5N-sulphuric acid and 50 ml. of water. Charge the burette with the 0-1N-potassium dichromate solution. Use the special saturated calomel electrode (Fig. VI, 4, 4) provided with the apparatus; place

* The commercial apparatus, Fig. VI, 3, 3 may be used, if available.
† The platinum electrodes should be thoroughly cleaned by immersion in boiling concentrated nitric acid and then thoroughly washed with distilled water.
saturated potassium chloride solution in the cup, fill the long capillary with the solution, wipe off the excess of solution from the tip with filter-paper, and clip the electrode into position in the titration stand. Use a bright platinum electrode as the indicator electrode. Set the stirrer in motion. Proceed with the titration as directed in Experiment 1. After each addition of the dichromate solution measure the e.m.f. of the cell. Determine the end point: (i) from the potential–volume curve and (ii) by the differential method. Calculate the normality of the ferrous ammonium sulphate solution, and compare this with the value computed from the actual weight of solid employed in preparing the solution.

Repeat the experiment using another 25 ml. of the ferrous ammonium sulphate solution but with a pair of polarised platinum electrodes; the latter are prepared with the aid of the special polarising switch provided on the apparatus. The first permanent deflection of the magic-eye indicator gives the end point. The experiment may also be repeated with the tungsten electrode (reference) and the platinum electrode (indicator) pair.

Numerous other determinations can, of course, be made by potentiometric titration. The reader is referred to the Bibliography (particularly Nos. 1, 2, 3, 5, 6, 7, and 8) in Section VI, 12 for further information. A few typical determinations are given in Sections VI, 8 to VI, 11.

VI, 8. Standardisation of sodium thiosulphate or of iodine solution with potassium permanganate or with potassium dichromate.—This and the succeeding experiments are best carried out with a commercial apparatus such as the Cambridge titration apparatus (potentiometric pattern, Fig. VI, 3, 3) or a thermionic-valve titrimeter. The brief experimental details apply to the former type of apparatus, but can be readily adapted to the apparatus which employs a magic-eye indicator for the determination of the end point. The mode of calculation of the result will be self-evident in the examples given, or will have been described in an earlier chapter.

Place, say, 25 ml. of the standard potassium permanganate or the standard potassium dichromate solution (ca. 0.01N) in the beaker, add about 100 ml. of 0.2–0.5N-sulphuric acid and excess of potassium iodide. Stir the mixture and allow the reaction to proceed for 5–10 minutes. Adjust the galvanometer spot to one end of the scale and introduce the sodium thiosulphate solution from a burette until the spot returns almost to zero, this being the end point: one further drop may be added, and no change in the rest position of the spot should be observed after it has come to rest. The concentration of the sodium thiosulphate solution may now be calculated.

Now introduce, say, 25 ml. of the iodine solution and 100 ml. of 0.2–0.5N-sulphuric acid into the beaker, and carry out the titration with the now-standardised sodium thiosulphate solution as before. Calculate the normality of the iodine solution.

Note. Titrations may be carried out in dilute solution (up to, say, $2 \times 10^{-3}N$) by the addition of sufficient potassium iodide solution (e.g., 5 ml. of a 10 per cent solution) to depolarise the anode.

VI, 9. Determination of the available chlorine in bleaching powder, etc.—Triturate a known weight of the bleaching powder in a clean glass mortar with a little water, and make up to a known volume with the
washings from the mortar. Transfer an aliquot portion of the solution (or suspension) to the titration beaker and acidify with acetic acid; the total volume should be about 100 ml. Add excess of potassium iodide solution, stir the mixture, and allow the reaction to proceed for a few minutes before commencing the titration. Adjust the galvanometer spot to the end of the scale. Run in the standard sodium thiosulphate solution until the spot returns to its initial rest point; this is the end point of the titration.

The determination may also be carried out with arsenious oxide. Place an aliquot portion of the bleaching-powder solution and 20 ml. of saturated sodium bicarbonate solution (this requires about 1·5 g. of the solid) in the beaker and dilute to about 100 ml. Run in the standard sodium arsenite solution from the burette until the galvanometer spot returns to its rest point; add a further drop to establish the permanency of the end point.

**VI, 10. Determination of copper.**—Prepare a solution of the sample, containing about 0·1 g. of copper and no interfering elements, by any of the usual methods,* any large excess of nitric acid and all traces of nitrous acid must be removed. Boil the solution to expel most of the acid, add about 0·5 g. of urea (to destroy the nitrous acid) and boil again. Treat the cooled solution with concentrated ammonia solution dropwise until the deep-blue cuprammonium compound is formed, and then add a further two drops. Decompose the cuprammonium complex with glacial acetic acid and add 0·2 ml. in excess. Too great a dilution of the final solution should be avoided, otherwise the reaction between the cupric acetate and the potassium iodide may not be complete.

Place the prepared copper acetate solution in the beaker and add 10 ml. of 20 per cent potassium iodide solution. Set the stirrer in motion and add distilled water, if necessary, until the two platinum electrodes are fully immersed in the solution. The galvanometer spot will now be deflected to one end of the scale, and will remain there whilst the standard sodium thiosulphate solution is run in until the equivalence point is approached; the light spot will then make temporary excursions across the scale to the rest point. At the equivalence point, the galvanometer spot will move to the rest point and remain there; this is the end point of the titration. Further addition of the reagent will result in movement of the light spot, but it will return to its former rest point.

**VI, 11. Determination of chromium.**—The chromium in the substance is converted into chromate or dichromate by any of the usual methods. † A platinum indicator electrode and a saturated calomel electrode are used. Place a known volume of the dichromate solution in the titration beaker, add 10 ml. of 10 per cent sulphuric acid or hydrochloric acid per 100 ml. of the final volume of the solution and also 2·5 ml. of 10 per cent phosphoric acid. Insert the electrodes, stir, and adjust the potentiometer controls to bring the galvanometer spot to the centre of the scale. Continue the stirring, add a standard solution of ferrous ammonium sulphate and observe the movement of the galvanometer spot. The light spot will move a little to the left during the

---

* The student may first employ A. R. cupric sulphate crystals to secure initial practice in the method.
† The student may obtain preliminary experience with the method by using A.R. potassium dichromate.
Potentiometric Titration Methods

first part of the titration; as the end point is approached the spot will return towards the zero and will occasionally make violent fluctuations to the right. Now add the ferrous salt solution cautiously until a full and permanent deflection is obtained; this is the equivalence point. The oxidation of the ferrous salt is not instantaneous, and decreases in speed as the end point is approached: care must therefore be taken that the full deflection obtained is permanent and not transitory.

VI, 12. Determination of manganese.—The method is based upon the titration of manganous ion with permanganate ion in neutral pyrophosphate solution:

\[ 4\text{Mn}^{2+} + \text{MnO}_4^- + 8\text{H}^+ + 15\text{H}_2\text{P}_2\text{O}_7^{-} = 5\text{Mn(H}_2\text{P}_2\text{O}_7)_3^{-}^- + 4\text{H}_2\text{O} \]

The manganic pyrophosphate complex has an intense reddish-violet colour, consequently the titration must be performed potentiometrically. A bright platinum indicator electrode and a saturated calomel reference electrode may be used. The change in potential at the equivalence point at a pH between 6 and 7 is large (about 300 millivolts); the potential of the platinum electrode becomes constant rapidly after each addition of the potassium permanganate solution, thus permitting direct titration to almost the equivalence point and reducing the time required for a determination to less than 10 minutes. With relatively pure manganese solutions, a sodium pyrophosphate concentration of 0.2-0.3 M, a pH between 6 and 7, the equivalence point potential is +0.47 ± 0.02 volt vs. the saturated calomel electrode. At a pH above 8 the pyrophosphate complex is unstable and the method cannot be used.

The method is at least as accurate as the bismuthate procedure (Section III, 60) and is even less subject to interferences. Large amounts of chloride, cobalt (II), and chromium (III) do not interfere; iron (III), nickel, molybdenum (VI), tungsten (VI), and uranium (VI) are innocuous; nitrate, sulphate, and perchlorate ions are harmless. Large quantities of magnesium, cadmium, and aluminium yield precipitates which may co-precipitate manganese and should therefore be absent. Vanadium causes difficulties only when the amount is equal to or larger than the amount of manganese; when it is present originally in the +4 state, it is oxidised slowly in the titration to the +5 state along with the manganese. Small amounts of vanadium (up to about one-fifth of the amount of manganese) cause little error. The interference of large amounts of vanadium (V) can be circumvented by performing the titration at a pH of 3-3.5. Oxides of nitrogen interfere because of their reaction with potassium permanganate: hence when nitric acid is used to dissolve the sample, the resulting solution must be boiled thoroughly and a small amount of urea or sulphamic acid must be added to the acid solution to remove the last traces of oxides of nitrogen before introducing the sodium pyrophosphate solution.

For initial practice in the method the student may determine the manganese content of anhydrous A.R. manganous sulphate. Heat A.R. manganese sulphate crystals to 280°, allow to cool, grind to a fine powder, reheat at 280° for 30 minutes, and allow to cool in a desiccator. Weigh accurately about 2.2 g. of the anhydrous manganous sulphate, dissolve it in water and make up to 250 ml. in a volumetric flask.

Prepare a 0.02 M solution of potassium permanganate and standardise it against A.R. sodium oxalate or A.R. arsenious oxide.
Prepare 5N-sodium hydroxide solution using the A.R. solid: test a 10-ml. sample for reducing agents by adding a drop of the permanganate solution; no green coloration should develop.

Prepare also a saturated solution of the purest available sodium pyrophosphate (do not heat above 25° C., otherwise appreciable hydrolysis may occur); 12 g. of the hydrated solid Na₄P₂O₇·10H₂O will dissolve in 100-150 ml. of water according to the purity of the compound. It is essential to employ freshly made sodium pyrophosphate solution in the determination.

Place 150 ml. of the sodium pyrophosphate solution in a 250-400-ml. beaker, adjust the pH to 6-7 by the addition of concentrated sulphuric acid from a 1-ml. graduated pipette (use the appropriate indicator test-paper or a glass electrode). Add 25 ml. of the manganous sulphate solution and adjust the pH again to 6-7 by the addition of 5N-sodium hydroxide solution. Introduce a bright platinum electrode into the solution, and connect the latter through a saturated potassium chloride bridge to a saturated calomel electrode; complete the assembly for potentiometric titration as in Fig. VI, 3, 1. (The Mullard—B.T.L. potentiometric titration apparatus, Fig. VI, 4, 2, or an equivalent apparatus, may also be used.) Stir the mixture, add the potassium permanganate solution in 2-ml. portions at first, reduce this to 0.1-ml. portions in the vicinity of the end point: determine the potential after each addition. Plot the e.m.f. values (ordinates) against the volume of potassium permanganate solution added (abscissae), and determine the equivalence point. From your curve read off the potential at the equivalence point; this should be + 0.47 volt. In the determination the permanganate ion undergoes only a 4-electron change to the + 3 state, hence a 0.02M solution is 0.08N. Calculate the percentage of Mn in the sample.

1 ml. 0.02M-KMnO₄ = 0.00439 g. Mn

Repeat the titration using polarised platinum electrodes and the magic-eye indicator (Fig. VI, 4, 2); the end point is readily detected.

Further practice may be obtained by determining manganese in a manganese ore and in a steel.

Pyrolusite. Dissolve 1.5-2 g., accurately weighed, of pyrolusite* in a mixture of 25 ml. of 1:1 hydrochloric acid and 6 ml. of concentrated sulphuric acid, and dilute to 250 ml. Filtration is unnecessary. Titrate an aliquot part containing 80-100 mg. of manganese; add 200 ml. of freshly prepared, saturated sodium pyrophosphate solution, adjust the pH to a value between 6 and 7, and perform the potentiometric titration as described above.

Steel. Dissolve 5 g., accurately weighed, of a steel† in 1:1 nitric acid with the aid of the minimum volume of hydrochloric acid in a Kjeldahl flask. Boil the solution down to a small volume with excess of concentrated nitric acid to re-oxidise any vanadium present reduced by the hydrochloric acid: this step is unnecessary if vanadium is known to be absent. Dilute, boil to remove gaseous oxidation products, allow to cool, add 1 g. of urea or sulphamic acid, and dilute to 250 ml. Titrate 50-ml. portions as above.

* Either Ridsdale's "Pyrolusite Mn Ore (dry)" or Bureau of Analysed Samples "Manganese Ore" (a British Chemical Standard) is suitable.
† Use either Ridsdale's "Medium Carbon Steel" or Bureau of Analysed Samples "Carbon Steel R" or British Standard Steel Sample, No. 11.
VI, 13. Determination of cobalt.—Cobaltous salts may be titrated potentiometrically by making use of the reaction with standard 0.1N(0.1M)-potassium ferricyanide solution in the presence of a high concentration of ammonium citrate and of ammonia solution. The reactants should preferably be covered with a layer of an immiscible solvent (e.g., petroleum ether, b.p. 100–120° C.); this serves to exclude air, shields the operator and equipment from the strongly ammoniacal vapours, and minimises the formation of incrustations on the burette tips: efficient mechanical stirring is essential. The cobaltous salt solution (e.g., cobaltous sulphate) of approximately 0.05M concentration should be placed in the burette: this may be prepared from pure cobalt or from a pure cobalt salt, and its concentration may be checked against the standard potassium ferricyanide solution or by a gravimetric method (as anthranilate, etc.—Section IV, 33). If a small concentration of cobalt is to be determined, the cobalt solution may be added to excess of standard potassium ferricyanide solution, etc., and then titrated with the standard cobaltous solution: a simple calculation will give the cobalt content of the unknown solution.

Nickel, copper, chromium, tungsten, and molybdenum do not interfere, and iron in concentration up to one-twentieth of the amount of cobalt is without effect; manganese must be removed before the titration is commenced, for it is said to be quantitatively oxidised to the trivalent state.

To obtain experience in the titration the student may employ a 0.05M-cobalt sulphate solution prepared from uneffloresced crystals of the A.R. heptahydrate. Alternatively, a sample of cobalt ammonium sulphate CoSO₄·(NH₄)₂SO₄·6H₂O (prepared by mixing concentrated solutions of the component sulphates in equimolecular proportions and crystallising) may be used. A useful check is provided by a gravimetric determination of the cobalt content (Section IV, 33).

Prepare the following solutions:

**Standard 0.05N(0.05M)-potassium ferricyanide.** Finely powder about 20 g. of A.R. potassium ferricyanide (molecular weight = 329.25), dry at 60–80° C., and allow to cool in a desiccator. Weigh out 16.46 g. of the dry solid, dissolve it in water, and dilute to 1 litre in a standard flask. Check the normality of the potassium ferricyanide solution by iodometric titration (Section III, 120) using sodium thiosulphate solution which has been standardised against pure potassium iodate.

**Ammonium citrate solution.** Dissolve 50 g. of pure citric acid in 100 ml. of water and add 67.5 ml. of concentrated ammonia solution (sp. gr. 0.88).

**Procedure.** Into a 250- or 400-ml beaker place 25 ml. of the 0.05N-potassium ferricyanide solution, 10 ml. of the ammonium citrate solution and 100 ml. of ca. 5N-ammonia solution (prepared by diluting 30 ml. of concentrated ammonia solution to 100 ml. with distilled water). Cover the resulting solution with a layer of 25 ml. of light petroleum, b.p. 100–120° C. Introduce a bright platinum and a saturated calomel electrode and also a glass stirrer into the solution; use the Mullard-B.T.L. potentiometric titration apparatus (Fig. VI, 4, 2) or an equivalent apparatus. Read the potential between the platinum and calomel electrodes with the aid of the magic-eye indicator after each addition of appropriate volumes (1–2 ml.) of the cobaltous sulphate (or cobaltous ammonium sulphate) solution from the burette. The potential falls from an initial value of about 300 millivolts (positive
Quantitative Inorganic Analysis

to S.C.E.) and falls slowly to within 0·5–1 ml. of the end point. When a reading of about 100 millivolts has been attained, add the cobalt sulphate solution dropwise, and allow sufficient time for the potential to become steady before proceeding to the next addition. The end point is sharp and is easily deduced from the potential $(E)/$volume of solution $(V_x)$ graph or, better, by plotting $dE/dV$ against $V_x$ (see Section VI, 7). Immediately after the end point has been passed, the readings become negative vs. S.C.E., and if a complete titration curve is required a reversing key should be included in the circuit; this is usually unnecessary, as the end point is attained before the reversal of polarity occurs.

Calculate the strength of the cobalt sulphate solution from the known normality of the potassium ferricyanide solution.

Dilute the standard solution of the cobalt salt $n$-fold, introduce a known volume of this diluted solution into a 400-ml. beaker, and repeat the titration exactly as detailed above. Calculate the concentration of the diluted solution from the new value of the end point, and compare this figure from that deduced from the dilution factor $(n)$. 
VI. 14. SELECTED BIBLIOGRAPHY

CHAPTER VII

CONDUCTOMETRIC TITRATION METHODS

VII. 1. General Considerations.—Ohm’s law states that the current $I$ flowing in an electric conductor is directly proportional to the electro-motive force $E$ and inversely proportional to the resistance $R$ in the conductor, or $I = E/R$. The reciprocal of the resistance is termed the conductance.* The resistance of a homogeneous material of uniform cross-section with an area of $a$ sq. cm. and length $l$ cm. is given by:

$$ R = \rho \cdot l/a $$

where $\rho$ is a characteristic property of the material termed the specific resistance. The reciprocal of the specific resistance is named the specific conductance $\kappa$, and is the conductance of a cube of material 1 cm. in length and 1 cm. in cross-section. The specific conductance of an electrolytic solution depends only on the ions present, and therefore varies with their concentration. When a solution of an electrolyte is diluted, the specific conductance will decrease, since fewer ions per ml. of solution are present to carry the current. If all the solution be placed between two electrodes 1 cm. apart and large enough to contain the whole of the solution, the conductance will increase as the solution is diluted. This is due largely to a decrease in inter-ionic effects for strong electrolytes and to an increase in the degree of dissociation for weak electrolytes. If 1 g. equivalent of the solute is present, the conductance of such a solution is termed the equivalent conductance $\Lambda$. The equivalent conductance will clearly be the specific conductance multiplied by the volume $V$ in cubic centimetres containing 1 g. equivalent weight, or

$$ \Lambda = \kappa V = 1000\kappa/C $$

where $C$ is the concentration of the solution expressed in gram equivalents per litre. For strong electrolytes the equivalent conductance increases as the concentration is decreased, but it appears to approach a limiting value known as the equivalent conductance at infinite dilution $\Lambda_\infty$; this quantity is sometimes written as $\Lambda_0$ when concentration, rather than dilution, is considered. The quantity $\Lambda_\infty$ can be determined by extrapolation for dilute solutions of strong electrolytes. For weak electrolytes the extrapolation method cannot be used for the determination of $\Lambda_\infty$ but it may be computed from the equivalent conductances at infinite dilution of the respective ions, use being made of the “law of independent migration of ions.” At infinite dilution the ions are independent of each other, and each contributes its part to the total conductance, thus:

$$ \Lambda_\infty = \ell_+^* + \ell_-^* $$

where $\ell_+^*$ and $\ell_-^*$ are the ionic conductances or ionic mobilities at infinite
dilution.

* The terms conductance and conductivity will be employed synonymously throughout this Chapter.
The increase of mobility of most ions is about 2 per cent for each 1°C. rise in temperature. It is therefore important to allow the contents of the conductivity cell to attain thermal equilibrium before proceeding with the conductance measurement. The conductance of weak electrolytes is largely dependent upon the degree of ionisation, which is itself also dependent upon the temperature.

The addition of an electrolyte to a solution of another electrolyte under conditions producing no appreciable change in volume will affect its conductance according as to whether or not ionic reactions have occurred. If no ionic interaction takes place, such as in the addition of one simple salt to another (e.g., potassium chloride to sodium nitrate), the conductance will rise. If ionic interaction does occur, as in the addition of a base to an acid, the conductance will decrease owing to the replacement of the hydrogen ion (high mobility) by a metallic ion (lower mobility). This is the principle underlying conductometric titrations, i.e., the substitution of ions of one mobility by ions of another mobility.

Let us consider how the conductance of a solution of a strong electrolyte $A^+B^-$ will change upon the addition of a reagent $C^+D^-$, assuming that the cation $A^+$ (which is the ion to be determined) reacts with the ion $D^-$ of the reagent. If the product of the reaction $AD$ is relatively insoluble or only slightly ionised, the reaction may be written:

$$A^+B^- + C^+D^- \rightarrow AD + C^+B^-$$

Thus in the reaction between $A^+$ ions and $D^-$ ions, the $A^+$ ions are replaced by $C^+$ ions during the titration. As the titration proceeds the conductance increases or decreases, depending upon whether the mobility of the $C^+$ ion is greater or less than that of the $A^+$ ion.

During the progress of neutralisations, precipitations, etc., changes in conductivity may, in general, be expected, and these may therefore be employed in determining the end points as well as the progress of the reactions. The conductivity is measured after the addition of each increment of the reagent, and the points thus obtained are plotted to give a graph which consists of two straight lines intersecting at the equivalence point. The accuracy of the method is greater the more acute the angle of intersection and the more nearly the points of the
Quantitative Inorganic Analysis

Graph line on a straight line. The volume of the solution should not change appreciably; this may be achieved by employing a titrating reagent which is 20 to 100 times more concentrated than the solution being titrated, and the latter should be as dilute as practicable. Thus if the conductivity cell contains about 100 ml. of the solution at the beginning of the titration, the reagent (say, of fifty times the concentration of the solution being analysed) may be placed in a 5-ml. micro burette, graduated in 0.01 or 0.02 ml. A correction for the dilution effect may, however, be made by multiplying the values of the specific conductance by the factor \((V + v)/V\), in which \(V\) is the original volume of the solution and \(v\) is the volume of reagent added.

In contrast to potentiometric titration methods (see Chapter VI) but similar to amperometric titration methods (see Chapter IX), measurements near the equivalence point have no special significance. Indeed, owing to hydrolysis, dissociation, or solubility of the reaction product, the values of the conductivity measured in the vicinity of the equivalence point are usually worthless in the construction of the graph, since one or both curves will give a rounded portion at this point. Even if the conductivity of the reaction product at the equivalence point is appreciable, the reaction may frequently be employed for conductometric titration if the conductivity of the reaction product \(AD\) is practically completely suppressed by a reasonable excess of \(A^+\) or \(B^-\). Thus conductometric methods may be applied where visual or potentiometric methods fail to give results owing to considerable solubility or hydrolysis at the equivalence point, for example, in many precipitation reactions leading to moderately soluble substances, in the direct titration of weak acids by weak bases, and in the displacement titration of salts of moderately weak acids or bases by strong acids or bases. A further important advantage is that the method is as accurate in dilute as in more concentrated solutions; it can also be employed with coloured solutions.

The relative change of conductivity of the solution during the reaction and upon the addition of an excess of reagent largely determines the accuracy of the titration; under optimum conditions this is about 0.5 percent. Large amounts of foreign electrolytes, which do not take part in the reaction, must be absent, since these have a considerable effect upon the accuracy. In consequence, the conductometric method has much more limited application than visual, potentiometric, or amperometric procedures.

VII. 2. Apparatus and measurements.—A conductivity cell for conductometric titrations may be of any kind that lends itself to thorough stirring (preferably by mechanical means) of the contents and permits the periodical additions of reagent. It should preferably be immersed in a thermostat controlled to ±0.1°C. or, better, to ±0.01°C.; if a thermostat is not available, the cell should be immersed in a large, well-lagged tank of water which has acquired the temperature of the laboratory and is gently stirred by mechanical means. The conductivity cell should be constructed of Pyrex or other resistance glass. The electrodes should, as a rule, be about 1 sq. cm. in area, and welded to thick platinum wires that are fused into glass tubes in which they make contact with mercury; the ends of the copper leads that dip into the mercury should be previously amalgamated. The distance between the electrodes will be determined by the change in conductance of the
solution being titrated. For low-conductance solutions (e.g., when extremely dilute), the electrodes should be large and close together. For precipitation reactions, the electrodes must be vertical. Several cells with different cell constants (i.e., with different size electrodes and at varying distances apart) should be available for measurements with solutions of widely different conductivities. For many purposes a cell with electrode separation of 2 cm. is satisfactory. The bright platinum electrodes should be platinised in order to minimise polarization effects.

The following procedure may be used for platinising the electrodes. The conductivity vessel and electrodes are thoroughly cleaned by immersion in a warm solution of potassium dichromate in concentrated sulphuric acid. After washing with distilled water until free from acid, the electrodes are plated from a solution containing 3 g. of chloroplatinic acid and 0.025 g. of lead acetate per 100 ml. The current may be obtained from two accumulators (4 volts), the poles of which are connected to the ends of a suitable sliding resistance. The current is adjusted so as to produce a moderate evolution of hydrogen. Each electrode should be used alternately as anode and cathode (i.e., the current should be reversed every half minute) and electrolysis should be continued until both electrodes are covered with a jet-black deposit. The time may vary from about two to about five minutes. After platinising, the electrodes must be freed from traces of chlorine by connecting the two electrodes together as cathode and electrolysising in dilute sulphuric acid, using another platinum electrode as anode, for about fifteen minutes. The electrodes are then washed with distilled water and afterwards kept immersed in distilled water until required for use.

A number of conductivity cells, suitable for conductometric titration, are depicted in Fig. VII, 2, 1.

A is a Pyrex bottle of suitable capacity, closed by a stopper which carries the two electrode leads and has a third opening through which the reagent may be added: mixing is achieved by gentle shaking of the contents of the bottle in a thermostat. The electrodes are stout horizontal platinum discs, previously lightly platinised, and the glass tube carrying the lower electrode passes through a hole in the upper one. If the tubes enclosing the electrode leads are firmly held by the stopper, the electrodes can be kept in the same relative positions for as long as is required; the cell can be easily adapted for use with more concentrated or more dilute solutions by increasing or decreasing the distance between the electrodes. This cell is not recommended for precipitation reactions.

B is a typical conductivity cell for titrations; it is usually provided with a mechanical stirrer.

C is the cell designed by Britton and German (1930): the electrodes are firmly fixed in the ebonite lid.

D is a schematic diagram of an "immersion type" of cell for dipping into the test solution; it will be observed that it is open at the bottom. E is a robust form of this cell, and is marketed as the Mullard conductivity cell, type GM.4221 (see also Fig. VII, 2, 5 for a slightly modified form). It consists of a glass container with apertures at the side and bottom for the circulation of the liquid under test. The platinum electrodes, approximately 1 cm. square, are positioned rigidly by means of a glass "bridge"; the volume of liquid between the
electrodes is about 2 ml. Cells are supplied with bright platinum electrodes or with electrodes coated with platinum black.

When absolute values of the conductivities are required, the so-called cell constant is determined. If the resistance of the liquid measured in the cell is \( R \) and the specific conductance is \( \kappa \), the cell constant is defined by the relationship:

\[
\kappa = \frac{\text{Cell Constant}}{R} \quad \text{or Cell Constant} = \kappa R
\]

If the cell is a tube of uniform cross-section with the electrodes at the ends, the cell constant can be determined from the geometrical measurements, i.e., length (cm.)/area (sq. cm.). It is usual, however, to calculate the cell constant from the measurement of the resistance (or conductance) of a solution of known specific conductance. Potassium chloride solutions are generally employed, since the specific conductances of aqueous solutions of this salt have been determined with a high degree of accuracy at several temperatures (Table II).

For conductometric titrations it is not essential to know the absolute conductance; it usually suffices to plot the reciprocal of the measured resistance (which is proportional to the conductance) against the volume of the reagent added.

The passage of a current through a solution of an electrolyte may
produce changes in the composition of the solution in the vicinity of the electrodes; potentials at the electrodes may thus arise, with the consequent introduction of serious errors in the conductivity measurements, unless such polarisation effects can be reduced to negligible proportions. Those difficulties are generally overcome by the use of alternating currents for the measurements so that the polarisation is constantly reversed. The platinum electrodes are covered electrolytically with a light coating of finely divided platinum, known as "platinum black"; this greatly increases the surface and materially reduces polarisation. The resistance (or conductance) can be measured with the aid of a Wheatstone bridge as shown diagrammatically in Fig. VII, 2, 2. The conductivity cell forms one arm of a Wheatstone bridge $ac$, a standard variable resistance box $R$ forms another arm, and a calibrated slide-wire resistance $bc$ constitutes the third and fourth arms, $bd$ and $dc$. Alternating current (1000 cycles) is supplied to the bridge by a valve oscillator $V^*$ across $bc$, and a telephone $T$ is connected across $ad$ and serves to detect the point of balance. A variable condenser $C$ is connected in parallel with the resistance $R$. When the position of the contact $d$ is adjusted as well as possible for minimum sound in the telephone $T$, various capacitances are inserted until the best setting is obtained. The following condition then holds:

$$R_{\text{cell}}/dc = R/db$$

from which the resistance of the cell $R_{\text{cell}}$ can be calculated, since the three other quantities are known. A disadvantage of the Kohlrausch Wheatstone bridge method for measuring resistance is that one must work in a quiet room undisturbed by noises; this may be largely overcome by the use of an additional valve amplifier. For conductometric work it is best to replace the telephone detector by a visual device, such as the magic-eye electronic detector. The Mullard conductivity bridge,*

* The oscillator, type GM.4260, supplied by Mullard Electronic Products, Ltd., Aboyne Road, London, S.W.17, is both satisfactory and inexpensive.
type E.7566,* incorporates a circuit of this kind; it is both simple and inexpensive. The instrument is shown in Fig. VII, 2, 3, and the basic circuit in Fig. VII, 2, 4; a photograph of the associated immersion

* Mullard Electronic Products, Ltd., Aboyne Road, London, S.W.17.
type of conductivity cell constitutes Fig. VII, 2, 5. Power is derived from a 100–245 volts A.C. mains, and a step-down transformer reduces the voltage applied to the bridge network to 1·5 volts; the frequency of the incorporated oscillator is 2900 cycles. The two ratio arms of the conventional bridge are combined in a single potentiometer, and the circuit is so arranged that for a maximum rotation of the dial, the ratio change is exactly 100:1. The scale is calibrated from 0·1 to 10; the scale reading must be multiplied by the factor shown on the range switch for direct measurement in conductance, and also by the cell constant if the specific conductivity is required. Another range switch selects any one of a number of standard resistances, and thus provides readings of the conductance for the ranges 0·1–10, 10–1000, and 1000–100,000 micro-mhos. To check the correct operation of the bridge, the instrument is set at the control position in which two equal resistances are connected across the bridge arms so that the main potentiometer balances in the centre “unity” position; it will be found that in the unbalanced condition the whole area of the magic-eye balance indicator will fluoresce brightly, but on rotating the main potentiometer a position will be found (exactly over the centre division marked “1”) where the area of fluorescence contracts to a minimum.

To measure the conductance of a solution, the latter is placed in a suitable conductivity cell, or a cell of the immersion type (e.g., Fig. VII, 2, 5) is supported in the solution, and then connected to the conductivity bridge. The selector switch is set at the appropriate conductance range, and the main potentiometer dial is rotated until a balance is indicated on the magic eye. The conductance in micro-mhos is the reading on the outside scale multiplied by the factor on the range switch: the specific conductivity is calculated by multiplying this reading by the cell constant.

VII. 3. Applications of conductometric titrations.—Some typical conductometric titration curves are collected in Fig. VII, 3, 1 a–h.

Strong acid with a strong base. The conductance first falls, due to the replacement of the hydrogen ion (mobility 350) by the added cation (mobility 40–80) and then, after the equivalence point has been reached, rapidly rises with further additions of strong alkali due to the large mobility of the hydroxyl ion (198·5). The two branches of the curve are straight lines provided the volume of the reagent added is negligible, and their intersection gives the end point (Fig. VII, 3, 1a). This titration is of practical interest when the solutions are dark or deeply coloured or if they are very dilute (10⁻³–10⁻⁴ N); in the latter case carbon dioxide must be excluded.
Quantitative Inorganic Analysis

(a) Conductance vs. equivalents of NaOH
(b) Conductance vs. equivalents of NH₄OH
(c) Conductance vs. equivalents of NaOH with 0.01N, 0.001N, and 0.01N solutions
(d) Conductance vs. equivalents of alkali
(e) Conductance vs. ml of alkali solution
(f) Conductance vs. equivalents of NaOH
(g) Conductance vs. equivalents of NH₄OH
(h) Conductance vs. ml of base

Fig. VII, 5, 1.
Conductometric Titration Methods 727

Strong acid with a weak base. The titration of a strong acid with a moderately weak base \((K \approx 10^{-5})\) may be illustrated by the neutralisation of dilute sulphuric acid by dilute ammonia solution (Fig. VII, 3, 1 b). The first branch of the graph reflects the disappearance of the hydrogen ions during the neutralisation, but after the end point has been reached the graph becomes almost horizontal, since the excess of ammonium hydroxide is not appreciably ionised in the presence of ammonium sulphate.

Weak acid with a strong base. In the titration of a weak acid with a strong base, the shape of the curve will depend upon the concentration and the dissociation constant \(K\) of the acid. Thus in the neutralisation of acetic acid \((K = 0.8 \times 10^{-5})\) with sodium hydroxide solution, the neutral salt (sodium acetate) which is formed during the first part of the titration tends to repress the ionisation of the acetic acid still present so that its conductance decreases. The rising salt concentration will, however, tend to produce an increase in conductance. In consequence of these opposing influences the titration curves may have minima, the position of which will depend upon the concentration and upon the strength of the weak acid. As the titration proceeds, a somewhat indefinite break will occur at the end point, and the graph will become linear after all the acid has been neutralised. Some curves for acetio acid–sodium hydroxide titrations are shown in Fig. VII, 3, 1 c.

For moderately strong acids \((K \approx 10^{-3})\) the influence of the rising salt concentration is less pronounced, but, nevertheless, difficulty is also experienced in accurately locating the end point. Thus curve 1 in Fig. VII, 3, 1 d is obtained upon titrating 0.005N-o-nitrobenzoic acid with 0.130N-potassium hydroxide; the neutralisation line is slightly curved in the neighbourhood of the end point. Righellato and Davies (1933) give two procedures for determining the end point in the titration of weak acids with strong bases. The acid is first titrated with ammonium hydroxide solution; if the end point cannot be obtained from the curve with the desired accuracy, a second titration is carried out using potassium hydroxide solution of the same concentration. The two curves are practically identical up to the neutralisation point, and beyond this straight lines are obtained in both titrations, the intersection of which gives the end point. In Fig. VII, 3, 1 d, curve 2 is obtained with 0.130N-ammonium hydroxide solution. If the end point is required with great accuracy, a correction should be applied for the fact that the conductance of the ammonium salt is approximately 0.6 per cent lower than that of the potassium salt solutions, and the point of intersection should therefore be found when the final section of curve 2 is raised by this amount.

In the second procedure the titration is commenced with a small amount of ammonium hydroxide solution (sufficient, say, to neutralise one-third of the acid), and is then completed with sodium hydroxide solution of the same concentration. A typical curve for 0.005N-mandelie acid is shown in Fig. VII, 3, 1 e. When all the acid has been neutralised the conductance of the mixture falls owing to the replacement of the ammonium ion by the more slowly moving sodium ion \((\text{NH}_4\text{M} + \text{NaOH} \rightarrow \text{NH}_4\text{OH} + \text{NaM})\); when the displacement of the ammonia is complete, the conductivity rises abruptly. At this end point \((S)\), the total amount of sodium hydroxide solution added \(QS\) is equivalent to the acid originally present \((PQ\) represents the first
stage of the titration performed with ammonium hydroxide solution. Alternatively, the acid present is also measured by the total alkali added to the point at which the conductivity falls, i.e., by $P_R$. A double check is thus obtained in the titration. The method may be employed to improve the end point of any titration if the acid is sufficiently strong to form an ammonium salt.

**Very weak acid with a strong base.** The initial conductance is very small, but increases as the neutralisation proceeds owing to the salt formed. The conductance values near the equivalence point are high because of hydrolysis; beyond the equivalence point the hydrolysis is considerably reduced by the excess of alkali. To determine the end point, values of the conductance considerably removed from the equivalence point must therefore be used. Some titration curves for boric acid and sodium hydroxide solution are given in Fig. VII, 3, 1f.

**Weak acids with weak bases.** The titration of a weak acid and a weak base can be readily carried out, and frequently it is preferable to employ this procedure rather than use a strong base. Fig. VII, 3, 1g is the titration curve of 0.003N-acetic acid with 0.0073N-ammonium hydroxide solution. The neutralisation curve up to the equivalence point is similar to that obtained with sodium hydroxide solution, since both sodium and ammonium acetates are strong electrolytes; after the equivalence point an excess of ammonium hydroxide solution has little effect upon the conductivity, as its dissociation is depressed by the ammonium salt present in the solution. The advantages over the use of strong alkali are that the end point is more easy to detect, and in dilute solution the influence of carbon dioxide may be neglected.

**Mixture of a strong acid and a weak acid with a strong base.** Upon adding a strong base to a mixture of a strong acid and a weak acid (e.g., hydrochloric and acetic acids), the conductance falls until the strong acid is neutralised, then rises as the weak acid is converted into its salt, and finally rises more steeply as excess of alkali is introduced. Such a titration curve is shown as $S$ in Fig. VII, 3, 1h. The three branches of the curve will be straight lines except in so far as: (a) increasing dissociation of the weak acid results in a rounding off of the first end point, and (b) hydrolysis of the salt of the weak acid causes a rounding off of the second end point. Usually, extrapolation of the straight portions of the three branches leads to definite location of the end points. Here also titration with a weak base, such as ammonium hydroxide solution, is frequently preferable to strong alkali for reasons already mentioned in discussing weak acids; curve $W$ in Fig. VII, 3, 1k, is obtained by substituting ammonium hydroxide solution for the strong alkali. The procedure may be applied to the determination of mineral acid in vinegar or other weak organic acids ($K < 10^{-5}$).

**Displacement (or replacement) titrations.** When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced by that of the stronger one and the weak acid itself is liberated in the undisassociated form. Similarly, in the addition of a strong base to the salt of a weak base, the cation of the weak base is replaced by that of the stronger one and the weak base itself is liberated in the undisassociated form. If, for example, $N$-hydrochloric acid is added to a 0.1N-solution of sodium acetate, the curve shown in Fig. VII, 3, 2 is obtained; the acetate ion is replaced by the chloride ion. The initial increase in conductivity is due to the fact that the mobility of the
chloride ion is slightly greater than that of the acetate ion. Until the replacement is nearly complete, the solution contains sufficient sodium acetate to suppress the ionisation of the liberated acetic acid and thereby render negligible its contribution to the conductivity of the solution. Near the equivalence point the acetic acid is sufficiently ionised to affect the conductivity, thus leading to higher values of the conductivity and the rounded portion of the curve. Beyond the equivalence point when excess of hydrochloric acid is present, the ionisation of the acetic acid is again suppressed and the conductivity rises rapidly. It has been calculated by Kolthoff (1941) that to titrate a 0·1N-salt solution the dissociation constant must not be greater than $5 \times 10^{-4}$, for a 0·01N-salt solution $K > 5 \times 10^{-5}$, and for a 0·001N-salt solution $K > 5 \times 10^{-6}$, i.e., the ionisation constant of the displaced acid or base divided by the original concentration of the salt must not exceed $5 \times 10^{-3}$. Fig. VII, 3, 2 also includes the titration curve of 0·01N-ammonium chloride solution with 0·1N-sodium hydroxide solution. The decrease in conductivity during the displacement is caused by the substitution of the faster ammonium ion by the slower sodium ion (see Table I in Section VII, 1).

Precipitation and complex formation reactions. A reaction may be made the basis of a conductometric titration if the reaction product is sparingly soluble or is a stable complex. The following factors must be considered in connexion with the usefulness and accuracy of the titration:

(a) In order to reduce the influence of errors in the conductometric titration to a minimum the angle between the two branches of the curve should be as small as possible. If the angle is very obtuse, a small error in the conductance data can cause a large deviation. Kolthoff (1941) gives the following rules:

(i) The smaller the mobility of the ion which replaces the reacting ion, the more accurate will be the result. (Thus it is preferable to titrate a silver salt with lithium chloride rather than with hydrochloric acid; cations may be titrated with lithium salts, and anions with acetates.)

(ii) The larger the mobility of the anion of the reagent which
reacts with the cation to be determined, or vice versa, the more acute is the angle.

(iii) The titration of a slightly ionised salt does not give good results, since the conductivity increases continuously from the commencement. Hence the salt present in the cell should be virtually completely dissociated; for a similar reason, the added reagent should also be a strong electrolyte.

(b) The solubility of the precipitate (or the dissociation of the complex) should be less than 5 per cent. The addition of alcohol is sometimes recommended to reduce the solubility, but its influence on the factors detailed in (a) must be borne in mind. An experimental curve is given in Fig. VII, 3, 3. If the solubility of the precipitate

were negligibly small, the conductance at the equivalence point would be given by AB and not the observed AC. The addition of excess of reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determined by continuing the straight portions of the two arms of the curve until they intersect.

(c) A slow rate of precipitation, particularly with micro-crystalline precipitates, prolongs the time of titration. Seeding or the addition of alcohol (concentration up to 30–40 per cent) may have a favourable effect.

(d) If the precipitate has pronounced adsorptive properties, the composition of the precipitate will not be constant, and appreciable errors may result. Occlusion may take place with micro-crystalline precipitates.

In spite of the obvious limitations of the method, quite a large number of conductometric titrations have been carried out: thus silver nitrate, lead nitrate, barium acetate or barium chloride, uranyl acetate, lithium sulphate, and lithium oxalate have been employed in precipitation reactions (for details, see references 4 and 8 in Selected Bibliography, Section VII, 5).

VII, 4. Some experimental details for conductometric titrations.—Any of the conductivity cells depicted in Fig. VII, 2, 1 may be used.
Conductometric Titration Methods

Conductivity measurements may be made with any available set-up similar to Fig. VII, 2, 2, but the inexpensive Mullard conductivity bridge (Fig. VII, 2, 3) is recommended. The titrating reagent (of concentration at least 10 times that of the solution being titrated) should be placed in a 5 or 10-ml. micro-burette; the reagent is added in small portions, and the solution is stirred or shaken after each addition. The conductivity is measured after the well-mixed solution has been allowed to stand for a minute or two. The addition of the titrating reagent is continued until at least five readings beyond the equivalence point have been made. It is often advisable to carry out a preliminary titration; this will provide information as to the increments of the reagent best suited for the particular titration, e.g., in increments of 0.5 ml., etc. The conductance is plotted as ordinates against the volume of the titrating reagent as abscissa; the two straight portions of the curve are extrapolated until they intersect and the point of intersection is taken as the equivalence point of the reaction. It may be necessary to multiply the specific conductance readings by the factor \((V + v)/V\), where \(V\) is the original volume of the solution and \(v\) is the volume of reagent added, in those cases where the straight-line portions of the curves are not altogether satisfactory.

**EXPERIMENT 1.** Strong acid with a strong base. Treat a suitable volume of 0.01N-hydrochloric acid (according to the capacity of the conductivity cell employed) with 0.1N-sodium hydroxide solution. Repeat the titration with 0.001N-hydrochloric acid and 0.01N-sodium hydroxide solution.

**EXPERIMENT 2.** Strong acid with a weak base. Use 0.01N-sulphuric or hydrochloric acid and 0.1N-ammonium hydroxide solution.

**EXPERIMENT 3.** Weak acid with a strong base. Titrate 0.1N-acetic acid with N-sodium hydroxide. Repeat the titration with 0.01N-acetic acid and 0.1N-sodium hydroxide. In order to determine the end point in the latter titration, repeat it with 0.1N-ammonium hydroxide solution.

It is instructive to carry out the above experiments substituting o-nitrobenzoic acid for acetic acid.

**EXPERIMENT 4.** Very weak acid with a strong base. Titrate 0.1N-boric acid with 1.0N-sodium hydroxide.

**EXPERIMENT 5.** Weak acid with a weak base. Titrate 0.01N-acetic acid with 0.1N-ammonium hydroxide solution.

**EXPERIMENT 6.** Mixture of a strong acid and a weak acid with a strong base. Prepare a mixture of 80 ml. of 0.01N-acetic acid and 20 ml. of 0.01N-hydrochloric acid. Titrate aliquot portions first with 0.1N-sodium hydroxide and then with 0.1N-ammonium hydroxide solution. Compare the percentage of strong acid actually found by conductometric titration (compare Fig. VII, 3, 1h) with that actually present.

**EXPERIMENT 7.** Displacement titrations. Titrate: (a) 0.1N-sodium acetate with N-hydrochloric acid and (b) 0.01N-silver nitrate with N-sodium hydroxide.

**EXPERIMENT 8.** Precipitation titrations. Carry out the following precipitation titrations:

(a) 0.01N-silver nitrate with N-potassium chloride.
(b) 0.001N-silver nitrate with 0.1N-potassium chloride.
(c) 0.001N-silver nitrate with 0.1N-lithium chloride.
(d) 0.01N-ferric ammonium sulphate with freshly prepared 6 per cent cupferron solution. Standardise the latter against a ferric salt solution prepared from a known weight of electrolytic iron.

$p$-Acetophenonitrile (0.3–0.4 g. per litre) has been proposed as a preservative for cupferron solutions.

(e) 0.01N-ferric ammonium sulphate (or any ferric salt solution produced by oxidising a ferrous salt with hydrogen peroxide or with bromine and boiling off the excess of oxidant) with 15 per cent sulphosalicylic acid solution or a 10 per cent solution of its ammonium salt (prepared by adding the solid acid to ammonia solution until acid to methyl red).
VII. 5. SELECTED BIBLIOGRAPHY

CHAPTER VIII

POLAROGRAPHY

VIII, 1. GENERAL INTRODUCTION

If a steadily increasing voltage is applied to a cell incorporating a relatively large quiescent mercury anode and a minute mercury cathode (composed of a succession of small mercury drops falling slowly from a fine capillary tube), it is frequently possible to construct a reproducible current–voltage curve. The electrolyte is a dilute solution of the material under examination (which must be electro-active) in a suitable medium containing an excess of an indifferent electrolyte (supporting electrolyte, or base or ground solution) to carry the bulk of the current and raise the conductivity of the solution, thus ensuring that the material to be determined, if charged, does not migrate to the dropping mercury cathode. From an examination of the current–voltage curve, information as to the nature and concentration of the material may be obtained (Heyrovsky, 1922). Heyrovsky and Shikata (1925) developed an apparatus which increased the applied voltage at a steady rate and simultaneously recorded photographically the current–voltage curve. Since the curves obtained with this instrument are a graphical representation of the polarisation of the dropping electrode, the apparatus was called a polarograph, and the records obtained with it, polarograms. It must be emphasised that, while this (or an equivalent pen-recording) instrument is valuable in routine determinations as a time saver, it is by no means essential for polarographic work: excellent results may be obtained by plotting current–voltage curves from readings obtained with a home-made polarograph (vide infra) or with the equivalent commercial apparatus. Throughout this chapter the term polarogram will be used, irrespective of whether it is recorded automatically or obtained by plotting a series of individual readings.

The basic apparatus for polarographic analysis is depicted in Fig. VIII, 1. 1. The dropping mercury electrode is here shown as the cathode (its most common function); it is sometimes referred to as the indicator or micro-electrode. The anode is a pool of mercury, and its area is correspondingly large, so that it may be regarded as incapable of becoming polarised, i.e., its potential remains almost constant in a medium containing anions capable of forming insoluble salts with mercury (Cl\(^-\), SO\(_4\)\(^{2-}\), etc.); it acts as a reference electrode. The polarisation of the cell is therefore governed by the reactions occurring at the minute dropping mercury cathode. Inlet and outlet tubes are provided in the cell for expelling dissolved oxygen from the solution by the passage of an inert gas (hydrogen or nitrogen) before, but not during, an actual measurement—otherwise the polarogram of the dissolved oxygen will appear in the current–voltage curve. \(P\) is a potentiometer by which any e.m.f. up to 3 volts may be gradually applied to the cell. \(S\) is a shunt for adjusting the sensitivity of the galvanometer \(G\) appropriate to the nature and concentration of the
substance being investigated. It may be mentioned that under these conditions the current-voltage curve is really a current-cathode potential curve, but displaced by a constant voltage corresponding to the potential of the anode. For some purposes it is advisable to employ an external anode of known potential (e.g., a saturated calomel electrode): an internal electrode is more convenient for most analytical work, since absolute values of the cathode potential are not usually required.

The initial potential of the dropping mercury cathode is indeterminate, and will assume any potential applied to it from an external source; when it acquires a potential different from that which it had in the absence of electrical connexions, the indicator electrode is said to be polarised.

Let us consider what will occur if an external e.m.f. is applied to the cell shown in Fig. VIII, 1, 1, charged with, say, a dilute, oxygen-free solution of cadmium chloride. All the positively charged ions present in the solution will be attracted to the negative-indicator electrode by: (a) an electrical force, due to the attraction of oppositely charged bodies to each other, and by (b) a diffusive force, arising from the concentration gradient produced at the electrode surface. The total current passing through the cell can be
regarded as the sum of these two factors. A typical simple current-voltage curve is shown in Fig. VIII, 1, 2. The indicator electrode, being perfectly polarisable, assumes the correspondingly increasing negative potential applied to it; from \( A \) to \( B \) practically no current will pass through the cell. At \( B \), where the potential of the micro-electrode is equal to the decomposition potential of the cadmium ions with respect to a metallic cadmium electrode, the current suddenly commences to increase and the indicator electrode becomes depolarised by the cadmium ions, which are then discharged upon the electrode surface to form metallic cadmium, consequently a rapid increase in the current flowing through the cell will be observed. At the point \( C \) the current no longer increases linearly with applied potential but approaches a steady limiting value at the point \( D \): no increase in current is observed at higher cathode potentials unless a second compound able to depolarise the indicator electrode is present in the solution. At any point on the curve between \( B \) and \( C \) (usually spoken of as the polarographic wave) the number of cadmium ions reaching the micro-electrode surface as a result of migration and diffusion from the main bulk of the solution always exceeds the number of cadmium ions which react at and are deposited upon the electrode. At the point \( C \) the rate of supply of the cadmium ions from the main bulk of the solution to the indicator-electrode surface has become equal to the rate of their deposition. Hence at potentials more negative than point \( D \), the concentration of undischarged cadmium ions at the micro-electrode surface is negligibly small relative to the cadmium-ion concentration in the bulk of the solution; no further increase in current passing through the electrolytic cell can be expected, since the limiting current is now fixed by the rate at which cadmium ions can reach the electrode surface.

A number of polarisable micro-electrodes (e.g., a rotating platinum wire, ca. 3 mm. long and 0.5 mm. diameter, suitably mounted, or stationary noble-metal electrodes) have been used in determining current-voltage curves, but the most satisfactory is a slowly growing drop of mercury issuing, under a head of 40-60 cm. of mercury, from a resistance-glass capillary (0.05-0.06 mm. in diameter and 6-7 cm. long) in small, uniform drops. The dropping mercury electrode has the following advantages: (i) its surface is reproducible, smooth, and continually removed; (ii) the surface area can be calculated from the weight of the drops; (iii) mercury amalgamates with most metals; (iv) the value of the overvoltage of hydrogen is highest on mercury, so that much work can be done in acid solutions and at large negative potentials without disturbance from the evolution of hydrogen; and (v) the current instantly assumes a steady value and is reproducible.

Reference has already been made to the convenience for routine analytical work of using a mercury pool covering the bottom of the electrolysis cell as the non-polarisable reference electrode. If the solution covering the mercury pool contains chloride or other similar depolarising ions of concentration \( c \), the mercury pool acts as a calomel or other type of reference electrode of approximate concentration \( c \). This potential, although constant, is not known with accuracy, and must therefore be determined after each current-voltage experiment by balancing against some standard half-cell, if a current-electrode potential curve is required. This additional determination may be avoided by the use of an external standard-reference electrode con-
Polarography

connected to the electrolysis vessel by a salt bridge; a large saturated calomel electrode is perhaps the most convenient. The potential of the polarised micro-electrode $E_m$ can then be calculated from the relationship:

$$E_m = E_r + V + IR$$

where $E_r$ is the potential of the non-polarisable reference electrode, $V$ is the applied voltage, $I$ is the observed current, and $R$ is the resistance of the electric circuit. (In polarography it is usual to regard the current as positive when the micro-electrode is the cathode, and negative when it is the anode.) The correction for $IR$ becomes necessary when the product of the current and the resistance exceeds 1 millivolt.

**VIII, 2. THEORETICAL PRINCIPLES**

We will now consider the factors affecting the limiting current with a dropping mercury cathode. Heyrovsky had early recognised the importance of the limiting current in quantitative analysis.

**Residual (or condenser) current.** Mercury is unique in remaining electrically uncharged when it is dropping freely into a solution containing an indifferent electrolyte, such as potassium chloride or potassium nitrate. If a current–voltage curve is determined for a solution containing ions with a strongly negative reduction potential (e.g., potassium ions), a small current will flow before the decomposition of the solution begins. This current increases almost linearly with the applied voltage, and it is observed even when the purest, air-free solutions are used, so that it cannot be due to the reduction of impurities. It must therefore be considered a non-Faradayic or condenser current, made appreciable by the continual charging of new mercury drops to the applied potential. It is known that metals, when submerged in an electrolyte, are covered with an electrical double layer of positively and negatively charged ions. The composition of the double layer and hence the charging current vary, depending upon the potential which is imposed upon the metal.

In practice, one often finds that the indifferent electrolyte contains traces of impurities so that small, almost imperceptible currents are superimposed upon the condenser current. It is customary to include all these in the residual current. As will be shown later, in practical polarographic work the residual current is automatically subtracted from the total observed current by proper extrapolation and placement of tangents to the wave.

**Migration current.** Electro-active material reaches the surface of the electrode largely by two processes. One is the migration of charged particles in the electric field caused by the potential difference existing between the electrode surface and the solution; the other is concerned with the diffusion of particles, and will be discussed in a succeeding paragraph. Heyrovsky (1934) showed that the migration current can be practically eliminated if an indifferent electrolyte is added to the solution in a concentration so large that its ions carry essentially all the current. (An indifferent electrolyte is one which conducts the current but does not react with the material under investigation, nor at the electrodes within the potential range studied.) In practice, this means that the concentration of the added electrolyte (supporting electrolyte) must be at least 100-fold that of the electro-active material.
An example will make this conception of supporting electrolyte clear. Let us imagine an electrolytic solution is composed of potassium ions 0.10 M and copper ions 0.01 M. If we assume that the equivalent conductances of each ion are approximately equal, then it follows that ca. 90 per cent of the current will be transported to the cathode by the potassium ions and only 10 per cent by the copper ions. Both ions will tend to diffuse towards any portion of the solution where a concentration gradient exists, but the rate of diffusion will be slow. If the concentration of the potassium ions be increased until it represents 99 per cent of the total cations present, practically all the current passing through the cell will be transported by the potassium ions. Under such conditions the electro-active material can reach the electrode surface only by diffusion. It must be emphasised that the supporting electrolyte must be composed of ions which are discharged at potentials which will not interfere or react chemically with the ions under investigation.

**Diffusion current.** When an excess of supporting electrolyte is present in the solution the electrical force on the reducible ions is nullified; this is because the ions of the added salt carry practically all the current and the potential gradient is compressed or shortened to a region so very close to the electrode surface that it is no longer operative to attract electro-reducible ions. Under these conditions the limiting current is almost solely a diffusion current. Ilkovic (1934) examined the various factors which govern the diffusion current and deduced the following equation:

\[ I_d = k \cdot nF \cdot C \cdot D^2 \cdot m \cdot t^4 \]

where \( I_d \) is the diffusion current at any given time, \( n \) is the number of electrons involved in the reduction of one molecule of the electro-active substance, \( F \) is the Faraday (96,500 coulombs), \( D \) is the diffusion coefficient of the reducible substance and \( C \) its concentration, \( m \) the weight of mercury flowing through the capillary per second, and \( t \) the time (in seconds) necessary for the formation of one drop of mercury; \( k \) is a constant. If \( I_d \) is expressed in microamperes (1 \( \mu \)A = \( 10^{-6} \) amp.), \( C \) as millimols. per litre, \( D \) in sq. cm./second, and \( m \) in grams, the Ilkovic equation becomes:

\[ I_d = 706 \cdot n \cdot C \cdot D^2 \cdot m^3 \cdot t^4 \mu A \]

The diffusion coefficient \( D \) of the reducible substance depends upon several factors, such as temperature, viscosity, ion mobilities, and ionic strength of the solution. For most metal ions the diffusion current increases about 2 per cent per degree rise in temperature; the temperature of the surrounding bath should therefore be controlled to about \( \pm 0.2^\circ \), although \( \pm 0.5^\circ \) suffices for most practical purposes. Unless the individual drops fall under their own weight when they are completely formed, the diffusion currents are not reproducible: stirring of the solution under investigation is therefore not permissible.

The drop time \( t \) depends not only upon the mercury pressure but also upon the interfacial tension at the mercury–solution interface. Fortunately \( t \) appears only as the sixth root in the Ilkovic equation, so that variation in this quantity will have a relatively small effect upon the diffusion current. The product \( m^3 \cdot t^4 \) is important because it permits results with different dropping electrodes to be compared.
An important deduction from the Ilkovic equation is:

\[ I_d = K \cdot C \]

i.e., with all other factors remaining constant, the diffusion current is directly proportional to the concentration of the reacting material.

**Adsorption current** (maxima on polarographic curves). Current-voltage curves obtained with the dropping mercury cathode frequently exhibit pronounced maxima, which are reproducible and which can be usually eliminated by the addition of certain appropriate "maximum suppressors." These maxima vary in shape from sharp peaks to rounded humps, which gradually decrease to the normal diffusion-current curve as the applied voltage is increased. A typical example is shown in Fig. VIII, 2, 1. Curve A is that for copper ions in 0.1M-potassium hydrogen citrate solution, and curve B is the same polarogram in the presence of 0.005 per cent acid fuchsin solution.

The maxima may be due to stirring of the liquid around the mercury drop or to adsorption of electro-active material on the electrode surface, but the exact cause is unknown. To measure the true diffusion current, the maxima must be eliminated. Fortunately this can easily be effected by the addition of small quantities of dye and indicator ions (e.g., sodium methyl red or acid fuchsin) of colloids (e.g., gelatin or agar). Gelatin is generally employed in concentrations of 0.002–0.01 per cent; higher concentrations will suppress the diffusion current.

**Half-wave Potentials.** We are now in a position to appreciate the significance of half-wave potentials. The salient features of a typical current–applied voltage curve (polarogram) are shown in Fig. VIII, 2, 2. The height of the curve (wave length) is the diffusion current, and is a function of the concentration of the reacting material; the potential
corresponding to the point of inflection of the curve (half-wave potential) is characteristic of the nature of the reacting material. This is the essential basis of quantitative and qualitative polarographic analysis.

The underlying theory may be simplified as follows. Polarography is concerned with electrode reactions at the indicator or micro-electrode, i.e., with reactions involving a transfer of electrons between the electrode and the components of the solution. These components are called oxidants when they can accept electrons, and reductants when they can lose electrons. The electrode is a cathode when a reduction can take place at its surface, and an anode when oxidation occurs at its surface. During the reduction of an oxidant at the cathode, electrons leave the electrode and enter the solution with the formation of an equivalent amount of the reductant. Similarly, during the oxidation of a reductant at the anode electrons pass from the solution to the electrode and form an equivalent amount of the oxidant. Free electrons cannot exist in solution, consequently any process of reduction at the cathode is accompanied by a simultaneous oxidation at the anode. We may summarise the above discussion as:

Oxidant $\rightarrow n$ Electrons $\Rightarrow$ Reductant

or

$$\text{Ox} + n\text{e} \Rightarrow \text{Red} \quad \ldots \ldots \quad (1)$$

The reductant differs from the oxidant merely by $n$ electrons, and together they form an oxidation-reduction system. We will consider the reversible reduction of an oxidant to a reductant at a dropping mercury cathode. The electrode potential is given by:

$$E = E_0 + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{red}}} \quad \ldots \ldots \quad (2)$$

where $a_{\text{ox}}$ and $a_{\text{red}}$ are the activities of the oxidant and reductant respectively as they exist at the electrode surface (henceforth called the electrode-solution interface and denoted by the subscript "i"), $R$ is the gas constant, $T$ the absolute temperature, $n$ the number of electrons involved in the reaction, and $F$ the Faraday; $E_0$ is the electrode potential of the system when the activities of the oxidant and the reductant are equal. Polarographic measurements are seldom more accurate than $\pm 1$ millivolt, hence substitution of concentrations for activities will not introduce any appreciable error. Equation (2) may therefore be written as:

$$E = E_0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]} \quad \ldots \ldots \quad (3)$$

Before the commencement of the polarographic wave only a small residual current flows, and the concentration of any electro-active substance must be the same at the electrode interface as in the bulk of the solution. As soon as the decomposition potential is exceeded, some of the reducible substance (oxidant) at the interface is reduced, and must be replenished from the body of the solution by means of diffusion. The reduction product (reductant) does not accumulate at the interface, but diffuses away from it into the solution or into the electrode material. If the applied potential is increased to a value at which all the oxidant reaching the interface is reduced, only the newly formed reductant will be present; the current then flowing will be the diffusion current.
The current \( I \) at any point on the wave is determined by the rate of diffusion of the oxidant from the bulk of the solution to the electrode surface under a concentration gradient \([\text{Ox}]\) to \([\text{Ox}]_i\):

\[
I = K([\text{Ox}] - [\text{Ox}]_i) . . . . . . (4)
\]

When \([\text{Ox}]_i\) is reduced to almost zero, equation (4) may be written:

\[
I = K[\text{Ox}] = I_d . . . . . . (5)
\]

where \( I_d \) is the diffusion current. From equations (4) and (5), it follows that:

\[
[\text{Ox}]_i = (I_d - I)/K . . . . . . (6)
\]

If the reductant (Red) is soluble in water and none was originally present with the oxidant, it will diffuse from the surface of the electrode to the bulk of the solution. The concentration of \([\text{Red}]_i\) at the surface at any value of \( I \) will be proportional to the rate of diffusion of the reductant from the surface of the electrode to the solution (under a concentration gradient \([\text{Red}]_i\)) and hence also to the current:

\[
I = k[\text{Red}]_i . . . . . . (7)
\]

If the reductant is insoluble in water but soluble in the mercury phase (amalgam formation), equation (7) still holds. Substituting in equation (3), we have:

\[
E = E_0 - \frac{RT}{nF} \ln \frac{K}{k} + \frac{RT}{nF} \ln \frac{I_d - I}{I}
= E'_0 + \frac{RT}{nF} \ln \frac{I_d - I}{I} . . . . . . (8)
\]

where \( E'_0 = E_0 - K' \) and \( K' = \frac{RT}{nF} \ln \frac{K}{k} \).

When \( I \) is equal to 0.5\( I_d \), equation (8) reduces to:

\[
E = E'_{0.5} = E'_0 + \frac{RT}{nF} \ln \frac{0.5I_d}{0.5I_d} = E'_0 . . . . . . (9)
\]

The potential at the point on the polarographic wave where the current is equal to one-half the diffusion current is termed the \textit{half-wave potential} and is designated by \( E'_{0.5} \). It is quite clear from equation (9) that \( E'_{0.5} \) is a characteristic constant for a reversible oxidation-reduction system and that its value is independent of the concentration of the oxidant \([\text{Ox}]\) in the bulk of the solution. It follows from equations (8) and (9) that at 25°:

\[
E = E'_{0.5} + \frac{0.0591}{n} \log \frac{I_d - I}{I} . . . . . . (10)
\]

This equation represents the potential as a function of the current at any point on the polarographic wave; it is sometimes termed the \textit{equation of the polarographic wave}.

The half-wave potential is also independent of the electrode characteristics, and can therefore sometimes serve for the qualitative identification of an unknown substance. Owing to the proximity of many different half-wave potentials, its use for qualitative analysis is of limited application unless the number of possibilities is strictly
limited by the nature of the unknown. The theoretical treatment for
anodic waves is similar to the above.

It follows from equation (10) that when \( \log \left( \frac{I_a - I}{I} \right) \) (where \( I \) is the current at any point on the polarographic wave minus the residual current) is plotted against the corresponding potential of the micro-
electrode (ordinates), a straight line should be obtained with a slope of
0.0591/\( n \) for a reversible reaction; the intercept of the graph upon
the vertical axis gives the half-wave potential of the system. Hence
\( n \), the number of electrons taking part in the reversible reaction, may
be determined. It also follows from equation (10) that the range of
potentials over which the polarographic wave extends decreases with
increasing values of \( n \); thus the wave is steeper in the reduction of
the trivalent aluminium or lanthanum ion than for the lead or cadmium
ion, which in turn are steeper than that of the alkali metal or thallous
ion.

If the reaction at the indicator electrode involves complex ions, satis-
factory polarograms can be obtained only if the dissociation of the
complex ion is very rapid as compared to the diffusion rate, so that
the concentration of the dissociated ion is maintained constant at the
electrode interface. Let us consider the general case of the dissociation
of a complex ion:

\[
MX_p^{(a-p)b^+} \rightleftharpoons M^{n^+} + pX^{-b}
\]  

(11)

The instability constant may be written:

\[
K_{\text{instab.}} = \frac{[M^{n^+}][X^{-b}]^p}{[MX_p^{(a-p)b^+}]}
\]  

(12)

(strictly, activities should replace concentrations).

We may imagine the amalgam reaction to be (assuming amalgam
formation):

\[
M^{n^+} + ne + \text{Hg} \rightleftharpoons M(\text{Hg})
\]  

(13)

Combining (11) and (13), we have:

\[
MX_p^{(a-p)b^+} + ne + \text{Hg} \rightleftharpoons M(\text{Hg}) + pX^{-b}
\]  

(14)

It can be shown * that the expression for the electrode potential can be
written:

\[
E_{0.5} = E_0 + \frac{0.0591}{n} \log K_{\text{instab.}} - \frac{0.0591}{n} \log [X^{-b}]^p.
\]  

(15)

Here \( p \) is the coordination number of the complex ion formed, \( X^{-b} \) in
the complexing agent and \( n \) is the number of electrons involved in the
electrode reaction. The concentration of the complex ion does not
enter into equation (15), so that the observed half-wave potential will
be constant and independent of the concentration of the complex metal
ion. Furthermore, the half-wave potential is more negative the smaller
the value of \( K_{\text{instab.}} \), i.e., the more stable the complex ion. The half-
wave potential will also shift with a change in the concentration of

* Kolthoff and Lingane, Polarography, 1946, p. 163.
the complex forming agent, and if the former is determined at two different concentrations of the complex forming agent, we have:

$$\Delta E_{a.5} = -p \cdot \frac{0.0591}{n} \times \Delta \log [X^{-b}]$$

This relationship enables one to determine the coordination number $p$ of the complex ion and thus its formula.

**VIII. 3. Quantitative technique.—General considerations.** Polarographic analysis is most conveniently carried out if the concentration of the electro-active substance is $10^{-4}$–$10^{-3}$ molar and the volume of the solution is between 2 and 25 ml. It is, however, possible to deal with concentrations as high as $10^{-2}$ molar or as low as $10^{-5}$ molar and to employ volumes appreciably less than 1 ml. Under normal conditions (in particular, concentrations of $0.0001$–$0.001M$) and with strict adherence to established technique, the reproducibility of duplicate analyses may be as good as ± 2 per cent.

Oxygen dissolved in electrolytic solutions is easily reduced at the dropping mercury electrode, and produces a polarogram consisting of

$$O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^- \quad \text{(neutral or alkaline solution)}$$

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2 \quad \text{(acid solution)}$$
The second wave is ascribed to the reduction of the hydrogen peroxide either to hydroxyl ions or to water:

\[
\begin{align*}
H_2O_2 + 2e & \rightarrow 2OH^- \quad \text{(alkaline solution)} \\
H_2O_2 + 2H^+ + 2e & \rightarrow 2H_2O \quad \text{(acid solution)}
\end{align*}
\]

It is therefore necessary to remove any dissolved oxygen from the electrolytic solution whenever cathodic regions are being investigated at which oxygen interferes. This is easily accomplished by bubbling an inert gas (nitrogen or hydrogen) through the solution for about 10-15 minutes before determining the current-voltage curve. Curve B in Fig. VIII, 3, 1, was obtained after the removal of the oxygen by unpurified nitrogen from a cylinder of the compressed gas. The gas stream must be discontinued during the actual measurements to prevent its stirring effect interfering with the normal formation of drops of mercury or with the diffusion process near the micro-electrode. By employing nitrogen and a cell with a glass dome incorporating a water seal (see Fig. VIII, 6, 5), the solution is largely protected from contact with air during the measurements; with other types of cells it may be advisable to pass the inert gas over the surface of the solution. For solutions of concentration $10^{-3}-10^{-2}M$ the writer has found that nitrogen derived from a cylinder of compressed gas (containing less than 0.05 per cent of oxygen) quite satisfactory without purification. For more dilute solutions ($< 10^{-3}$ molar) traces of oxygen should be removed from nitrogen or hydrogen derived from cylinders of the compressed gas (e.g., by passage over heated copper gauze or turnings at 400-450° or through chromous chloride solution); it is more convenient, however, to employ pure nitrogen ("white spot," oxygen content $< 0.0001$ per cent) supplied by the British Oxygen Company in cylinders. If chemical purification of the gas is employed, it should be passed through a small wash-bottle or glass "bubbler" charged with the same type of solvent as is used for the test solution, so that the gas stream will become saturated and thereby prevent change in concentration of the solution in the cell. In a neutral or alkaline supporting electrolyte and with no lead or other interfering ions present in the solution, the oxygen may be rapidly removed (ca. 10 minutes) by the addition of sodium sulphite (about 0.1 g. of $Na_2SO_3$ per 10 ml.).

The influence of temperature has already been discussed. The electrolytic cell should be immersed in a thermostat bath maintained at $\pm 0.2^\circ C$; for many purposes a temperature of $\pm 0.5^\circ C$ is permissible. A temperature of 25° C. is usually employed.

As a precautionary measure to prevent the appearance of maxima, sufficient gelatin to give a final concentration of 0.005 per cent should be added. The gelatin should preferably be prepared fresh each day; bacterial action usually appears after a few days. Other maximum suppressors (e.g., methyl red and methyl cellulose) are sometimes used.

Two or more electro-active ions may be determined successively if their half-wave potentials differ by at least 0.4 volt for univalent ions and 0.2 volt for bivalent ions provided that the ions are present in approximately equal concentrations. If the concentrations differ considerably, the difference between the half-wave potentials must be correspond-
ingly larger. If the waves of two ions overlap or interfere, various experimental devices may be employed. The half-wave potential of one of the ions may be displaced to more negative potentials by the use of complex-ion formation reagents, which are incorporated in the supporting electrolyte, for example, cupric ions by the addition of potassium cyanide. Sometimes one ion may be removed by precipitation (e.g., with lead and zinc, the lead can be rendered harmless by precipitation as sulphate; the lead sulphate formed need not be removed by filtration); the possibilities of adsorption or co-precipitation of part of the other ions must, however, be borne in mind. When one or more of the noble metals predominates (e.g., copper), this is conveniently removed by electrolysis with a mercury cathode at a carefully controlled potential; the minor base metals may then be determined in the residual solution.

VIII. 4. Evaluation of quantitative results.—Three methods which have been widely used in practice will be described.

Wave height–concentration plots. Solutions of several different concentrations of the ion under investigation are prepared, the composition of the supporting electrolyte being the same as that in which the unknown is situated. The heights of the waves obtained are measured in any convenient manner and plotted as a function of the concentration. The polarogram of the unknown is produced exactly as the standards, and the concentration is read from the graph. The method is strictly empirical, and no assumptions, except correspondence with the conditions of the calibration, are made. The wave height need not be a linear function of the concentration, although this is frequently the case. For results of the highest precision the unknown should be bracketed by standard solutions run concurrently, so that the analysis becomes a simple interpolation process.

Pilot-ion method. The relative diffusion currents of ions in the same supporting electrolyte are independent of the characteristics of the capillary electrode and, to a close approximation, of the temperature. Hence upon determining the relative wave heights of the unknown ion and of some standard or “pilot” ion added to the solution in known amount, and comparing these with the ratio for known amounts of the same two ions, previously determined, the concentration of the unknown ion may be computed. This procedure has limited application, primarily because only a small number of ions are available to act as pilot or reference ions. The main requirement for such an ion is that its half-wave potential should differ by at least 0.2 volt from the unknown or any other ion in the solution with which it might interfere. When a single unknown is present, this condition can usually be satisfied, but in complex mixtures there is seldom sufficient difference between the half-wave potentials to introduce additional waves.

Method of standard addition. The polarogram of the unknown solution is first recorded, after which a known volume of a standard solution of the same ion is added to the cell and a second polarogram is taken. From the magnitude of the heights of the two waves, the known concentration of ion added, and the volume of the solution after the addition, the concentration of the unknown may be readily calculated as follows. If \( I_1 \) is the observed diffusion current (= wave height) of the unknown solution of volume \( m \) ml. and of concentration \( X \), and \( I_2 \) is the observed diffusion current after \( n \) ml. of a standard solution
Quantitative Inorganic Analysis

of concentration $c$ have been added, then according to the Ilkovic equation:

$$I_1 = kX$$

and

$$I_2 = k(mX + nC)/(m + n)$$

from which it can be deduced that:

$$X = C \cdot \frac{\frac{nI_1}{I_2(m + n) - nI_1}}$$

The accuracy of the method depends upon the precision with which the two volumes of solution and the corresponding diffusion currents are measured. The material added should be contained in a medium of the same concentration as the supporting electrolyte, so that the latter is not altered by the addition. The assumption is made that the wave height is a linear function of the concentration in the range of concentration employed. The best results would appear to be obtained when the wave height is about doubled by the addition of the unknown amount of standard solution.

VIII, 5. Simple homemade polarograph.—Excellent current-voltage curves may be obtained with a home-made polarograph. Such an instrument is comparatively inexpensive and will enable even the smallest college to provide instruction in polarography. The essential requirements of a circuit for obtaining polarograms are: (a) a means of applying a known e.m.f. to the electrolytic cell, and (b) a device for measuring the resulting current, which is usually less than $5 \times 10^{-4}$ amps. The circuit used by the author, which is a modification of that of Müller (1941), is shown schematically in Fig. VIII, 5, 1. It can easily be
assembled from readily available components. The circuit incorporates normal cathodic and anodic polarising units. With the double-pole two-way switch $S_2$ in position $q$, the normal polarising unit is connected. It consists of an accurate voltmeter $V$, a slide wire $V_4$, a tapping key $T$, and a regulating resistance $V_3$. The 3-volt voltmeter $V$ is connected across the ends of the slide wire $V_4$, and indicates the total drop in potential across the wire; the potential drop across the wire may be varied, as indicated by the voltmeter $V$, by means of the variable resistance $V_3$ (500 ohms). The slide wire was constructed from a meter rule and a No. 36 gauge "eureka" wire (with a uniform resistance of 4.95 ohms per foot) and was mounted on a hardwood base; the sliding contact, guided by a length of curtain rail fixed parallel to the wire, was provided with a light spring in order to maintain good contact with the wire. (Any good-quality commercial slide wire of resistance 15–20 ohms will serve equally well; the slide wire of the type used for conductivity measurements, provided it has the correct resistance, is particularly suitable.)

By placing switch $S_3$ in position $p$ the cathodic and anodic polarisation unit is brought into circuit. It adds to the normal polarising unit two variable resistances $V_1$ and $V_2$ (22 ohms each) and two fixed resistances $R_{12}$ and $R_{13}$ (100 ohms each), all of which are in series: a fine-adjustment control $V_o$, consisting of a 2200-ohm carbon-track potentiometer with a 3-ohm wire-wound resistance $R_{14}$ in parallel, is inserted in series with one of the variable and the corresponding fixed resistance. They are connected (in parallel) to the slide wire $V_4$. The reference electrode is connected to the junction of the two fixed resistances $R_{12}$ and $R_{13}$: the last-named were introduced to prevent short-circuiting of the power supply across $V_3$ when the variable resistances $V_1$ and $V_2$ are set at zero. If the resistance $(R_{12} + V_1)$ is exactly equal to $(R_{13} + V_2)$, the voltage applied from $V_4$ to the electrolytic cell is zero when the slide-wire contact is set at the centre position (50 cm.): above 50 cm. the dropping mercury electrode is negatively polarised, and below 50 cm. it is positively polarised. By this means a decreasing anodic polarisation may be followed, without interruption, by an increasing cathodic polarisation. (In practice, the slide-wire contact is set at the 50-cm. mark and the variable resistances $V_1$ and/or $V_2$ are adjusted to a zero deflection on the galvanometer.)

The Cambridge spot galvanometer $G$ (with enclosed lamp and scale) employed had an internal resistance of 552 ohms, a critical damping resistance of 10,500 ohms, and a maximum sensitivity of 175 mm. per $\mu A$ or $5.7 \times 10^{-9}$ amp. per mm. A galvanometer is critically damped when it indicates the flow of current in as short a time as possible without overshooting its mark. In polarography the galvanometer is generally used to measure currents and not as a null instrument, and therefore should be critically damped at all times: this is especially important in automatically recording polarographs. The effect of the damping resistance may be visualised by recalling that a galvanometer, deflected from its zero position, will generate electricity in its coil while it is moving in its stationary magnetic field on its return to the zero position. A critical resistance or Ayrton shunt can then be found which, when placed across the terminals of the galvanometer, will slow down the movement of the coil so that it will reach its zero position without overshooting; the galvanometer is then always...
critically damped regardless of the setting of the shunt. The shunt consists of a series of accurate resistances so chosen as to render possible the selection of a convenient known fraction of the maximum sensitivity by the mere turning of a switch; the values employed were $1, \frac{1}{2}, \frac{1}{3}, \frac{1}{4}, \frac{1}{5}, \frac{1}{6}, \frac{1}{7}, \frac{1}{8}, \frac{1}{9}$, and $\frac{1}{10}$. The magnitudes of the resistances (in ohms) were computed from the formula:

$$R = (x + y)F$$

where $R$ is the total resistance between the variable contact and position 12, $x$ is the galvanometer resistance, $y$ the critical damping resistance, and $F$ is the sensitivity factor. The galvanometer employed had $x = 552$ ohms, and $y = 10,500$ ohms. The corresponding values of the fixed resistances $R_1$ to $R_{10}$ are therefore 5000, 3300, 1100, 600, 220, 110, 66, 22, 7-4, 3-7, and 11-0 respectively. In position 1 the galvanometer is short-circuited, while position 12 is that of maximum sensitivity. The twelve-way switch $S_1$ is ganged to the twelve-way switch $S_2$; the latter brings into circuit a 4000-microfarad reversible condenser $C_1$ (1 volt) in positions 2 to 11: in positions 1 and 12 the condenser is disconnected and discharged. The condenser reduces the galvanometer oscillations due to the periodic growth and fall of the mercury drops at the dropping mercury electrode. A 5000-ohm variable pre-set resistance may be connected in series with this condenser so that the amount of damping in positions 2 to 11 can be adjusted, if necessary, to a suitable value. The dropping mercury electrode is connected to the $+$ terminal of the galvanometer and to position 1 on switch $S_1$ and position 2 on switch $S_2$.

The source of e.m.f. may be either a 6-volt storage battery (< 50 ampere-hours capacity) or the power pack operating from the 200–250-volt, 50-cycle mains. Details of the power-pack circuit are shown at the right of Fig. VIII, 6, 1. The choice of power supply is made by means of the double-pole two-way switch $S_4$. In the $x$ position power is connected to the terminals on the case of the instrument. In the $y$ position power is derived from a low-voltage mains transformer $T$ working in conjunction with a bridge rectifier, the condensers $C_2$, $C_3$, and $C_4$, and the low-resistance choke $O_4$. The condensers $C_2$ and $C_3$ serve to smooth out A.C. ripple when the power pack is in use, and condenser $C_2$ tends to counteract any small changes in voltage when storage batteries are employed.

The components are mounted in a wooden cabinet provided with a sloping metal panel (see Fig. VIII, 6, 4). A signal-lamp fitting (e.g., Bulgin, type D54) with a mains indicator neon lamp (Osram or Philips) is connected in parallel with the mains on/off switch to the primary winding of the transformer; this light therefore indicates whether the power pack is switched on irrespective of whether it or batteries are being employed in the polarograph.

**Details of Components.**

- $S_1$ and $S_2$: twelve-way, one-pole, two-bank rotary selector switch (Yaxley or Oak).
- $S_3$ and $S_4$: double-pole, change-over toggle switch (Bulgin).
- $R_1$ 11-0; $R_2$ 3-7; $R_3$ 7-4; $R_4$ 22; $R_5$ 66; $R_6$ 110; $R_7$ 220; $R_8$ 660; $R_9$ 1100; $R_{10}$ 3300; and $R_{11}$ 5000 ohms: all, except $R_3$ and $R_4$, are Dubilier or Erie "gold spot" type. $R_3$ and $R_4$ were constructed from
nichrome resistance wire, 6.24 ohms per foot, 26 S.W.G., and wound
on asbestos or bakelite rod, ca. \(\frac{3}{8}\) in. diameter, shellac-lacquered and
"baked."

\[ R_{12} \text{ and } R_{13} : 100\text{-ohm (Dubilier or Erie "gold spot" type).} \]
\[ R_{14} : 3\text{-ohm wire-wound resistance (home-made).} \]
\[ K : \text{tapping key (Bulgin).} \]
\[ V_1 \text{ and } V_2 : 22\text{-ohm, variable (Bulgin).} \]
\[ V'_4 : 500\text{-ohm, variable (Bulgin).} \]
\[ V_8 : 2200\text{-ohm carbon-track potentiometer (Centralab, from Radio}
\text{Corporation, U.S.A.). (A 5000-ohm carbon-track potentiometer}
\text{(Erie or Dubilier) may also be used if the Centralab component is not}
\text{available.)} \]
\[ C_1 : 4000\text{-microfarad, 1-volt, reversible (Telegraph Condenser Co.).} \]
\[ C_2 \text{ and } C_3 : 50\text{-microfarad, 50-volt (Telegraph Condenser Co.).} \]
\[ C_4 : 0.5\text{-microfarad, 500-volt (Telegraph Condenser Co.).} \]
\[ V : \text{M.R. voltmeter, No. D. 0–3 volts in 0.1 volt, 2.5-in. dial (Elliott).} \]
\text{(The moving-coil voltmeter, type B.42, supplied by Ferranti, Ltd., is}
\text{also satisfactory.)} \]
\[ G : \text{Spot galvanometer, resistance 552 ohms, critical damping}
\text{resistance 10,500 ohms, 175 mm. deflection per } \mu \text{A, period 2.7 seconds}
\text{(Cambridge).} \]
\[ T : \text{Transformer, type OST; primary 240/220/200/0 volts, secondary}
16/11/7/0 volts, 2 amps. (M.R. Supplies).} \]
\[ RC_1, RC_2, RC_3, \text{and } RC_4 : \text{Sentercel bridge rectifier, type B15/1/IBIL}
\text{(Standard Telephones).} \]
\[ Ch_1 : \text{Low-resistance (\(\geqslant 20\) ohms), low-current, smoothing choke,}
\text{inductance about 3 henries (Garland Radio or Zenith Electric).} \]
\text{Plugs and sockets for external connexions (Bulgin).} \]

A. F. Bulgin and Co., Ltd., Bye Pass Road, Barking, Essex.
Dubilier Condenser Co., Ltd., Ducon Works, Victoria Road, North Acton,
London, W.3.
Elliott Brothers (London), Ltd., Century Works, Lewisham, London,
S.E.13.
Ferranti, Ltd., Moston, Manchester, 10.
Standard Telephone and Cables Co., Ltd., Brimar Valve Works, Foots Cray,
Kent.
"Yaxley" or "Oak" switch from British N.S.I. Co., Ltd., Keighley,
Yorks.
Zenith Electric Co., Ltd., Villiers Road, London, N.W.2.

Note on calibration of voltmeter. It is recommended that the voltmeter
be calibrated by either or both of the following methods.

With a standard resistance. Adjust the Cambridge spot galvanometer
so that the central line of the illuminated spot is accurately at the zero
position of the scale. Set up the polarograph with a potential drop
of 3.0 volts across the slide wire, and allow 15 minutes for the attain­
ment of a steady state. Replace the electrolytic cell by a standard
resistance large enough to prevent the galvanometer deflection at full
sensitivity extending beyond the full length of the scale. Place the sensitivity switch at zero, i.e., sensitivity = 1. Depress the tapping key and observe the deflection of the galvanometer spot. The current passing through the galvanometer may be computed from its known sensitivity (supplied by the manufacturers; the instrument employed gave a deflection of 175 mm. per μA). By assuming that the resistance of the galvanometer is negligible relative to the external standard resistance, the voltage across the latter may be calculated, and this value is compared with the reading on the voltmeter. This procedure may be repeated with the voltmeter set at suitably spaced values, and a calibration chart drawn up for the voltmeter.

With a standard cell. Adjust the galvanometer spot to the zero position whilst out of circuit. Set up the polarograph with a potential drop of 3.0 volts across the slide wire, and leave for 15 minutes. Replace the electrolytic cell by a standard Weston cell, taking care that the negative pole of the cell is connected to the negative lead, i.e., in opposition to the e.m.f. in the slide wire. With a suitable shunt in circuit, move the slide-wire contact gradually until the depression of the tapping key produces no deflection of the galvanometer spot; reduce the value of the shunt slowly as the balance point is approached. Read the exact position of the sliding contact (x cm.). The potential across the slide wire (100 cm.) is therefore 100 × 1.0183/x. Compare this value with the exact voltmeter reading, and thus determine the correction to be applied to the latter. Repeat the calibration for other values of the slide-wire potential.

VIII, 6. Ancillary Equipment

Mercury. Doubly distilled mercury is usually recommended for polarographic work. The re-distilled mercury of commerce is generally satisfactory for most determinations; it should be filtered through a filter-paper cone with a small pin-hole in the tip (or through a sintered-glass funnel) before use in order to remove any surface oxides or dust. Used mercury should be washed with water, thoroughly agitated for about 12 hours in contact with 10 per cent nitric acid (a filter-flask, arranged to admit air through the bottom of the mercury and connected to a water-pump, is satisfactory), then thoroughly washed with distilled water, dried with filter-paper, and re-distilled under reduced pressure (air-bath, Claisen flask with capillary, etc.).

Caution. Mercury vapour is a cumulative poison. All vessels containing mercury should be stoppered. Any spilled mercury should be immediately collected and placed in a flask containing water. Employ a tray under all vessels containing mercury and for all operations involving the transfer of mercury.

Dropping mercury electrode assembly. The assembly consists of a mercury reservoir (e.g., a 100-ml. levelling bulb), a connecting-tube between the reservoir and the capillary tube, and a small glass electrolysis cell in which the unknown solution is placed. A simple arrangement is shown in Fig. VIII, 6, 1. The heavy-walled rubber tubing, 80–100 cm. long, should be sulphur-free. Neoprene tubing is generally employed; the inside surface should be steamed out for 30 minutes before use, followed by air-drying through a cotton filter-plug. The electrolysis cell shown in the figure is the original type devised by
Heyrovsky. Electrical connexion to the mercury in the reservoir is effected by a platinum wire sealed into the end of a soft-glass tube, which is partly filled with mercury and held in place by the stopper of the reservoir.

The effective capillary tube has a length of 5–8 cm. and a bore diameter of about 0·05 mm.; the delivery tip is cut accurately horizontal. Capillaries may be made by drawing down a fine-bore tip on Pyrex thick-walled tubing having a bore diameter of about 1 mm., or they can be prepared from round-bore thermometer tubing of resistance glass; alternatively, they may be purchased, ready for use, from any manufacturer of commercial polarographs. The form of capillary electrode in which the narrow capillary tube (ca. 0·05 mm. bore) is sealed to (or has been prepared from) a length of wide-bore capillary (about 10 cm. long, internal bore 1·5 mm., external bore 7 mm.) is particularly convenient in practice, since the wide-bore capillary can be readily clamped or introduced through a rubber stopper, etc.; the risk of breakage is thus considerably reduced. The dropping rate in normal potassium chloride solution with a mercury head of about 50 cm. should be one drop in 2·5–3·5 seconds. With a drop time shorter than about 2·5 seconds the diffusion currents of very small concentrations of a reducible substance are not strictly proportional to the concentration; if the drop time is greater than 5–6 seconds the oscillations of the galvanometer, due to the periodic growth and fall of the mercury drops, become too large.

With careful treatment one capillary will remain serviceable for several months. When not in use the capillary should be kept immersed in distilled water. The flow of mercury from the capillary must be started before removing it from the distilled water; the flow after an analysis has been completed should not be stopped until the tip has been thoroughly rinsed and returned to the distilled-water vessel. Great care must be taken not to allow water or the solution to enter the capillary. If the capillary becomes partly choked, it can usually be cleared by drawing strong nitric acid through it, followed by distilled water and drying with air filtered through a cotton-wool plug.

For reproducible results with the same dropping mercury electrode it is important that the height of the mercury in the reservoir above the capillary tip should be kept constant, i.e., the same pressure on the dropping mercury tip be maintained; the small quantity of mercury passing through the capillary does not appreciably affect the volume.
in the reservoir. In the home-made polarograph assembly this condition is achieved at the upper end either by supporting the mercury bulb in a ring and clamping the mouth of the bulb or by removing a small portion of the metal from an ordinary retort ring (thus enabling the metal ring to be covered with thick-walled rubber tubing) and fitting a small metal bar with central hole through which the narrow end of the bulb passes (see figure). The clamp for the capillary is fixed to the upper of two metal rings, which can slide along the rod of the retort stand. The lower ring can be clamped in position by means of a suitable screw; the upper ring is provided with a short metal pin, and this fits tightly into a hole drilled in the lower ring, thus ensuring that the two metal rings can always be returned to the same position relative to one another. Fig. VIII, 6, 2 will make these devices clear. It may be noted that when once the upper mercury reservoir and the lower ring have been fixed to give a convenient rate of dropping for the particular capillary in use, the screw holding the support for the mercury reservoir is tightened with the aid of the special key and all further adjustments (e.g., to stop the flow of mercury drops when a determination has been completed) are made by raising the clamp holding the capillary: in this way the dropping electrode can always be returned to the original position.
An excellent stand for polarographic work is marketed by the Cambridge Instrument Company, and is shown in Fig. VIII, 6, 3. The capillary and reservoir are fixed to a carriage adjustable along the vertical rod of the stand. The capillary can thus be lifted out of the cell and replaced without altering the height of the mercury. The position of the reservoir can be adjusted to give the correct mercury height for the particular capillary in use and then secured in position with the aid of a clamping screw. The clamp holding the capillary can be swung aside and the tip of the capillary lowered into a beaker of distilled water when not in use. This dropping electrode stand is so convenient in practice, that the author strongly recommends it even with the home-made polarograph described above.

A photograph of the home-made polarograph, constructed according to the details given in the previous Section, is reproduced in Fig. VIII, 6, 4; the metre scale has been omitted, as has also the thermostat surrounding the electrolytic cell.

Numerous electrolysis cells have been described or are available commercially. A number of these, including a simple saturated calomel electrode (a), are collected in Fig. VIII, 6, 5.

(a) is the original electrolysis cell devised by Heyrovsky: common sizes are for 10 and 15 ml. respectively (diameters 30 and 40 mm.).

(b) is the Heyrovsky micro-type for very small samples.
(c) and (d) are 2-ml. and 20-ml. Cambridge cells provided with a side tube as an inlet for the gas stream and a bell-shaped cover (attached to the dropping electrode) which dips into a little water placed in the annular portion surrounding the upper part of the cell; this permits the ready escape of the inert gas but prevents entry of air. A mercury pool is used as anode, connexion being made by a sealed-in platinum wire; the latter dips into a small pool of mercury in a cell holder (see Fig. VIII, 6, 3). These cells cannot be used in a thermostat.

(e) and (f) are similar to (c) and (d), but are designed for use in a thermostat. Electrical connexion is made through a little mercury contained in the right-hand side tube.

(g) and (h) are similar to (e) and (f) except that the wide side tube on the right is employed for the introduction of a small saturated calomel electrode (e.g., (j)) or of an agar salt bridge.
(i) is the Tinsley cell for use with a quiescent mercury pool; the glass ring neck of the cell is supported in a special metal stand. The two small holes in the anode dome constitute the gas outlet and prevent a large gas pressure building up inside the dome.

(j) is a saturated calomel electrode (Cambridge) which may be used with cells (e) to (h); the small glass spiral in the constricted portion effectively prevents the saturated potassium chloride solution from running into the electrolysis cell.

An H-type of cell has found wide application; it is similar to Fig. IX, 2, 2, except that the burette is omitted.

Preparation of gelatin suppressor. Three methods of preparation are available.

(a) Dissolve 0.20 g. of powdered gelatin in a flask containing 100 ml. of distilled water which has previously been boiled for 10 minutes and then cooled to about 50° C. Stopper firmly. This solution does not usually keep for more than about a day.

(b) Dissolve 0.20 g. of powdered gelatin as under (a), add a few drops of sulphur-free toluene, and stopper firmly. This solution will keep for a few days.

(c) Dissolve 0.20 g. of powdered gelatin and 0.20 g. of A.R. phenol in warm distilled water and make up to 100 ml. in a volumetric flask. This solution is stable for at least a week.

VIII, 7. COMMERCIAL MANUAL NON-RECORDING POLAROGRAPHs

An excellent manually operated instrument, termed a voltamoscope, is manufactured by the Cambridge Instrument Company; it is comparatively inexpensive. The basic circuit is presented in Fig. VIII, 7, 1, and the actual instrument is shown in Fig. VIII, 7, 2. The voltammetric consists of a moulded case with a sloping panel carrying all the necessary control knobs, and, on the top of the case, a Cambridge spot

**Fig. VIII, 7, 1.**
galvanometer (resistance about 450 ohms) for measuring the current. On the panel a potentiometer slide wire $A$ controls the voltage applied to the electrodes; this covers the range $+0.3$ to $-2.7$ volts. The current through the potentiometer is adjusted by means of the rheostat $B$ and a standard cell, which is incorporated in the polarograph. The electrode current is measured either by the direct deflection on the galvanometer or by a second graduated potentiometer $C$; in the latter case the galvanometer is employed as a null instrument, and it may be stated that this is particularly valuable for measurements upon very dilute solutions ($10^{-5}N$ or less) when readings of the actual galvanometer deflections often become difficult. The sensitivity, controlled by the sensitivity switch $D$, can be varied over the range 1, 3, 5, 7, 10, 15, 20, 30, 50, 70, 100, 150, 200, 300, 500, 700, 1000, and 2000.

It indicates the fraction of the total current actually passing through the galvanometer. The zero adjustment knob $E$ operates a special rheostat. A rheostat $F$, marked “Damping,” is employed to vary the rate of response of the galvanometer by altering a resistance in series with the electrolytic condenser. It is important to remember that calibration should be done with the same damping control and the same sensitivity as is to be used for the test solutions. The rheostat $G$, marked “Counter Current,” controls a small reverse current through the galvanometer, which varies linearly with the voltage. On occasion it is advantageous to apply a potential (or current) through the galvanometer circuit which is in opposition to that arising from the electrode system in order, for example, (a) to balance out a large diffusion wave preceding a smaller one of a less noble ion, and (b) to reduce the effect of “condenser current” in the determination of small concentrations of substances. It is important to return the “Counter Current” to the “off” position after use. The apparatus is normally operated from the A.C. mains supply. The voltamoscope is used in conjunction with the special electrode stand depicted in Fig. VIII, 6, 3.
The Cambridge Instrument Company supply a special thermostat bath (Fig. VIII, 7, 3), designed to accommodate four cells of the type shown in Fig. VIII, 6, 5, e and f. The thermostat gives automatic temperature control to ± 0.1°C, and the control temperature can be set to any point between 25° and 35°C; it operates directly from the A.C. mains. A special feature is a device (of importance in routine measurements) by which two cells can be flushed out with hydrogen or nitrogen whilst measurements are made in a third, and the solution in the fourth cell is replaced. By rotating the top plate each cell can be brought in turn under the dropping mercury electrode.

General Note. In the description of expensive commercial apparatus it is not proposed to give detailed directions for their operation. These instructions are always supplied by the manufacturers with the instruments.

The elecdropode (Fig. VIII, 7, 4) supplied by the Fisher Scientific Company, is similar in many respects to the Cambridge instrument. Currents can be measured only on the galvanometer scale across the top of the polarograph: the simple cell and dropping electrode assembly are mounted directly on the cabinet. No provision is made for a constant-temperature bath for surrounding the cell.

The Model III manual polarograph, manufactured by E. H. Sargent and Company of Chicago, is another example of a good commercial instrument for operation on 115-volt, 50-cycle mains. The galvanometer has a sensitivity of ca. 0.005 microampere per mm., the curved galvameter scale is 315 mm. long, and the voltmeter (0–3 volts) has an accuracy of 1 per cent.
The original polarograph, designed by Heyrovsky and Shikata (1925), made use of automatic photographic recording. The underlying principle of the instrument will be evident from Fig. \textit{VIII, 8, 1}.

The Cambridge polarograph (Heyrovsky pattern) is depicted in Fig. \textit{VIII, 8, 2}, whilst the circuit diagram of the instrument is shown in Fig. \textit{VIII, 8, 3}. In the latter, \textit{A} is a milliammeter, \textit{E} is a rheostat and
current control, C a galvanometer, D the sensitivity adjustment, E the damping adjustment, F the counter-current adjustment, G the tensimeter, and H is the zero adjustment. It is similar to the Cambridge voltammetry already described, except that it is equipped for the photographic recording of the polarogram. The beam of light reflected from the galvanometer mirror falls on a ground-glass scale seen through a window in the front of the apparatus (which is used for visual observation) and also on a cylindrical lens: this lens which forms part of the camera, covers the length of a cylindrical drum around which

![Diagram of polarograph](image)

Fig. VIII, 8, 3.

gaslight photographic paper can be clamped for taking the records. The drum rotates on the same axis as the potentiometer and can be turned by hand by means of a knob at the side of the instrument, its position being shown by a scale alongside the potentiometer scale; for taking records, the drum can be driven at constant speed by a synchronous motor. It is also possible to take records at any constant potential for use in amperometric titrations.

The Sargent-Heyrovsky polarograph,* model XII, is similar to the Cambridge instrument.

The disadvantages of photographic-recording polarographs include the necessity of loading and development in a dark room and the consequent delay in obtaining and examining the polarogram. The pen-recording instruments enable one to see the graph in detail while being traced (thus permitting rapid change in adjustments, if necessary) and completely avoid the cumbersome photographic process. The mechanism of a pen recorder is necessarily more robust than that of a photographic recorder, and the current must be amplified to operate the ink recorder. The Tinsley pen-recording polarograph † is an excellent and comparatively inexpensive instrument. Fig. VIII, 8, 4 is a photograph of the polarograph, Fig. VIII, 8, 5 is a simplified schematic diagram of

* Supplied by E. H. Sargent and Company, 155 East Superior Street, Chicago 30, Illinois, U.S.A.
† Manufactured by Tinsley (Industrial Instruments), Ltd., North Circular Road, West Twyford, London, N.W.10.
the apparatus, and Fig. *VIII, 8, 6* depicts the dropping-electrode assembly normally supplied. The instrument incorporates a polarising

* This figure has not been drawn to scale; the electrolysis cell (mercury not shown) utilises only a small volume of solution and is easily repaired if broken.
unit, an amplifier, and a pen recorder. The various controls detailed below are mounted on the operating panel. The auto-potentiometer has a circular scale 6 in. in diameter, which is graduated in 0.05 volts from +0.5 to -3.0 volts. It is normally driven by a synchronous motor at the rate of 0.5 volt per minute corresponding to a movement of 1 in. on the recorder chart. The potentiometer scale and the recorder chart can also be set by hand to any desired position. The auto-potentiometer produces a linearly increasing polarising potential which is applied across the polarographic cell. The resulting current is amplified by the mirror galvanometer D.C. amplifier, the output of which operates the moving-coil recorder. Linearity and high speed of operation are achieved by a feedback circuit which controls the galvanometer. Electrical zero controls are provided for centralising the chart record and for working with solutions in which the residual current of the base electrolyte is high and also when a small diffusion step is to be measured in the presence of a larger one. The damping control introduces electrolytic condensers across the recorder, and thus provides variable damping of the pen-excursions due to the mercury drops. The polarising voltage is standardised directly against a standard cell by the standardising rheostat. There are two switches, one for the simultaneous operation of the potentiometer and the pen recorder, and one to cut out the potentiometer drive and thus permit the recorder to operate with constant voltage across the electrolysis cell. The potential for the electrolysis cell is provided by two 2-volt accumulators in series; power for the motor, galvanometer, etc., is provided from the A.C. mains (200–250 volts, 50 cycles).

The recorder is a moving-coil D.C. pen-type milliammeter; it has a continuous roll chart 3.5 in. wide calibrated in 100 units, and divided into 50 parts on the current axis and in 0.1 volt along the potential axis. The recorder is driven by a synchronous motor (200–250 volts, 50 cycles) and the standard speed is 1 in. per minute corresponding to a voltage change of 0.5 volt.
In the dropping-electrode system (Fig. VIII, 8, 6) the mercury reservoir and the electrode assembly are mounted on a counterbalanced sliding carriage, which is operated by a lever. The reservoir can be locked in position at any required height, the distance between the capillary jet and the mercury level in the reservoir remaining constant when the capillary is removed from the electrolysis cell.

The Sargent polarograph, model XXI (visible chart recording), is an elaborate recording instrument producing a record measuring 280 mm. on the current axis and 343 mm. on the voltage axis. The Leeds and Northrup Electro-ohemograph, type E,* incorporates the well-known type G Speedomax microammere recorder, and produces a visible polarogram of considerable size. Both instruments are excellent, but are, of necessity, expensive by British standards.

VIII, 9. Determination of the half-wave potential of the cadmium ion in $N$-potassium chloride solution.—Preliminary adjustments. Use either the home-made polarograph (Fig. VIII, 6, 4), the Cambridge voltam­oscope, or an equivalent manually operated instrument. Charge the reservoir with filtered, re-distilled mercury (about 1 kg.). Use, preferably, a fine capillary sealed to a thick-walled ca. 1.5-mm. capillary (compare Section VIII, 6) and carefully fit the latter into a glass bell (compare Fig. VIII, 6, 5 c) by means of a small rubber stopper. Connect the mercury reservoir to the capillary by means of neoprene tubing, prepared for use as detailed in Section VIII, 6.

Raise the mercury reservoir holder as high as possible in the stand after releasing the clamping screw and allow the mercury to drop into distilled water for 5–10 minutes. Replace the beaker of water by one containing $N$-potassium chloride solution and adjust the rate of dropping by varying the height of the mercury reservoir until the dropping rate is 20–24 per minute; then fix the mercury reservoir in position. When not in use, immerse the capillary in a small beaker of distilled water; after a few minutes lower the reservoir on the special Cambridge stand (Fig. VIII, 6, 3) without changing the position of the stop. For the home-made instrument raise the ring clamp (Fig. VIII, 6, 2) holding the dropping electrode (since the upper clamping screw is fixed when once the assembly has been adjusted for a particular capillary) and also the beaker containing water supported on a special flat ring; the latter can be attached to the vertical rod in the usual way.

Preparation of solutions. Heat 5 g. of finely-powdered A.R. cadmium sulphate in a crucible at 250° C. until anhydrous, and allow to cool in a desiccator. Weigh out 1.856 g. and dissolve it in 1 litre of water in a volumetric flask. This solution contains 1.000 g. of Cd$^{++}$ per litre.

Prepare a 2$N$ solution of potassium chloride from the A.R. salt. Dissolve 0.20 g. of powdered gelatin in warm, boiled-out, distilled water and, when cold, make up to 100 ml. in a volumetric flask.

Prepare the solution for the electrolysis cell as follows. Pipette 10 ml. of the cadmium solution into a 100-ml. measuring-flask, add 2-5 ml. of 0.2 per cent gelatin solution, 50 ml. of 2$N$-potassium chloride solution and dilute to the mark. The resulting solution (A) will contain 0.100 g. Cd$^{++}$ per litre in a base solution (supporting electrolyte) of $N$-potassium chloride with 0.005 per cent gelatin solution as suppressor.

* Supplied by the Leeds and Northrup Company, 4807 Stanton Avenue, Philadelphia, Pa., U.S.A., or by the Integra Co., Ltd., 183 Broad Street, Birmingham, 16
Measurements. Place 5 ml. of the solution A in an electrolysis cell (e.g., Fig. VIII, 6, 5 g) and immerse it in a thermostat at 25° C. Pass pure nitrogen through the solution at the rate of about two bubbles per second for 10–15 minutes in order to remove dissolved oxygen. Meanwhile renew the junction of a small saturated calomel electrode (this will be abbreviated in all subsequent discussions to S.C.E.), Fig. VIII, 6, 5 j, by introducing a little saturated potassium chloride solution from the reservoir, carefully closing the stopcock, and removing any excess of solution from the lower end of the electrode by lightly touching with quantitative filter-paper: support the S.C.E. in the wider side arm of the cell, taking care that it is in contact with the solution in the electrolytic cell. Also raise the mercury reservoir to the previously determined height (Cambridge stand; for the home-made stand (Fig. VIII 6, 2), lower the upper ring clamp to the previously determined position) and allow mercury to drop into distilled water for 5 minutes, wipe off (filter-paper) the water carefully from the capillary tip and lower the glass bell supporting the capillary (compare Fig. VIII, 6, 5 c) into the cell so that the capillary tip is immersed in the solution. Fill the annular space between the bell and the cell with distilled water to a depth of a few millimeters. Connect the saturated calomel electrode to the positive terminal and the mercury in the reservoir to the negative terminal of the polarograph. After about 15 minutes stop the passage of inert gas through the solution; the electrical measurements may now be commenced.

Carry out a preliminary test to ascertain the correct position of the galvanometer shunt. Move the slider gradually along the wire (or slowly turn the applied potential dial) and depress the tapping key at intervals. It will be found that at a certain point the current (as indicated by the deflection of the galvanometer spot) will increase rapidly. Decrease the galvanometer sensitivity by means of the shunt switch until the spot remains on the scale even at maximum applied potential.

Now, with the desired sensitivity in circuit and commencing from zero, increase the applied potential in suitable steps (say, in 0·05 volt) and read the galvanometer deflection for each value of the applied voltage. (If the voltameter is used, it is more convenient to measure the current with the aid of the cell-current dial: the galvanometer spot is brought back to zero after each reading.) When the decomposition potential of the cadmium ion is reached, the galvanometer deflection (i.e., current) increases rapidly, and smaller increments of the applied voltage (say, in 0·01 volt steps) are then advisable until the rate of change decreases considerably. It should be noted that the maximum deflection of the spot must be recorded. Plot the applied voltage (abscissa) against current (ordinates) as represented by the galvanometer deflections. (The actual current flowing at each value of the applied voltage may be easily computed, if desired, from the known sensitivity of the galvanometer, as determined by the manufacturers, and the position of the sensitivity switch.) The graph should have the form shown in Fig. VIII, 2, 2. Measure the maximum height of the diffusion wave after correction has been made for the residual current: this is the diffusion current $I_d$, and is proportional to the total concentration of cadmium ions in the solution.

Measure the height of the diffusion wave $I$, after correcting for...
the residual current, at each increment of the applied voltage. Plot values of log \( \frac{I_a - I}{I} \) as abscissae against applied voltage as ordinates as in Fig. \( \text{VIII, 9, 1.} \) Determine the slope of the graph, which should be equal to about 0.30, and read off the intercept on the voltage axis. The latter is the half-wave potential for the cadmium ion in \( \mathcal{N} \)-potassium chloride solution and should be about \(-0.64\) volt vs. the S.C.E.

**VIII, 10. Determination of the half-wave potentials of the zinc and manganese ions in \( \mathcal{N} \)-potassium chloride solution.**—This determination is conducted in \( \mathcal{N} \)-potassium chloride solution as the supporting electrolyte; the external reference electrode (S.C.E.) is now replaced by a quiescent mercury pool anode, and the cadmium ion is employed as a reference ion. The large mercury pool anode is not at a definite reproducible potential, since the value will depend upon the anions being discharged upon it; however, by utilising the known half-wave potential of the cadmium ion (previous Section), the half-wave potentials of the zinc and manganese ions can be readily computed from the resulting polarogram.

Prepare the following stock solutions:

(a) 1·000 g. of Cd\(^{++}\) per litre (from 1·856 of anhydrous cadmium sulphate), \( 2\mathcal{N} \)-potassium chloride, and 0·2 per cent gelatin solution (see previous Section).

(b) 1·000 g. of Zn\(^{++}\) per litre (from 2·4693 g. of anhydrous zinc sulphate, made by heating A.R. zinc sulphate crystals at 280° C. and cooling in a desiccator).

(c) 1·000 g. of Mn\(^{++}\) per litre (from 2·7488 g. of anhydrous manganous sulphate, made by heating A.R. manganous sulphate at 280° and cooling in a desiccator).

Prepare the test solution by introducing 10 ml. of each of the stock solutions of cadmium, zinc, and manganese sulphates, 50 ml. of \( 2\mathcal{N} \)-potassium chloride solution, and 2·5 ml. of 0·2 per cent gelatin solution into a 100-ml. volumetric flask, and diluting to the mark with distilled water. The resulting solution contains cadmium, zinc, and manganese
ions (each 0·1 g. per litre) in a base solution of \(N\)-potassium chloride and containing 0·005 per cent gelatin solution as suppressor.

Place 2–3 ml. of the test solution in an electrolytic cell of the type depicted in Fig. VIII, 6, 5 e (if cells a, f, or i are employed, larger volumes of the test solution will be required), and remove the dissolved oxygen by passing nitrogen through the solution for 10–15 minutes. The electrolysis cell should be immersed in a thermostat at 25\(^\circ\) C. Insert the glass bell carrying the dropping electrode, taking care that the fine capillary is well immersed in the solution; place 2–3 ml. of water in the annular space between the bell and the cell so as to form a water-seal. Stop the passage of nitrogen before commencing the readings. Adjust the galvanometer sensitivity as before to ensure that the maximum current will not produce too great a deflection of the galvanometer spot. Then proceed to measure current (galvanometer deflection) at gradually increasing negative applied voltages up to about \(-2.0\) volts. Plot the polarogram from the results. Determine the half-wave potentials of the three ions from the resulting polarogram; these occur in the order cadmium, zinc, and manganese with increasing negative applied potential. Utilising the previously determined value for the half-wave potential of cadmium ions with reference to the S.C.E., compute the corresponding figures for zinc and manganous ions vs. S.C.E. These constants should be of the order of 1·0 and 1·5 volts.

VIII, 11. Determination of cadmium in solution.—Two procedures may be employed: (i) that dependent upon wave height–concentration plots and (ii) the method of standard additions. The theory has been given in Section VIII, 4.

(i) Wave height–concentration plots. Prepare from the stock solution containing 1·000 g. Cd\(^{++}\) per litre (Section VIII, 9) solutions containing respectively 0·1, 0·05, 0·025, and 0·01 g. Cd\(^{++}\) per litre by transferring to 100-ml. volumetric flasks 10, 5·0, 2·5,* and 1·0* ml. of the stock solution, adding 50 ml. of 2\(N\)-potassium chloride solution and 2·5 ml. of 0·2 per cent gelatin solution to each flask and then diluting to the mark with distilled water. Mix 10 ml. of the unknown solution (which may contain, say, about 0·04 g. of cadmium per litre) in a 100-ml. measuring-flask with 50 ml. of 2\(N\)-potassium chloride solution and 2·5 ml. of 0·2 per cent gelatin solution and dilute to the mark. Record the polarograms of the four standard solutions and of the unknown solution following the procedure described in Section VIII, 9, and determine the wave heights from each polarogram. Draw a calibration curve (wave heights as ordinates, concentrations as abscissae) for the four standard solutions: read off from the curve the concentration corresponding to the wave height of the unknown solution.

(ii) Method of standard additions. The polarogram of the unknown solution will have been determined under (i). A new polarogram must now be recorded after the addition of a known volume of a standard solution containing the same ion, care being taken that in the resulting solution the concentration of the supporting electrolyte and the suppressor are maintained constant.

* More accurate results are obtained by first diluting 10 ml. of the stock solution to 100 ml. in a graduated flask, and then using 25 ml. and 10 ml. respectively of the diluted solution for the preparation of solutions containing 0·025 g. and 0·01 g. of cadmium per litre.
Place 10 ml. of the unknown solution, 5 ml. of the stock solution (1.000 g. Cd/litre), 50 ml. of 2N-potassium chloride solution, and 2.5 ml. of 0.2 per cent gelatin solution in a 100-ml. graduated flask, and dilute to the mark with distilled water. Transfer a suitable volume to the electrolytic cell in a thermostat, remove the dissolved air with nitrogen, and record the polarogram in the usual way. It is important that the galvanometer sensitivity be kept at the previous value. Determine the new wave height \( x \). If \( y \) is the wave height obtained with the unknown solution, the increase in height \( (x - y) \) is proportional to the concentration of cadmium ions added (0.05 g. Cd\(^{++}\) per litre). The concentration of the unknown solution will therefore be \( 0.05 \times y / (x - y) \) g. of cadmium per litre. Compare this value of the concentration with that found by method (i).

VIII, 12. Investigation of the influence of dissolved oxygen.—The solubility of oxygen in water at the ordinary laboratory temperature is about 8 mg. (or \( 2.5 \times 10^{-4} \) mol.) per litre. Oxygen gives two polarographic waves \( \left( O_2 \rightarrow H_2O_2 \rightarrow H_2O \right) \) which occupy a considerable voltage range, and their position depends upon the pH of the solution. Unless the test solution contains a substance which yields a large wave or waves compared with which those due to oxygen are negligible, dissolved oxygen will interfere. In general, particularly in dilute solution, dissolved oxygen must be removed by passing pure nitrogen or hydrogen through the solution; in alkaline solution the addition of a little sodium sulphite (0.1 g. per 10 ml.) is effective.

Place some \( N \)-potassium chloride solution containing 0.005 per cent gelatin in an electrolytic cell (for example, Fig. VII, 6, 5 e, or i) immersed in a thermostat. Make the usual preliminary adjustments with regard to sensitivity control of the galvanometer, observe the current (galvanometer deflection) at increasing values of applied voltage, and plot the current-applied voltage curve. Now pass oxygen-free nitrogen through the solution for 10–15 minutes, taking care that the electrolysis cell is water-sealed. Plot the polarogram using the same galvanometer sensitivity. It will be observed that the two oxygen waves are absent in the new polarogram (compare Fig. VII, 3, 1).

VIII, 13. Determination of magnesium with 8-hydroxyquinoline.—The polarogram of a dilute solution of oxine in 5 per cent ethyl alcohol consists of two waves, the first with a half-wave potential \( (E_{0.5}) \) of \(-1.39 \) volts vs. S.C.E., which does not shift appreciably with concentration in the range 0.25–2.8 \( \times 10^{-4} \) mols. per litre, and the second with a half-wave potential of \(-1.61 \) volts vs. S.C.E.; the latter shifts slightly with concentration, and considerably with changes in pH. The height of the wave at \( E_{0.5} = 1.39 \) is proportional to the concentration, and is used as the basis of the method for the determination of magnesium. In effect, the procedure consists in determining the decrease in wave height of a polarogram of a solution containing a given concentration of oxine due to precipitation of part of the oxine by magnesium ions in a buffered solution (pH, 10): the removal of the precipitated magnesium complex is unnecessary, but all elements which are precipitated by oxine must be absent or be rendered inactive. Concentrations of magnesium of the order 0.5–5 mg. per litre can be readily determined with an oxine solution of concentration 0.5 g. per litre.

Dissolve 0.2500 g. of pure magnesium in the minimum volume of
PoZa1'Ography

0·01N-hydrochloric acid and dilute to 250 ml. in a measuring-flask. Dilute 10 ml. of this solution to 100 ml. in a volumetric flask: the resulting solution will contain 100 mg. of magnesium per litre.

Dissolve 0·5 g. of A.R. oxine in 50 ml. of rectified spirit and dilute to 1 litre with water.

Prepare the buffer solution by dissolving 2·0 g. of A.R. ammonium chloride in water, adding 10-12 ml. of concentrated ammonia solution (sp. gr. 0·88) and diluting to 1 litre: adjust to pH 10 by the addition of a few drops of ammonia and the assistance of pH test strips or a pH meter. This solution is ca. 0·25M in total ammonia and 0·04M in ammonium chloride.

Into each of three 100-ml. volumetric flasks introduce 20 ml. of the standard oxine solution, 40 ml. of the buffer solution, and a little gelatin (0·2 per cent solution) suppressor. Dilute the first flask to the mark with distilled water; add 1·00 ml. (use a micro-burette) of the standard magnesium solution to the second and dilute to the mark, thus giving a solution containing 1 mg. of magnesium per litre; add a suitable volume of the unknown magnesium solution, such that the final concentration is between 0·5 and 5 mg. per litre, to the third and dilute to the mark. Shake the two flasks at intervals during 2 hours; the magnesium 8-hydroxyquinolate will gradually precipitate.

Record the polarogram of each solution using a mercury pool anode and the dropping mercury cathode over the range 0-2 volt in the usual manner. Determine the wave heights in each case for the first wave (at ca. 1·3 volts) after correction for the residual current. With a knowledge of the decrease in height of the wave produced by the standard magnesium solution (1 mg. per litre), calculate the magnesium concentration of the unknown solution from the observed reduction in height of the wave.

Space does not permit the description of the numerous other determinations for which the polarograph is particularly suitable, for example, (a) lead, cadmium, and tin in high-purity zinc and zinc alloys (8), (b) traces of cobalt in nickel, (2) (c) traces of barium in “pure” strontium preparations (3), (d) traces of copper, lead, and zinc in pure aluminium (9), and (e) small amounts of nitrobenzene in aniline (6). Full details will be found in the selected bibliography given in the following Section.
SELECTED BIBLIOGRAPHY

CHAPTER IX

AMPEROMETRIC TITRATIONS

IX, 1. THEORETICAL CONSIDERATIONS

It has been shown in the previous chapter (compare Fig. VIII, 2, 2) that the limiting current is independent of the applied voltage impressed upon the dropping mercury electrode (or other indicator micro-electrode). The only factor affecting the limiting current, if the migration current is almost eliminated by the addition of sufficient supporting electrolyte, is the rate of diffusion of electro-active material from the bulk of the solution to the electrode surface. Hence the diffusion current \((= \text{limiting current} - \text{residual current})\) is proportional to the concentration of the electro-active material in the solution. If some of the electro-active material is removed by interaction with another reagent, the diffusion current will decrease. This is the fundamental principle of amperometric titrations. The observed diffusion current at a suitable applied voltage is measured as a function of the volume of the titrating solution; the end point is the point of intersection of two lines giving the change of current before and after the equivalence point.

It may be noted that when during a titration the potential is measured between an indicator electrode and a reference electrode, the titration is termed a potentiometric one; here it is important to measure the potential relatively accurately near the end point, the latter being characterised by a maximum of the differential \(\Delta E/\Delta v\), the rate of change of potential, say, per 0.1 ml. In conductometric titrations the electrical conductance of the solution is measured during the titration, and the end point is found graphically as the point of intersection of two straight lines giving the change of conductivity before and after the equivalence point. In amperometric titrations (derived from ampere, the unit of current) the current which passes through the titration cell between an indicator electrode (e.g., the dropping mercury electrode) and the appropriate depolarised reference electrode (e.g., the saturated calomel electrode) at a suitable applied e.m.f. is measured as a function of the volume of the titrating solution. Such titrations have also been termed polarographic, polarometric, and voltammetric; the term amperometric titration will be used throughout this book.

Some advantages of amperometric titrations may be mentioned:

(i) The titration can usually be carried out rapidly, since the end point is found graphically; a few current measurements at constant applied voltage before and after the end point suffice.

(ii) Titrations can be carried out in cases in which the solubility relations are such that the potentiometric or visual-indicator methods are unsatisfactory, for example, when the reaction product is markedly soluble (precipitation titration) or appreciably hydrolysed (acid-base titration). This is because the readings near the equivalence point have no special significance in amperometric titrations. Readings are
Quantitative Inorganic Analysis

recorded in regions where there is excess of titrant, or of reagent, at which points the solubility or hydrolysis is suppressed by the mass-action effect; the point of intersection of these lines gives the equivalence point.

(iii) A number of amperometric titrations can be carried out at dilutions (ca. $10^{-4} \text{N}$) at which visual or potentiometric titrations no longer yield accurate results. (It must be noted, however, that in more concentrated solutions the potentiometric method is superior.)

(iv) "Foreign" salts may be present without interference and are, indeed, usually added as the supporting electrolyte in order to eliminate the migration current.

(v) The results of the titration are independent of the characteristics of the capillary.

(vi) The temperature need not be known as it is kept constant during the titration.

If the current–voltage curve of the reagent and of the substance being titrated are not known, the polarograms must first be determined in the supporting electrolyte in which the titration is to be carried out. The voltage applied at the beginning of the titration must be such that the total diffusion current of the substance to be titrated, or of the reagent, or of both, is obtained. In Fig. IX, 1, 1 are collected the most common types of curves encountered in amperometric titrations together with the corresponding hypothetical polarograms of each individual substance; $S$ refers to the solute to be titrated and $R$ to the titrating reagent. The slight "rounding off" in the vicinity of the equivalence point is due to the solubility of the precipitate; this curvature does not usually interfere, since the end point is located by extending the linear branches to the point of intersection. For each amperometric titration the applied voltage is adjusted to a value between $X$ and $Y$ shown in Fig. IX, $I$, $A$–$D$. In $A$ only the material being titrated gives a diffusion current (see $A'$), i.e., the electro-active material is removed from the solution by precipitation with an inactive substance (for example, lead ions titrated with oxalate or sulphate ions). In $B$ the solute gives no diffusion current but the reagent does (see $B'$), i.e., an electro-active precipitating reagent is added to an inactive substance (for example, sulphate ions titrated with barium or lead ions). In $C$ both the solute and the titrating reagent give diffusion currents (see $C'$) and a sharp V-shaped curve is obtained (for example, lead ions titrated with dichromate ions). Finally, in $D$ the solute gives an anodic diffusion current (that is, is oxidised at the dropping mercury cathode) at the same potential as the titrating reagent gives a cathodic diffusion current (see $D'$); here the current changes from anodic to cathodic or vice versa and the end point of the titration is indicated by a zero current. Examples of $D$ include the titration of halide ions with mercuric or silver ions, but some difficulty may be experienced in determining the end point; another example is the titration of tervalent titanium in acidified tartrate solution with tervalent iron.

To take into account the change in volume of the solution during the titration, the observed currents should be multiplied by the factor $(v + x)/v$, where $v$ is the initial volume of the solution and $x$ is the volume of the titrating reagent added. Alternatively, this correction may be avoided (or considerably reduced) by adding the reagent from
FIG. IX, 1, 1.
Quantitative Inorganic Analysis

a micro-burette in a concentration at least ten times that of the unknown solute. The use of concentrated reagents has the additional advantage that comparatively little dissolved oxygen is introduced into the system, thus rendering unnecessary prolonged bubbling with inert gas after each addition of the reagent. The migration current is eliminated by adding sufficient supporting electrolyte; if necessary, a suitable maximum suppressor is also introduced.

IX, 2. Technique of amperometric titrations with the dropping mercury electrode.—An excellent and inexpensive titration cell consists of a commercial resistance glass (e.g., Hysil), 100-ml., three-necked, flat or round-bottomed flask to which a fourth neck is sealed. The complete assembly is depicted schematically in Fig. IX, 2, 1. The burette (preferably of the micro-type), dropping electrode, a two-way gas-inlet tube (thus permitting the nitrogen to be bubbled either through the solution or over its surface), and an agar-potassium salt bridge (not shown in the figure) are fitted into the four necks by means of rubber stoppers. The agar–salt bridge is connected through an intermediate vessel (a weighing-bottle may be used) containing the saturated potassium chloride solution to a large saturated calomel electrode. The agar–salt bridge is made from a gel which is 3 per cent in agar and contains sufficient potassium chloride to saturate the solution at the room temperature; when chloride ions interfere with the titrations, the connexion is made with an agar-potassium nitrate bridge.

Another cell, due to Lingane and Laitinen, is shown in Fig. IX, 2, 2: the special feature of this H-cell is the sintered-glass disc and the 3 per cent agar–salt plug which separates the saturated calomel electrode from the solution being titrated. A minor disadvantage would appear to be the possibility of breaking the fragile capillary or the burette tip upon removal from the rubber stopper.

Thermostatic control is not essential provided the cell is maintained at a fairly constant temperature during the titration. It is advantage-
Amperometric Titrations

ous to store the reagent beneath an atmosphere of inert gas: this precaution is not absolutely necessary if the reagent solution has ten to twenty times the concentration of the solution being titrated and is added from a micro-burette. If the solute is electro-reducible, sufficient electrolyte should be added to eliminate the migration current; if the reagent is electro-reducible and the solute is not, the addition of a supporting electrolyte is usually not required, since sufficient electrolyte is formed during the titration to eliminate the migration current beyond the end point. It may be necessary to add a suitable maximum suppressor, such as gelatin. If the polarographic characteristics of the solute and the reagent are not known, the current-voltage curve of each must be determined in the medium in which the titration is being carried out. The applied voltage is then adjusted at the beginning of the titration to such a value that the diffusion current of the unknown solute, or of the reagent, or of both, is obtained; frequently the voltage range is comparatively large and, in consequence, great accuracy is not required in adjusting the applied voltage.

The general procedure is as follows. A known volume of the solution under test is placed in the titration cell, which is then assembled as in Fig. IX, 2, 1: the electrical connexions are completed (dropping mercury electrode as cathode; saturated calomel half-cell as anode), and dissolved oxygen is removed by passing a slow stream of pure nitrogen for about 15 minutes. The applied voltage is then adjusted to the desired value, and the initial diffusion current is noted. A known volume of the reagent is run in from a micro-burette, nitrogen is bubbled through the solution for about 2 minutes to eliminate traces of oxygen from the added liquid and to ensure complete mixing. The flow of gas through the solution is then stopped, but is allowed to pass over the surface of the solution (thus maintaining an inert, oxygen-free atmosphere). The current and burette readings are both noted. This procedure is repeated until sufficient readings have been obtained to permit the end point to be determined as the intersection of the two linear parts of the graph.

IX, 3. Determination of lead with standard potassium dichromate solution.—Both lead ions and dichromate ions yield a diffusion current at an applied potential to a dropping mercury electrode of —1.0 volt against the saturated calomel electrode (v vs. S.C.E.). Amperometric titration gives a V-shaped curve (Fig. IX, 1, 1, C). For convenience in its application to large classes of students, the exercise has been adapted to the determination of lead in A.R. lead nitrate; the application to the determination of lead in dilute aqueous solutions (10^-4-10^-4N) is self-evident.

Solutions Required. Dissolve an accurately weighed amount of A.R. lead nitrate in 250 ml. of water in a volumetric flask to give an approximately 0.01 M solution. For use in the titration, dilute 10 ml. of this solution (use a pipette) to 100 ml. in a volumetric flask, thus yielding a ca. 0.001 M solution of known strength.

Prepare a ca. 0.05 M solution of potassium dichromate using the appropriate quantity, accurately weighed, of the dry A.R. solid. Dilute this solution to ca. 0.005 M.

Prepare also a ca. 0.01 M solution of potassium nitrate from the A.R. solid, for use as the supporting electrolyte.

Procedure. Use the home-made polarograph (Fig. VIII, 6, 4 or an
Quantitative Inorganic Analysis

equivalent commercial instrument) previously described in Chapter VIII. Set up the dropping mercury electrode assembly and allow the mercury to drop into distilled water for at least 5 minutes. Meanwhile, place 25 ml. of the ca. 0·001M-lead nitrate solution in the titration cell (Fig. IX, 2, 1), add 25 ml. of 0·01M-potassium nitrate solution, complete the cell assembly and bubble nitrogen slowly through the solution for 15 minutes. Make the necessary electrical connexions. Set up the slide wire with a potential drop of 2·0 volts across it as indicated by the voltmeter, move the sliding contact to the 50-cm. position and thus apply — 1·0 volt to the cathode. Turn the three-way tap so that the nitrogen now passes over the surface of the solution. Adjust the galvanometer sensitivity so that the spot is on the scale and take the reading. Do not alter the position of the sliding contact during the determination. Add the ca. 0·005M-dichromate solution in 0·5-ml. portions until within 1 ml. of the end point, and henceforth in 0·1-ml. portions until about 1 ml. beyond the end point, and continue with additions of 0·5 ml. After each addition pass nitrogen through the solution for 1 minute to ensure thorough mixing and also deoxygenation, turn the tap so that the nitrogen passes over the surface of the solution, and note the deflection of the galvanometer spot, i.e., measure the current. It will be observed that a large initial current will decrease as the titration proceeds to a small value at the equivalence point, and then increase again beyond the equivalence point. Correct the readings of the galvanometer deflection for the change in volume of the solution due to the added reagent using the formula 

$$i_{\text{corr}} = \frac{i_{\text{obs}} (v + x)}{v},$$

where $v$ is the initial volume of the solution and $x$ is the volume of the titrating reagent. Plot the values of the corrected current (galvanometer deflections) as ordinates against the volume of reagent added as abscissae: draw two straight lines through the branches of the "curve." The point of intersection is the equivalence point. Calculate the percentage of lead in the sample of lead nitrate.

1 ml. 0·01M-K$_2$Cr$_2$O$_7$ = 0·002072 g. Pb

**IX, 4. Determination of sulphate with standard lead nitrate solution.** — Solutions as dilute as 0·001M with respect to sulphate may be titrated with 0·01M-lead nitrate solution in a medium containing 30 per cent ethyl alcohol with reasonable accuracy. For solutions 0·01M or higher in sulphate the best results are obtained in a medium containing about 20 per cent ethanol. The object of the alcohol is to reduce the solubility of the lead sulphate and thus minimise the magnitude of the rounded portion of the titration curve in the vicinity of the equivalence point. The titration is performed in the absence of oxygen at a potential of — 1·2 volts (vs. S.C.E.) at which potential lead ions yield a diffusion current. A "reversed L" graph (compare Fig. IX, 1, B) is obtained: the intersection of the two branches gives the end point. A supporting electrolyte need not be added, since the current does not increase appreciably until an excess of lead is present in the solution, and the amount of salt formed during the titration suffices to completely suppress the migration current of lead ions.

Solutions required. Prepare an approximately 0·01M solution of potassium sulphate in a 100-ml. volumetric flask using an accurately weighed quantity of the dry A.R. solid. Similarly prepare an approxi-
mately 0.1M-lead nitrate solution in a 100-ml. volumetric flask from a known weight of the dry A.R. solid.

Procedure. Use the apparatus and technique described in the previous Section. Introduce 25 ml. of the potassium sulphate solution into the cell, add 2 to 3 drops of thymol blue followed by a few drops of concentrated nitric acid until the colour is just red (pH 1.2); finally, add 25 ml. of rectified spirit or methylated spirit. Connect the saturated calomel electrode through an agar-potassium nitrate bridge to the cell. Fill the micro-burette with the standard lead nitrate solution. Pass nitrogen through the solution in the cell for 15 minutes and then over the surface of the solution. Meanwhile adjust the applied voltage to —1.2 volt (this will require setting the sliding contact at 60 cm. on the slide wire used with the home-made polarograph). Set the sensitivity control at the appropriate value and also the galvanometer spot at zero. Introduce the lead nitrate solutions from the burette in 0.5-ml. portions until within 1 ml. of the equivalence point, then in 0.1-ml. quantities for the following 2 ml., and subsequently in 0.5-ml. portions. Pass the gas stream through the solution for about 1 minute after each addition (more dilute solutions will require up to 3 minutes to assist the precipitation of the lead sulphate) and then over the surface before reading the galvanometer deflection (current). Correct the current readings for the change in volume of the solution due to the added reagent as in the previous experiment. Read off the equivalence point from the amperometric titration curve drawn from your results.

Calculate the percentage of SO₄ in the sample of A.R. potassium sulphate.

\[ 1 \text{ ml. } 0.1M\text{-Pb(NO₃)₂} = 0.009606 \text{ g. } \text{SO}_4 \]

IX, 5. Determination of nickel with dimethylglyoxime.—The nickel solution (concentration less than 0.002M) is introduced into an ammonium hydroxide-ammonium chloride supporting medium and, after deoxygenation, titration is carried out at an applied voltage (—1.85 volts) at which both nickel and dimethylglyoxime are reducible. A V-shaped titration graph (Fig. IX, 1, 1, 0) is obtained.

Solutions required. (i) Prepare a 0.02M-dimethylglyoxime solution by dissolving 0.2322 g. of A.R. dimethylglyoxime in 95 per cent ethyl alcohol (rectified spirit) and make up to 100 ml. in a measuring-flask with the same solvent.

(ii) Prepare an approximately 0.01M solution of nickel ammonium sulphate by weighing out accurately about 0.395 g. of the salt (preferably of A.R. quality) and dissolving in 100 ml. of water in a volumetric flask. Dilute 25 ml. of this solution to 250 ml. in a 250-ml. volumetric flask, thus giving a ca. 0.001M solution.

(iii) Prepare the base solution by dissolving 8.0 ml. of concentrated ammonia solution (sp. gr. 0.88) and 10.70 g. of A.R. ammonium chloride in water and dilute to 1 litre in a volumetric flask. The resulting solution is 1.0M in ammonium hydroxide and 0.2M in ammonium chloride.

Procedure. Use the four-necked 100-ml. titration flask depicted in Fig. IX, 2, 1 including an agar-potassium nitrate bridge and a micro-burette. Place 25 ml. of the ca. 0.001M-nickel solution, 25 ml. of the base solution, and 1 ml. of 0.2 per cent gelatin solution in the clean, dry titration vessel; the base solution will now be ca. 0.5M in ammonium
hydroxide and ca. 0.1 M in ammonium chloride. Pass oxygen-free nitrogen through the solution for 15 minutes. Raise the dropping mercury electrode reservoir and allow the mercury to drop into distilled water for 5 minutes. Meanwhile connect a saturated calomel electrode through an intermediate saturated potassium chloride solution by means of an agar-salt bridge to the titration vessel. Fill the micro-burette with the 0.02 M-dimethylglyoxime solution and insert the tip inside the titration flask. The instrumental experimental details refer to the home-made polarograph (Fig. VIII, 6, 4) and are similar to those given in Section IX, 4; they can be readily adapted for a commercial instrument such as the Cambridge voltammetry.

Set the applied potential at $-1.85$ volts versus the saturated calomel electrode, commence the flow of mercury from the dropping electrode and note the maximum deflection of the galvanometer spot. Add the dimethylglyoxime solution from the micro-burette in suitable increments (e.g., 0.2 ml.) until within 1 ml. of the end point; then reduce the additions to 0.05–0.1 ml. and continue well beyond the equivalence point. After each addition pass nitrogen through the solution for 1 minute to deoxygenate and to mix the solution, and then observe the galvanometer deflection (current). It will be observed that the galvanometer deflection (current) decreases linearly to the end point and then increases more rapidly. Plot current (ordinates) against volume of dimethylglyoxime solution (abscissa), making the appropriate correction for the volume of reagent added at each reading. The equivalence point is the point of intersection of the two linear branches of the graph. Calculate the percentage of nickel in the sample of nickel ammonium sulphate.

$$1 \text{ ml. } 0.02M\text{-dimethylglyoxime} = 0.0005869 \text{ g. Ni}$$
IX. 6. SELECTED BIBLIOGRAPHY

Accounts of Amperometric Titrations are to be found in references 1, 2, 3, 4, 6, and 7 in Section VIII, 15.

CHAPTER X

GAS ANALYSIS

X. 1. General discussion.—The methods of gas analysis may be classified as follows:

1. Volumetric methods.* A measured volume of the gas mixture, at a known temperature and pressure, is subjected to selective chemical reagents (absorbents) to remove the various constituents in succession, the quantities so removed being determined by the resultant diminution in volume. When there is no suitable absorbent for the gas to be determined (e.g., methane), it is frequently possible to mix it with excess of another gas (e.g., oxygen) with which it reacts chemically (often in the presence of a catalyst) and under proper conditions to determine the change in volume which takes place.

In a precision form of apparatus, due to Bone and his co-workers (see Section X, 6E), the gas is expanded to a fixed volume and the pressure exerted is measured, as is also the diminution in pressure of the gas after each absorption when expanded to the same fixed volume. The constant-volume method may also be employed with the Ambler portable apparatus (Section X, 6D).

2. Titration methods. The constituent sought is absorbed in a liquid reagent of known concentration. This method is frequently employed for gases, such as sulphur dioxide, which are soluble in water. An interesting example is the determination of small quantities of carbon monoxide by passage over heated iodine pentoxide:

\[ \text{I}_2\text{O}_5 + 5\text{CO} = 5\text{CO}_2 + \text{I}_2 \]

the liberated iodine is titrated with dilute standard sodium thiosulphate solution.

3. Gravimetric methods. The gas is absorbed by, or reacts with, a weighed amount of the reagent, or else is absorbed in a liquid and a precipitate is subsequently weighed. Thus sulphur is determined in coal gas (Referees' method) by burning a known volume in a special Bunsen burner; the air for the combustion passes over a shelf containing ammonium sesquicarbonate, and the liberated ammonia carries the sulphur dioxide with it. The gases are absorbed in water, the resultant solution treated with a little pure bromine, acidified with dilute hydrochloric acid, warmed to remove excess of bromine, and the sulphur determined by precipitation as barium sulphate in the usual manner.

4. Physical methods. The constituents are determined by measurement of their physical properties, such as density, thermal conductivity, viscosity, and refractivity.

The following account of gas analysis is intended merely as an introduction to the subject, and will be considered under two headings: (a) analysis of gaseous mixtures, and (b) the determination of the volume

* The term volumetric in this connexion is restricted to processes in which gas volumes are measured.
of a gas produced in a chemical reaction and its application to the analysis of solids and liquids. For further details, the reader is referred to the standard text-books on gas analysis (see Section X, 17).

X, 2. **Sampling.**—The first step in the analysis of a gaseous mixture is the collection of a representative sample of the gas in a suitable vessel. If a large quantity of the gas is available it may be either passed or aspirated through a sample tube of the type shown in Fig. X, 2, 1 (a) or (b). The former has two two-way capillary taps; the latter has two three-way capillary stopcocks, which permit the flushing out of the connecting tubes with the sample itself or with a confining liquid. When the quantity of gas available is limited, the apparatus shown in Fig. X, 2, 2 may be used: the connexions are cleared of air by blowing or aspirating some of the gas through the upper tap, or alternatively by evacuating the connexions from the same place and filling them with mercury. The gas is collected in \( S \) by lowering the reservoir \( R \).

If a sample of the gas is to be collected and kept for analysis for a considerable time, the portions of gas taken for analysis must be displaced with mercury. A small gasometer that is suitable for prolonged storage is shown diagrammatically in Fig. X, 2, 3. The gas is contained in the large glass bulb \( A \), which carries a capillary U-tube \( B \) at the top, and at the bottom is connected to the levelling bulb \( C \) by means of a rubber tube; the capillary is closed by means of a rubber tube and pinch-cock \( D \). The apparatus is first filled with mercury: by
lowering or raising the levelling-bulb, gas can be drawn in or driven out as desired. If the gas sample is to be kept for some time, the capillary tube $B$ is filled with mercury by inserting a small pipette at $D$. A simple gasometer may also be constructed from a round-bottomed flask fitted with a two­holed rubber stopper and bent glass tubes as shown in Fig. $X$, 2, 4: the right-hand tube is connected to a levelling-bulb by means of rubber tubing as in Fig. $X$, 2, 3.

**X, 3. Purification of mercury.**—The mercury employed in analysis should be carefully purified. If impure, it clings to the glass, and accurate readings are impossible. The principal impurities in ordinary mercury are copper, cadmium, and zinc. The impurities are largely removed by allowing the mercury to run in a fine stream through a length of 5 per cent nitric acid in the apparatus shown in Fig. $X$, 3, 1. A glass tube of about 1 in. bore and 20–30 in. length is fused to an S-shaped glass capillary of about 2 mm. bore. The main tube is filled with 5 per cent nitric acid, and the siphon is so shaped that the bottom of the tube always contains a little mercury. An ordinary funnel containing a filter-paper folded in the usual way is supported above the apparatus with the stem just dipping into the nitric acid. A small hole is then made in the apex of the filter-paper by means of a pin, and the mercury poured into the filter. The mercury usually takes a zig-zag course as it flows in the form of a fine spray through the dilute acid; any dust, etc., contaminating the mercury is retained in the filter, together with a little mercury. The mercury collects in the bottom of the tube, and siphons over into the collecting-bottle or beaker. The process should be repeated a second time, and the mercury finally passed through a column of water in a similar apparatus. The mercury may be dried by heating to 100–150°C. (preferably under reduced pressure) in a fume cupboard provided with an efficient draught. MERCURY VAPOUR IS HIGHLY POISONOUS AND THE EFFECT IS CUMULATIVE; hence exposure of mercury to the open atmosphere should be reduced to the absolute minimum, and all operations with mercury at elevated temperatures must be conducted in a fume cupboard. All bottles containing mercury should be stoppered.

For most purposes the mercury obtained by the above process is suitable for use. If mercury is to be used for calibrating measuring apparatus, it is best distilled under reduced pressure in a slow stream of air; under these conditions the volatile metals, cadmium, zinc, etc., form non-volatile oxides, and complete purification of the mercury from these metals can be obtained.
All apparatus utilising mercury should be set up on a wooden base having a raised edge, which will serve to retain any mercury spilt during any of the operations. The base should be provided with a small hole, ordinarily closed with a cork, through which the mercury may be swept and recovered. For picking up spilled globules of mercury, the special pipette shown in Fig. X, 3, 2 is useful: suction may be applied by filter-pump or mouth through a rubber tube. The bulb forms a reservoir or safety trap.

**X, 4.** Correction of volume of gas for temperature and pressure.—The volume of a gas depends upon the temperature and pressure to which it is subjected. In all cases where a gaseous volume is measured the observed volume must be reduced to the corresponding value under normal conditions of temperature and pressure. The most generally employed temperature is 0° C., and the most generally employed pressure is that due to a column of mercury 76·0 cm. in height and of density 13·596 (i.e., at 0° C.): these are usually termed N.T.P. The variation of the density of mercury over the range 0–30° C. is 0·0738, thus an error of about 0·5 per cent would be introduced by a variation of 30° C. in the temperature of the barometer. Table I contains the values of the density of mercury at various temperatures.

**Table I.—Density of Mercury (in grams per ml.)**

<table>
<thead>
<tr>
<th>Temp. °C.</th>
<th>0.</th>
<th>2.</th>
<th>4.</th>
<th>6.</th>
<th>8.</th>
<th>10.</th>
<th>12.</th>
<th>14.</th>
<th>16.</th>
</tr>
</thead>
<tbody>
<tr>
<td>−20°</td>
<td>13·645</td>
<td>13·640</td>
<td>13·635</td>
<td>13·630</td>
<td>13·625</td>
<td>13·620</td>
<td>13·615</td>
<td>13·610</td>
<td>13·605</td>
</tr>
<tr>
<td>0°</td>
<td>13·596</td>
<td>13·591</td>
<td>13·586</td>
<td>13·581</td>
<td>13·576</td>
<td>13·571</td>
<td>13·566</td>
<td>13·561</td>
<td>13·556</td>
</tr>
<tr>
<td>20°</td>
<td>13·546</td>
<td>13·541</td>
<td>13·536</td>
<td>13·532</td>
<td>13·527</td>
<td>13·522</td>
<td>13·517</td>
<td>13·512</td>
<td>13·507</td>
</tr>
<tr>
<td>40°</td>
<td>13·497</td>
<td>13·492</td>
<td>13·488</td>
<td>13·484</td>
<td>13·479</td>
<td>13·474</td>
<td>13·469</td>
<td>13·463</td>
<td>13·458</td>
</tr>
<tr>
<td>60°</td>
<td>13·449</td>
<td>13·444</td>
<td>13·440</td>
<td>13·436</td>
<td>13·432</td>
<td>13·427</td>
<td>13·422</td>
<td>13·417</td>
<td>13·412</td>
</tr>
<tr>
<td>80°</td>
<td>13·400</td>
<td>13·395</td>
<td>13·390</td>
<td>13·386</td>
<td>13·381</td>
<td>13·376</td>
<td>13·371</td>
<td>13·366</td>
<td>13·362</td>
</tr>
<tr>
<td>100°</td>
<td>13·352</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The formula for applying the correction is:

\[ H_o = H_t \left(1 - (\beta - \alpha)t\right) \]

where \( H_t \) is the height of the barometer at \( t \)° C., \( H_o \) is the reduced height at 0° C., \( \beta \) is the coefficient of linear expansion of mercury, and \( \alpha \) is the coefficient of expansion of the material of the barometer scale.

If \( V \) is the volume of dry gas measured at a pressure of \( P \) mm. of mercury (corrected for temperature as already explained) and a temperature of \( t \)° C., then it follows by application of Boyle's and Charles' laws that the volume \( V_o \) at N.T.P. is given by:

\[ V_o = V \times \frac{P}{760} \times \frac{273}{(273 + t)} \]

If the gas is measured wet, i.e., saturated with water vapour, the pressure \( P \) must be reduced by the vapour pressure of water at the
temperature of the measurement. Table II contains the values of the vapour pressure of water at various temperatures.

**TABLE II.—PRESSURE OF AQUEOUS VAPOUR (IN MM. OF MERCURY)**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>4.80</td>
<td>10°</td>
<td>9.17</td>
<td>20°</td>
<td>17.39</td>
</tr>
<tr>
<td>1°</td>
<td>4.94</td>
<td>11°</td>
<td>9.70</td>
<td>21°</td>
<td>18.50</td>
</tr>
<tr>
<td>2°</td>
<td>5.30</td>
<td>12°</td>
<td>10.46</td>
<td>22°</td>
<td>19.66</td>
</tr>
<tr>
<td>3°</td>
<td>5.89</td>
<td>13°</td>
<td>11.16</td>
<td>23°</td>
<td>20.89</td>
</tr>
<tr>
<td>4°</td>
<td>6.10</td>
<td>14°</td>
<td>11.91</td>
<td>24°</td>
<td>22.18</td>
</tr>
<tr>
<td>5°</td>
<td>6.63</td>
<td>15°</td>
<td>12.70</td>
<td>25°</td>
<td>23.55</td>
</tr>
<tr>
<td>6°</td>
<td>7.00</td>
<td>16°</td>
<td>13.54</td>
<td>26°</td>
<td>24.90</td>
</tr>
<tr>
<td>7°</td>
<td>7.49</td>
<td>17°</td>
<td>14.42</td>
<td>27°</td>
<td>25.51</td>
</tr>
<tr>
<td>8°</td>
<td>8.02</td>
<td>18°</td>
<td>15.35</td>
<td>28°</td>
<td>26.10</td>
</tr>
<tr>
<td>9°</td>
<td>8.57</td>
<td>19°</td>
<td>16.35</td>
<td>29°</td>
<td>27.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30°</td>
<td></td>
<td>30°</td>
<td>29.55</td>
</tr>
</tbody>
</table>

When the determinations are made rapidly and comparative values only are required (as in a technical analysis), the correction for temperature and pressure is often omitted; provided no appreciable variations have occurred during the analysis. It may be mentioned that a variation of 7 mm. in pressure or of 3° C. in the temperature introduces an error of the order of 1 per cent in the percentage analysis of the gas.

**Automatic correction to N.T.P.** Various instruments have been devised with the object of eliminating the above calculations of a volume of gas to N.T.P. One of the best known is Lunge's gas volumeter: this is particularly useful where a large number of volume measurements have to be made as, for example, in the measurement of the volume of gas evolved from a weighed quantity of solid or liquid. The device is capable, however, of general application. The apparatus is shown in Fig. X, 4, 1. A is the graduated tube in which the gas is to be measured, B is the "control" or "compensation" tube, which has a spherical or cylindrical bulb at the upper end; the volume to the first mark of the latter is 100 ml., the remaining narrow portion of the tube being calibrated up to 130-140 ml. in 0.1 ml. The "control" tube is set once for all at the beginning of the work by observing the temperature and pressure, and calculating the volume which 100 ml. of dry (or moist) air at N.T.P. would occupy under these conditions.* The necessary volumes \( V \) are given by the expressions:

for dry gases \( V = \frac{100 (273 + t)}{273 \times P} \times 760 \)

for moist gases \( V = \frac{100 (273 + t)}{273 \times (P - p)} \times 760 \)

where \( P \) is the atmospheric pressure expressed in mm. of mercury, \( t \) is the temperature in °C., and \( p \) is the vapour pressure of water in mm. of mercury at \( t^\circ \) C.

* The necessary volumes \( V \) are given by the expressions:

for dry gases \( V = \frac{100 (273 + t)}{273 \times P} \times 760 \)

for moist gases \( V = \frac{100 (273 + t)}{273 \times (P - p)} \times 760 \)

where \( P \) is the atmospheric pressure expressed in mm. of mercury, \( t \) is the temperature in °C., and \( p \) is the vapour pressure of water in mm. of mercury at \( t^\circ \) C.
Gas Analysis

"control" tube is then filled to the volume so calculated. If now the levelling tube \( C \) is adjusted so that the mercury in \( B \) is levelled on this 100-ml mark, and the measuring-tube \( A \) is adjusted so that the mercury levels in \( A \) and \( B \) are the same, the gas in \( A \) is under the same conditions of temperature and pressure as that in \( B \). The reading on \( B \), however, is known to represent the true volume of the gas in \( B \) corrected to N.T.P., hence the volume read on the graduated tube \( A \) will correctly represent the volume at N.T.P. \( B \) is kept dry or wet according as to whether the gas in \( A \) is dry or wet: the tubes are kept dry or wet by means of a drop of concentrated sulphuric acid or of water respectively. The instrument should be used in a room at uniform temperature, and care must be taken to avoid heating one limb unequally either by contact with the hands or by unequal exposure to heat or draught. It may be mentioned that a difference of only 1° C. would mean a variation of 0.3 per cent in the gas volume.

There are large numbers of automatic compensators, but for these the reader is referred to treatises on gas analysis.

**X, 5. Calibration of gas measuring vessels.**—For work of only moderate precision the calibration of gas burettes, etc., is usually unnecessary, since instruments can be obtained with fairly accurate graduations. If, however, high accuracy is required, or the graduation is suspect, or the apparatus has been made or repaired in the laboratory, calibration must be carried out. Either the direct weighing method or that employing a "burette calibrator" (Section II, 22) may be used. The liquid employed in calibration should be the same liquid as is subsequently to be used in the burette, etc. In the majority of cases mercury is employed. A cathetometer is to be preferred for viewing the meniscus. The temperature of the mercury is, of course, noted, and the volume is calculated from the weight with the aid of Table I.

**Meniscus correction.** Gas burettes are usually calibrated inverted (see Fig. X, 5, 1). If we consider the calibration of the burette in Fig. X, 5, 1 (a) with mercury (which forms a convex meniscus), the volume desired is up to the plane \( CD \); it is evident that the volume of mercury weighed did not include the space \( ABC \) and \( BED \). Moreover, since the instrument is to be used in the reverse position, the error is really twice as great, as is clear by inspection of Fig. X, 5, 1 (b). This is called the double-meniscus correction, and will obviously depend upon the internal diameter of the tube: the correction will be positive. If water is used in the burette for analysis and calibration purposes the meniscus is concave upwards, and the correction, instead of being positive, as in the case of mercury, will be negative. Table III, due to H. Göckel (1903), gives the values for the double-meniscus correction with mercury and water respectively for tubes of various diameters.
TABLE III.—DOUBLE MENISCUS CORRECTION FOR WATER AND MERCURY

<table>
<thead>
<tr>
<th>Diameter of Tube (Mm.)</th>
<th>Double Meniscus Correction (ml.)</th>
<th>Diameter of Tube (Mm.)</th>
<th>Double Meniscus Correction (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mercury</td>
<td>Water</td>
<td>Mercury</td>
</tr>
<tr>
<td>1</td>
<td>0.0026</td>
<td>0.0091</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>0.0052</td>
<td>0.0043</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>0.0090</td>
<td>0.0093</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>0.0128</td>
<td>0.0144</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>0.0200</td>
<td>0.026</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>0.027</td>
<td>0.039</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>0.035</td>
<td>0.062</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>0.043</td>
<td>0.084</td>
<td>21</td>
</tr>
<tr>
<td>9</td>
<td>0.056</td>
<td>0.114</td>
<td>22</td>
</tr>
<tr>
<td>10</td>
<td>0.058</td>
<td>0.144</td>
<td>23</td>
</tr>
<tr>
<td>11</td>
<td>0.080</td>
<td>0.190</td>
<td>24</td>
</tr>
<tr>
<td>12</td>
<td>0.091</td>
<td>0.235</td>
<td>25</td>
</tr>
<tr>
<td>13</td>
<td>0.104</td>
<td>0.263</td>
<td></td>
</tr>
</tbody>
</table>

X, 6. Apparatus employed in gas analysis.—Numerous forms of apparatus have been designed for gas analysis, and all that can be attempted in this Section is to give a brief account of the construction of only a few typical forms of apparatus.

A. Hempel's apparatus. This apparatus was formerly extensively employed for analyses of an accuracy of about 0.5 per cent. It consists of two parts, the burette, which includes a measuring-tube and a levelling-tube, and the pipette. The gas is usually measured over water or some aqueous solution.

The Hempel-Winckler gas-burette consists of two glass tubes mounted on feet, one tube being graduated to 100 ml. in 0.2 ml. (the burette proper) and the other plain (the pressure tube). They are connected at the feet by a long rubber tube as in Fig. X, 6, 1. Here the burette is shown with a two-way tap at the upper end and a three-way tap at the lower end (this is the Winckler modification of the original Hempel burette, and must be employed for gases which are soluble in water). The original Hempel burette contained no glass taps, but was closed by a pinch-cock on a rubber tube at the upper end (this is shown in Fig. X, 6, 9 in connexion with the method of manipulation); the upper end consists of a capillary tube of 1 mm. internal and 6 mm. external diameter. The glass-tap burette is, however, more convenient in practice and more accurate.

A simple Hempel gas pipette is shown in Fig. X, 6, 2. This consists of two large bulbs A and B joined by the tube D; C is a capillary U-tube of 1 mm. internal diameter and about 6 mm. external diameter. Bulb A holds about 150 ml. and bulb B about 100 ml., so that when 100 ml. of gas is brought into A, sufficient space for the absorbing liquid will remain. The pipette is securely fastened to a wooden or iron stand; an iron stand with a four-sided base is generally preferable to wood because: (i) its greater weight renders the apparatus more stable and
(ii) it cannot warp. This pipette is employed for submitting the gas originally present in the burette to the action of a special liquid absorbent. The bulb $A$ is filled with the absorbent liquid by pouring the latter into $B$ and then sucking the air out of the apparatus at the capillary $C$; the liquid should reach the siphon bend of the capillary tube, and bulb $B$ should be nearly empty. It is convenient to keep a number of these pipettes filled with various absorbents (see Section X, 7), well corked (or closed by rubber "policemen") and labelled with the date on which fresh reagent was introduced. On each occasion that the pipette is used, the fact is noted on the label; in this way it is possible to know approximately when it is necessary to re-charge the apparatus.

A pipette suitable for solid (and liquid) reagents, such as phosphorus in water, is shown in Fig. X, 6, 3. The solid reagent is introduced through $D$, which is then closed with a rubber stopper; the latter is securely wired into place. This pipette is also useful for liquid reagents.
(e.g., potassium hydroxide for carbon dioxide determinations), for it may be filled with rolls of wire gauze or with fine glass rods before filling the pipette with the reagent; the gas is thus exposed to a larger surface of the reagent, and absorption is more rapid.

For solutions which undergo change upon exposure to the air, such as an alkaline solution of pyrogallol or an ammoniacal solution of cuprous chloride, the double-absorption pipette (Fig. X, 6, 4) is employed.

Here the reagent in B is in contact with an atmosphere free from oxygen, the indifferent gas being confined over water in the bulbs C and D. This pipette is filled as follows. Tube E is first closed with a rubber stopper, and the apparatus is filled with hydrogen or nitrogen by passing the gas through it. The reagent is introduced by pouring it through the tube E, and air-free water in through G until the bulb C is almost full—in order to form a water-seal. The tube E is then closed by a rubber stopper, and wired on. Fig X, 6, 5 is a double-absorption pipette, but adapted for use with a solid (or liquid) absorbent.

Fig. X, 6, 6 shows the simple absorption pipette used for fuming sulphuric acid. This has an upper small bulb, about 5 cm. in diameter, filled with
gas beads or broken glass in order to increase the absorbing surface. The ends of this pipette are closed when not in use by small glass caps, which can be made air-tight with rubber bands; a considerable improvement is effected by the use of ground-glass caps.

Fig. X, 6, 7 depicts a Hempel explosion pipette: this contains mercury instead of water. A slow-combustion pipette is illustrated in Fig X, 6, 8. The latter consists of a Hempel pipette for solid reagents with iron (or nichrome) electrodes inserted through the tubulation; the electrodes terminate in a platinum spiral $P$, which is heated by a current of 2–3 amps. at 6 volts.

Manipulation of the Hempel apparatus. The complete apparatus is shown in Fig. X, 6, 9. The experimental details for a simple Hempel burette (with pinch-cock) will be given; the student should have no difficulty in modifying these to the use of the Hempel-Winckler burette. It is recommended that the pinch-clamp at $E$ be of the Day type,* as this is far superior to the simple pinch-cock usually employed with burettes. If the burette has been in use, clean it thoroughly in the usual manner (Section II, 22), and rinse it well with distilled water. Make sure that the thick rubber tubing ("pressure tubing") joint at the

upper end of the burette is securely wired.* Open the pinch-clamp at 
E, and slip it down over the capillary tube. Pour water that has been 
saturated with the gas mixture to be analysed into the burette until 
A and B are rather more than half-full. Drive out all the air from the 
rubber tubing connecting A and B by raising and lowering the tubes 
alternately, keeping the rubber tubing taut during the process. Raise 
A until the water begins to flow out of the top of B, then close the 
rubber tube of the burette with the pinch-clamp, which is placed close 
to the end of the capillary. Compress the rubber tubing at C between 
the thumb and fingers of the left hand, and pour out the excess of water 
that is in A.

The next step is to measure out exactly 100 ml. of the gas sample. Insert 
into the rubber tubing at E a capillary tube connected with the supply 
of the gas to be analysed, after first displacing the air in this connecting 
capillary by the gas. Hold the upper part of A in the left hand, lower 
it below B, and open the pinch-clamp E with the right hand. Introduce 
somewhat more than 100 ml. of gas into the burette. Close the 
pinch-cock E, level A and B, and allow the water in the burette to drain 
for 2 minutes. Disconnect the capillary tube from the source of gas, 
and adjust the volume of the gas by suitably manipulating the pinch-
clamp until it is exactly 100 ml., when the levels of the liquids in the 
two tubes are the same.

The next stage is the absorption of one of the gaseous components of 
the mixture. Connect the burette and absorption pipette exactly as in 
Fig. X, 6, 9: the burette and levelling tube should be on a flat table. Insert 
into the rubber tubing G the bent capillary tube F. This connect-
ing capillary has the same dimensions as the capillary tubes of the 
burette and pipette, viz., 6 mm. external and 1 mm. internal diameter; 
the horizontal portion is about 6 cm. long and the legs each about 2·5 
cm. long. Slip a long piece of rubber tubing over the tube H of the 
pipette. Grasp F between the thumb and fingers of the right hand, 
squeeze the rubber tube E on the capillary tube of the burette between 
the thumb and fingers of the left hand, blow gently through H until the 
liquid in the pipette is driven over to a mark on the farther end of the 
horizontal portion of the capillary tube F, and then insert the end of 
F into the rubber tube on the burette. If the connexion is properly 
made, there will be practically no movement of the reagent in the 
capillary. Even if the air enclosed in the connexion between the burette 
and pipette should occupy about 1 cm. length of the capillary, the error 
may be neglected, since capillary tubing of about 1 mm. bore occupies 
only about 0·01 ml. per cm. length. If, however, more than 1 cm. 
length of air remains in F, F should be slipped out of E and the opera-
tion repeated.† The apparatus is now ready for the absorption of a gas.

* When joining together glass tubes by rubber tubing, the ends of the tubes should 
be rounded off in the flame, and then brought close together within the piece of rubber 
tubing. The rubber tubing is secured in place by means of wire ligatures, composed of 
copper wire about 1–2 mm. in diameter. Each ligature should consist of only one turn 
of the wire around the tube, the ends being drawn and tightly twisted together by means 
of a pair of pliers. Long rubber connections should be avoided, not only because the 
rubber tubing is somewhat porous, but also because air in the tube tends to adhere 
tenaciously to the walls.

† Certain reagents must never be allowed to come into contact with the rubber 
connexion at G; in such cases, the liquid from the pipette is forced upwards until it 
stands just below this rubber connexion and allowance is made for the air remaining 
in the capillary tubes. The correction is readily made, since 10 cm. of the 1-mm. bore 
capillary corresponds to ca. 0·1 ml. of air.
Open the pinch-clamp $E$, and slowly raise the levelling-tube $A$, thus driving the gas over into the pipette. Allow the water to flow into the capillary tube $F$ until it reaches the point to which the reagent has been driven over, and then close the pinch-clamp. A thin layer of the reagent adheres to the walls of the capillary, and this is sufficient to remove most of the absorbable constituent of the gas mixture remaining in the capillary. With some gases (e.g., carbon dioxide) absorption occurs rapidly in the pipette, but with others (e.g., oxygen and carbon monoxide) it is necessary to shake the pipette after the gas has been transferred into it. In the latter case, place another pinch-clamp on $G$, hold the burette in the left hand and gently rock the pipette stand backward and forward on the front edge of the base. After the constituent that is to be removed is completely absorbed, the gas is transferred back into the burette. This is done by holding the levelling-tube in the left hand and in such a position that the confining liquid in it stands at a slightly lower level than in the burette, open pinch-clamp $E$ (and, if necessary, that at $G$) and lower the levelling-tube slowly until the gas is drawn back into the burette and the liquid in the pipette reaches a point on $F$ at which it originally stood; close the pinch-clamp $E$, level approximately, allow the water to drain for 2 minutes, level accurately, and take the reading of the volume of the gas in the burette. Absorption may not be complete in one operation. It is therefore advisable to transfer the gas back to the absorption pipette and to repeat the process until no further diminution in volume occurs.

By the use of a series of Hempel pipettes the gas is subjected to the action of various absorbents, one after another, until the complete composition is ascertained. As already pointed out, the connexions must in all cases be made with stout rubber tubing ("pressure" tubing) which are secured with copper-wire ligatures.

For gases which are appreciably soluble in water, the levelling-tube containing water cannot, of course, be used. The clean burette, which must be of the Hempel–Winckler type, is first thoroughly dried by washing it successively with alcohol and ether (alternatively by acetone alone) and then drawing air through it. The dry burette is filled with the gas either by the pressure of the gas or by using an aspirator bottle attached to the three-way tap to draw out the air and replace it with the gas; when the burette is full, the taps are turned off, care being taken that the gas is at atmospheric pressure. Connexion may then be made with the levelling-tube $A$, which is then filled with water, the lower tap opened so that the water flows into the burette and absorbs the soluble gases present. As the burette holds exactly 100 ml. between the three-way tap and the upper tap, the percentage of soluble gas can be read off directly.

The manipulation of the Hempel apparatus may be considerably
Quantitative Inorganic Analysis

simplified by utilising a special Hempel burette as shown in Fig. X, 6, 10, and extending the capillary tube of the pipette so that it has a horizontal arm. The burette has a special three-way tap with capillary tube arms; only one rubber connexion is required for attachment to the pipette.

Attention is directed to the fact that the Hempel apparatus has been modified for the exact analysis of gaseous mixtures chiefly by (a) the use of a special burette with a device for automatically compensating for variations in temperature and barometric pressure, and (b) by the use of mercury as the confining liquid; the latter necessitates that the bulb $B$ (see Fig. X, 6, 2) is attached by means of "pressure" tubing to the bulb in which the actual absorption takes place.* It is doubtful whether such apparatus now finds a wide use because of the introduction of other more convenient apparatus for precision gas analysis (see below).

B. Bunte's apparatus. The apparatus is shown in Fig. X, 6, 11 (a).

The absorbent is introduced directly into the apparatus, and absorption takes place in the measuring-vessel itself. Analyses are only of a

second-order accuracy, but the apparatus is of great value for the preliminary training of large classes of students in gas manipulation.

The Bunte burette, in an improved form, has a capacity of 100 ml. from the zero graduation to the upper three-way tap, and is also graduated downwards from zero to 10-15 ml. for measuring the absorbing solution, if desired. In one form the tube is of uniform bore and is graduated in 0.2-ml. divisions; in another form (not shown in the figure) there is an upper bulb (capacity 50 ml.) graduated in 1-ml. divisions, and the lower half of the apparatus (50 ml. + 10-15 ml.) is the ordinary cylindrical tube graduated in 0.2 ml. C is a small cup-shaped vessel which is somewhat over 25 ml. in capacity, and is provided with a 25-ml. (and sometimes also a 20-ml.) graduation mark. For more accurate results, the burette is surrounded by a water-jacket, but this is ordinarily omitted. The capillary below B may be connected by means of rubber tubing to a levelling-reservoir or bottle containing water; this is adjustable to any height and is supported on a small circular platform fitted to a tall burette stand. Fig. X, 6, 11(b) is a gas wash-bottle, fitted with short lengths of "pressure" tubing at F and G, which can be closed by means of screw clips or pinch-clamps.

Manipulation of the apparatus. Fill the levelling-bottle, preferably saturated with the gas to be analysed, and connect it to the burette below B. Open taps B and A and allow the water to run up to the upper mark in the cup C. Connect the stopcock A through D to the supply of the gas, open B, lower the levelling-bottle, turn tap A to the proper position and draw 101-103 ml. of the gas into the burette, and close tap A. Raise the levelling-bottle, and compress the gas until the water exactly reaches the zero mark on the burette; close tap B, open tap A cautiously so that the excess of gas bubbles through the water in the cup. The gas in the burette is now under atmospheric pressure plus the pressure of the water in the cup C; these conditions must be reproduced in all subsequent measurements. Place a screw clip or pinch-clamp on the rubber tubing connecting the burette to the levelling-bottle, and pull off the end of the tubing attached to the burette.

Almost fill the wash-bottle, Fig. X, 6, 11(b), with water. Blow up the water into the rubber tube F and close it with a screw clip. Attach the upper end of F to the lower end of the Bunte burette. Open tap B, and connect the wash-bottle to a filter-pump (at G); open the screw clip at G and suck the water in the burette until it is just above the tap B, which is then closed. The gas is now under less than atmospheric pressure, and when the tip of the burette is dipped under the absorbent in a shallow dish and the tap B opened, the absorbent will rise in the burette. Disconnect the wash-bottle, place the end of the burette below the surface of a suitable absorbent contained in a shallow dish, and allow a suitable volume to enter; then close tap B. Hold the burette above the upper tap and below the lower tap (to prevent heating of the gas), and shake well for a few minutes. Dip the tip of the burette under the absorbent, open tap B, and allow a little more of the absorbing solution to enter. Repeat the process until no more of the absorbent is sucked up into the burette. Empty most of the water from the wash-bottle, and arrange so that water is contained only in the central tube and the rubber tubing F. Attach the water-bottle to the lower end of the burette and connect G to a filter-pump; suck out the absorbent from the burette until the absorbent just reaches tap B, and then
close the tap. Dip the end of the burette into a dish containing water, which then rises in the tube. Close tap \( B \), open tap \( A \) so that water flows into the burette from the cup \( \mathcal{C} \) until the original pressure is produced. Add more water until it stands at the upper mark in the cup, and open tap \( A \) cautiously to reproduce the original pressure. Read the volume of the residual gas: the difference in volume gives the concentration directly in percentage by volume of the constituent absorbed.

The Bunte burette may be employed \textit{inter alia} for the determination of carbon dioxide (by aqueous potassium hydroxide), heavy hydrocarbons (by bromine water), oxygen (by an alkaline solution of pyrogallol or, better, by alkaline sodium hyposulphite solution), and carbon monoxide (by ammoniacal cuprous chloride solution).

C. Orsat's apparatus. This apparatus, introduced by Orsat in 1874 and since modified by numerous workers, is widely used where an accuracy of about 0.5 per cent suffices, \textit{e.g.}, for furnace-gas analysis. The method of analysis is essentially similar to that with the Hempel apparatus, but the burette, pipettes, and accessories are so designed that the whole apparatus, including three or four absorption pipettes, fits into a portable box.

The Orsat-Lunge apparatus is shown in Fig. X, 6, 12. It consists of a water-jacketed burette of 100 ml. capacity, attached by means of a capillary tube manifold to four pipettes, three of which contain absorbents for carbon dioxide, oxygen, and carbon monoxide respectively, and which are usually filled with glass tubes or rods to present a greater surface of the reagent to the gas; the fourth pipette contains water only and is used in conjunction with a tube containing purified asbestos impregnated with palladium and heated by means of a small spirit lamp. The last pipette and palladium-asbestos tube are omitted in some forms of the apparatus. The burette and reservoir to which it is attached contain acidulated water coloured with a suitable indicator, so that an indication is given at once of any accidental fouling with reagents. The gas mixture is drawn into the apparatus through the filter shown on the outside of the case (the filter may be dispensed with when working with gases free from dust) and through the three-way stopcock. If the gas to be sampled is at less than atmospheric pressure, the sampling tubes and filter are filled with gas by operation of a rubber aspirator (not shown in the figure) before the stopcock is connected with the measuring-burette. The first sample of gas drawn into the burette is discarded, it being employed to expel the air from the capillary connecting tubes. The reagent in each pipette is adjusted to a standard line just below the rubber connexion, and in no circumstances must any of the reagent be drawn above the tap.

The method of carrying out the absorptions for carbon dioxide, oxygen, and carbon monoxide is obvious (it is similar to that employed with the Hempel apparatus), and need not be further described. For the determination of hydrogen, which must be carried out after the above gases have been removed from the gaseous mixture, air is allowed to enter the burette until the total volume is approximately 100 ml. and the exact volume is read. The small capillary containing palladiniised asbestos (situated at the left of the bulb containing water) is gently heated by means of a small spirit lamp, and the gas is passed very slowly from the burette into the pipette: the hydrogen will com-
bine with the oxygen at the surface of the catalyst. The gas is returned to the burette and the process repeated, after which the volume of the residual gas is measured. Two-thirds of the contraction represents the volume of hydrogen. If the temperature is not allowed to rise above 200° C., the volume of any methane and its homologues present which is burnt may be neglected in technical analyses. Various improvements for the determination of hydrogen and methane, either alone or in admixture, have been introduced. The most important of these are: (i) a Pyrex U-tube containing cupric oxide and which can be heated in a small electric furnace at 270–300° C. (fractional-combustion "pipette"), and (ii) a pipette provided with a platinum wire spiral which can be heated electrically and its temperature controlled by a rheostat (slow-combustion pipette). The fractional-com-
bustion pipette is employed to oxidise both carbon monoxide and hydrogen: at 270–300° C, the oxidation may be effected in the presence of saturated hydrocarbons, such as methane and ethane (compare Section X, 8). The diminution in volume gives the volume of hydrogen directly, whilst the combustion of carbon monoxide produces an equal volume of carbon dioxide ($2\text{CO} + \text{O}_2 = 2\text{CO}_2$), which can be determined by absorption; in the latter case mercury must be employed as the confining liquid. As a general rule in the analysis of mixtures containing methane and ethane, it is best to determine the carbon monoxide by absorption and the hydrogen by fractional combustion over cupric oxide at about 290° C. The gas is passed through the copper oxide U-tube maintained at 290–300° C at a rate of 10 ml. per minute and back into the measuring-vessel, and the process is repeated until there is no further contraction. The slow-combustion pipette with, preferably, mercury as the confining liquid is employed for the determination of methane and/or ethane. A commercial form of portable apparatus is available which incorporates absorption pipettes of improved design, a fractional-combustion “pipette,” and a slow-combustion pipette; this apparatus can therefore be employed for the determination of carbon dioxide, unsaturated hydrocarbons, carbon monoxide, hydrogen, methane, ethane, and nitrogen (by difference).

A serious drawback of the Orsat–Lunge and similar apparatus is that the absorption of oxygen and carbon monoxide is not complete unless the absorbent and gas are shaken together or unless the gas is brought into prolonged and intimate contact with the absorbent. Shaking is, of course, not very practicable with this apparatus; however, the use of pipettes packed with glass tubes considerably improves the absorption, but is, nevertheless, not quite satisfactory. Various improvements in the design of pipettes have been introduced, for example, by Dennis (spiral type) and by others, but perhaps the best of these is due to M. Shepherd (1930). The latter is shown in Fig. X, 6, 13 and is of the bubbling type; the gas passes through a capillary tube, at the lower end of which a platinum gas-distributing disc (containing about 200 individual minute perforations) is sealed. The gas is thoroughly atomised, intimate contact is thus ensured, and absorption is complete.

The Orsat apparatus has been so modified and improved by M. Shepherd (1931) that it may be employed as a precision instrument for the analysis of gaseous mixtures. Mercury is employed as the confining liquid. The Shepherd apparatus in Pyrex glass is available commer-

* This is the “Fisher” gas analyser, technical universal model; made by the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.
† L. M. Dennis and M. L. Nichols, \textit{Gas Analysis}, 1929, p. 76.
‡ See the apparatus catalogues of the Fisher Scientific Co., E. H. Sargent and Company, Baird and Tatlock (London), Ltd., A. Gallenkamp and Co., Ltd., etc. The first-named Company has introduced many improvements in the apparatus for gas analysis and their catalogue merits careful examination.
§ Manufactured by the Fisher Scientific Co., Pennsylvania, Pa., U.S.A.
D. Ambler's portable apparatus. The apparatus, designed by H. R. Ambler (1931), is portable (the size complete in case is 15 × 4·5 in., and the weight is 8·5 lb.), inexpensive, and can be used either for precision work or for routine determinations.† Mercury is employed as the confining liquid. The instrument is eminently suitable for the training of students in gas analysis.

The chief details of the apparatus are shown in Fig. X, 6, 14, whilst Fig. X, 6, 15 is a line diagram of the actual apparatus. Essentially the apparatus consists of: (i) a 10-ml. burette A, surrounded by a water-jacket, in which the gas is measured, (ii) a vessel B in which the gases are absorbed or combusted, and (iii) a graduated mercury manometer M. A and B are connected to mercury reservoirs R₁ and R₂ respectively; T₁ and T₂ are three-way and two-way taps respectively; refer-

* Supplied by E. H. Sargent and Co., Chicago, Ill., U.S.A.
† The apparatus, and also a "works model" (with manometer omitted), is supplied by A. Gallenkamp and Co., Ltd., Sun Street, London, E.C.2, England.
ence marks are etched at $F$ and $K$; $B$ contains a thin platinum coil, made from 1·5 cm. of platinum wire of 1·25 mm. diameter, and current is obtained from a 4·5-volt dry battery which is fixed on the base of the instrument and is controlled by a 3-ohm rheostat of the wireless-component type; the reservoir $R_2$ is provided with two rests (shown in Fig. X, 6, 15) at levels near the top and bottom of the manometer scale.

The general mode of use of the apparatus is as follows:

1. Introduce the gas sample (up to 10 ml.) into the vessel $B$ by means of the capillary tube $H$, the tap $T_1$ and the reservoir $R_2$.

2. Reverse the tap $T_1$, and transfer the gas to the measuring-vessel $A$. Run the mercury to the mark $K$, and thus seal the gas in the burette.

3. Introduce a quantity of the appropriate absorbent into $B$ from $H$ by suitably manipulating $T_1$ and $R_2$.

4. Transfer the gas to $B$ with the aid of $R_1$ and $T_2$. Absorption will take place.

5. Transfer the residual gas back into the measuring-burette $A$ by raising $R_2$ and suitably turning $T_1$. As soon as the absorbent liquid has reached the left-hand side of the tap $T_1$, reverse the latter, and drive out the reagent through $H$. Then reverse the tap, and adjust the mercury to the mark $K$ as before.

The method of measurement of the gas varies according as to whether precision results (within 0·1 per cent) or moderately accurate ("technical," i.e., within 0·5 per cent) are required. The measuring-vessel consists of a burette of 10 ml. capacity, calibrated in 0·1 ml. Below the 10-ml. mark the burette narrows to a bore of 3 mm., and a mark $F$
is etched round the lower part. Either varying volumes or varying pressures may be measured; the temperature is assumed constant, but may be corrected for if variations occur. The constant-volume method is the more accurate. Three procedures will be described.

(a) Varying volume and constant pressure. This is the quickest procedure and yields results of "technical" accuracy. Level the mercury in the burette with the mercury in \( R_1 \), which is held in the hand, and read the volume.

(b) Varying volume and approximately constant pressure (corrected). This modification of the constant pressure method is the most satisfactory for precision work. Bring the gas in the burette to approximately atmospheric pressure (say, to within 2 mm.), close the tap \( T_2 \), and read both the burette and manometer. The pressure in the burette is then equal to the atmospheric pressure, plus the difference between the manometer reading and the reading of the manometer when the burette is filled to the same mark at atmospheric pressure. Let us call this difference \( \Delta P \).

The manometer readings corresponding with the different burette readings at atmospheric pressure are a constant of the apparatus, and are determined once and for all by measuring a few points with the tap \( T_1 \) removed. These are plotted in the form of a graph, which is a straight line.

The correction to the burette reading is applied as follows. Let \( P \) be the atmospheric pressure, \( p \) the vapour pressure of water, \( V \) the burette reading (i.e., the volume of moist gas at the experimental pressure), and \( V_a \) what the burette reading would have been if the mercury had been levelled to exactly atmospheric pressure. Then:

\[
V_a = V \times \frac{P - p + \Delta P}{P - p}
\]

or

\[
V_a - V = V \times \frac{\Delta P}{P - p}
\]

If \( \Delta P \) is not greater than 1 cm., then any deviation of \( P - p \) from the average approximate figure \((76 - 1) = 75\) cm. will not affect the correction sufficiently to introduce an error of more than 0.1 per cent on the total gas. In practice, \( \Delta P \) does not exceed 2 mm.; the magnitude of the correction, for 1 mm. of \( \Delta P \), is:

\[
V \times (0.1/75) = V \times 0.0013, \text{ i.e., 0.13 per cent of } V
\]

(c) Varying pressure and constant volume. Many gas samples which occur in practice do not involve contractions greater than about 30 per cent of the total gas; for this purpose a manometer of 30 cm. length will suffice. In such cases the maximum accuracy is obtained by the constant-volume method. A knowledge of the volume is not required, and the result will be independent of any errors in the graduation of the burette. The mark \( F \) serves as a levelling-mark for this purpose, and the bulb below the water-jacket enables a sufficient volume of gas to be taken in the measuring-burette at atmospheric pressure to be compressed to ca. 10·5 ml. (volume to mark \( F \)) at about 100 cm. pressure. It can be shown that the volume of the gas (at normal pressure) contained in the burette is proportional to:

\[
P + A - K - p/76\]
where $A$ is the manometer reading and $K$ is the manometer reading with the burette at atmospheric pressure (all pressures are expressed in cm. of mercury).

Any other graduation may, of course, be employed, as in the case of samples which are not large enough to fill the burette. The precision then is somewhat less, since any error in levelling in the wider tube causes a greater error in volume.

Mention must be made of the fact that the vessel $B$ may be fitted either with a spark gap or with a platinum spiral for the burning of hydrogen and other combustible gases; the platinum spiral is of greater general utility. Gas mixtures containing more than 10 per cent of hydrogen or 3 per cent of hydrocarbons should be diluted with air before combustion.

The apparatus is applicable to all gases commonly dealt with. It can be used equally well for precise general analysis and for rapid technical analysis, and the volume of the sample required is small (normally 10 ml.). The use of mercury as the confining liquid increases the speed of transference of the gas, and determinations are correspondingly rapid.

**E. Bone and Wheeler apparatus.** This, in its simple or one of its modified forms, is probably the most widely used instrument for exact analysis in Great Britain, and is applicable to most classes of gaseous mixtures. The usual form of Bone-Wheeler apparatus is shown in Fig. X, 6, 16. The gas mixture is measured at constant volume in limb $A$ of the water-jacketed U-tube, the pressure being measured by the height of the mercury column in the limb $B$, which is graduated upwards in millimetres. The limb $A$ has a series of graduations coinciding in level with each integral 100-mm. mark on $B$. The heights of $A$ and $B$ are such, that when a measurement is being made, the closed space above the mercury in $B$ is a Torricellian vacuum except for water vapour; both limbs are kept saturated with water by means of a small quantity of dilute sulphuric acid (2–5 per cent). The pressure of the gas in $A$ is equal to the difference in the level of the mercury in $B$ and $A$. Variations in the atmospheric pressure during the analysis do not affect the results, but variations in temperature do affect the readings, and corrections must be calculated (see Section X, 4). Mercury is raised or lowered by
means of the reservoir $D$, which is connected to a windlass and ratchet; fine adjustment in levelling on to the marks is obtained by means of a special tap $C$, which separates the limbs $A$ and $B$ from $D$.

Absorption is carried out in the vessel (or pipette) $F$, which stands in a mercury trough; the capillary three-way tap at the top connects to the measuring-vessel and to a bottle or other container connected to a filter-pump or other exhausting apparatus, by means of which the
reagent, introduced into $F$ by means of a special bent pipette, may be removed after absorption has taken place. Combustible gases are determined by explosion with air in the vessel $K$, which is provided with a spark gap.*

Various modifications have been introduced, notably by J. G. King (1922), who incorporated a copper oxide tube for combustions,† and by Bone and Newitt (1929). The Bone and Newitt apparatus is shown in Fig. X, 6, 17; ‡ the chief distinctive feature is the provision of a three-way water-tap of special design, by means of which the mercury levels are controlled from the water supply with ease and delicacy. The levels are read with a cathetometer. Otherwise the procedure is similar to that with the Bone and Wheeler apparatus.§

F. Other precision forms of apparatus. Most of these are of the “absorption-pipette” type and employ mercury as the confining liquid. They are based upon the design originally introduced by Burrell and Oberfell (1916) and are often spoken of as U.S. Bureau of Mines apparatus. The Shepherd apparatus (Section X, 60) belongs to this class. Commercial forms of these gas analysers are marketed by several manufacturers.¶

X. 7. Absorbents for the various gases.—With all the types of apparatus described in the previous Section, the methods of determination of the constituent gases are essentially similar. The main sources of error by absorption methods are: (a) incomplete absorption due to insufficient time of contact, the use of an exhausted solution, or a chemical equilibrium between the gas and the compound formed by its action on the absorbent; (b) physical solution of constituent gases in reagents designed for the absorption of other constituents. The latter error is reduced to a minimum by the use of as small quantities of reagents as possible, and by saturating the reagents with the gases with which they come into contact: this is particularly necessary with instruments of the Hempel and Orsat type, where small volumes of reagents are not practicable.

The components of the gas mixture are usually determined in the following order by the methods detailed below.

A. Carbon dioxide. The most common reagent is a 25–33 per cent aqueous solution (by weight) of A.R. potassium hydroxide. For use in the Orsat apparatus a 40–50 per cent solution is recommended in order to reduce the number of times necessary to refill the apparatus. Sodium hydroxide should not be employed owing to the tendency of the bicarbonate to crystallise out; the potassium salt is much more soluble. It will be appreciated that acid gases, such as hydrogen sulphide, sulphur dioxide, and hydrogen cyanide, are also absorbed by the alkaline solution, and must be removed first.

* For further details, see G. Lunge and H. R. Ambler, Technical Gas Analysis, 1934 (Gurney and Jackson); A. McCulloch, Gas Analysis, 1938 (Witherby); F. Sutton and A. D. Mitchell, Volumetric Analysis, 1935 (Churchill).
¶ For further details, see, for example: (i) Dennis and Nichols, Gas Analysis (1929); (i) the apparatus catalogues of E. H. Sargent and Co., Chicago, U.S.A., and of Fisher Scientific Co., Pittsburgh, Pa., U.S.A.; (iii) the booklet of the last-named firm entitled Fisher Gas Analysis Manual (revised edition).
B. Unsaturated hydrocarbons. The most satisfactory absorbent is fuming sulphuric acid, containing 20–25 per cent of free SO₃; the specific gravity is about 1.94. This absorbs all the olefines, acetylenes, and aromatic hydrocarbons. The reagent must be employed at temperatures above 15°C, since below this temperature pyrosulphuric acid may crystallise out. Absorption is usually complete in 2–5 minutes; the rate of absorption is greatly accelerated by increasing the surface of the reagent by the use of glass rods or spheres (compare Fig. X, 0, 0). The gas must be subsequently treated with potassium hydroxide solution to absorb acid vapours. Fuming sulphuric acid must not be kept for long periods over mercury, although it is quite safe to allow it to remain in contact with mercury for a few minutes, as in the Bone and Wheeler absorption pipette.

A solution of bromine in 10 per cent potassium bromide solution is also employed to absorb unsaturated hydrocarbons. Bromine water attacks mercury much more readily than oleum, and is to be avoided, where possible, if mercury is used as the confining liquid for the gas. It is said (Himus, 1932) that the concentration may be so adjusted (to a deep-yellow solution) that it absorbs effectively whilst having little action upon mercury. The gas must be washed subsequently with alkali to remove bromine vapour.

In technical practice the heavy hydrocarbons are usually absorbed together, but they may be absorbed separately by suitable means.

(i) Acetylene. This gas is absorbed by ammoniacal cuprous chloride solution with the formation of cuprous acetylide Cu₂C₂, but the reagent cannot be used in the presence of carbon monoxide and oxygen. With potassium mercuric iodide reagent only acetylene is absorbed and carbon monoxide is unaffected. The latter reagent (1 ml. absorbs 20 ml. of acetylene) is prepared by dissolving 25 g. of mercuric iodide and 30 g. of potassium iodide in 100 ml. of water, and mixing it with potassium hydroxide solution immediately before use.

(ii) Benzene. Benzene is readily absorbed by concentrated sulphuric acid, and can thus be separated from ethylene (which is not appreciably absorbed), but not from the higher olefines. Benzene may be removed by ammoniacal nickel cyanide reagent; ethylene is not absorbed.

The ammoniacal nickel cyanide reagent is prepared as follows. Add a solution of 25 g. of potassium cyanide in 40 ml. of water to a solution of 50 g. of crystallised nickel sulphate in 75 ml. of water. Introduce 125 ml. of concentrated ammonia solution into the mixture, and shake until the nickel cyanide dissolves completely. Cool to 0°C, and allow to stand at this temperature for 20 minutes. Decant the clear liquid from the potassium sulphate that has separated, and treat with a solution of 18 g. of crystallised citric acid in 10 ml. of water. Allow the mixture to stand at 0°C. for 10 minutes, decant the greenish-blue supernatant liquid, and transfer to the absorption pipette (e.g., a Hempel double-absorption pipette, Fig. X, 0, 3, with the large bulb filled with broken glass). Add 2 drops of pure benzene to the reagent and shake the pipette until the benzene has combined with the reagent (2–3 minutes); this is shown by the appearance of fine, white, granular precipitate. The addition of a little benzene is necessary because it has been found that the freshly prepared reagent does not rapidly remove benzene vapour until some of the compound between benzene and the ammonium nickel cyanide has been formed.

DD
C. Oxygen. The three absorbents which are commonly employed for the absorption of oxygen are a strongly alkaline solution of pyrogallol, a solution of sodium hyposulphite, and phosphorus respectively.

**Alkaline pyrogallol.** For the Orsat and Hempel type of apparatus a solution of 15 g. of pyrogallol in 100 ml. of 50 per cent aqueous potassium hydroxide (prepared from A.R., i.e., electrolytic, KOH) is satisfactory. For the Ambler and Bone-Wheeler type of apparatus 40 per cent potassium hydroxide solution and 25 per cent aqueous pyrogallol solution are mixed in the ratio of 4 : 1 as required. At 20° C. about 3 minutes' shaking is required for complete absorption; below 15° C. absorption is inconveniently slow. With gases containing more than 25 per cent of oxygen, some carbon monoxide is always evolved, thus giving low results. A little carbon monoxide is also stated to be evolved with certain alkaline solutions of pyrogallol, but Haldane (1933) has shown that with the solution recommended above for the Orsat type of apparatus the effect is negligible if the solution is kept for 3 days before use or, alternatively, is heated at 100° C. for an hour.

**Sodium hyposulphite.** The reaction which occurs is:

$$\text{Na}_2\text{S}_2\text{O}_4 + \text{O}_2 + \text{H}_2\text{O} = \text{NaHSO}_4 + \text{NaHSO}_3$$

A suitable solution for general use is prepared by dissolving 50 g. of commercial sodium hyposulphite in 250 ml. of water, 30 g. of sodium hydroxide in 40 ml. of water, and mixing the solutions.* One ml. of this solution will absorb 10·5 ml. of oxygen. The absorption of oxygen is slower than with alkaline pyrogallol, but absorption also takes place at low temperatures at which the latter reagent is ineffective. Furthermore, no carbon monoxide is evolved or absorbed, and the reagent is unaffected by unsaturated hydrocarbons.

The rate of absorption can be considerably increased by the addition of sodium anthraquinone-β-sulphonate. Fieser (1924) recommends a solution of 16 g. of sodium hyposulphite, 6·6 g. of sodium hydroxide, 2 g. of sodium anthraquinone-β-sulphonate, and 100 ml. of water. When this solution is exhausted, its colour changes from blood-red to brown; vigorous shaking is unnecessary. The reagent should not be kept for more than one week.

**Solid phosphorus.** Yellow phosphorus in the form of thin sticks may be employed for the absorption of oxygen in the Hempel pipette for solid reagents (Fig. X, 6, 3) and in Orsat pipettes. A great advantage is that once a pipette has been charged with the reagent, it does not require renewing except after long periods. Absorption generally takes about 3 minutes: the oxygen content of the gas should not exceed 50 per cent., otherwise explosions may occur. During the absorption white clouds of oxide are produced and dissolve in the water: the clearing of these is a sign that absorption is complete. The water in which the phosphorus is immersed should be changed from time to time in order to remove the phosphoric and phosphorous acids which are formed. The phosphorus should be shielded from light, otherwise a layer of red phosphorus will be formed on the surface. The temperature should be above 15° C.—below this temperature absorption is extremely slow. Even small quantities of

* For use in the Bunte burette, a solution of 10 g. of Na$_2$S$_2$O$_4$ in 80 ml. of water mixed with 50 ml. of 10 per cent sodium hydroxide solution is preferable.
acetylene and unsaturated hydrocarbons must be absent, for these inhibit the reaction.

D. Carbon monoxide. The usual reagent for the absorption of carbon monoxide is ammoniacal cuprous chloride solution, which forms a complex CuCl₂H₂O,CO. The reagent may be prepared for use in the Ambler or Bone-Wheeler type of apparatus by adding 75 g. of white cuprous chloride to a solution of 15 g. of ammonium chloride in 80 ml. of water, and then adding sufficient concentrated ammonia solution until solution is complete. The solution should be kept in contact with copper wire or turnings in a stoppered bottle. For use in Hempel pipettes or in the Orsat type of apparatus, 125 ml. of concentrated hydrochloric acid are added to 40 g. of cuprous chloride in a suitable flask, followed by the cautious addition of 130 ml. of concentrated ammonia solution, the flask being cooled to atmospheric temperature: a little more ammonia solution (ca. 15 ml.) is then introduced until the white precipitate just dissolves.

The absorption of carbon monoxide by either of the above solutions is slow, and intimate contact between the gas and liquid is necessary. If the gaseous mixture contains more than 10 per cent of carbon monoxide, it should be treated a second time with a fresh solution. After the absorption ammonia must be removed from the gas by washing with water or with dilute sulphuric acid. Oxygen, acetylene, and to some extent, olefins are absorbed by the reagent, and must previously be removed as already described.

A better reagent is cuprous sulphate-β-naphthol, with which a stable compound Cu₂SO₄·2CO is formed. The reagent is prepared by cautiously adding 200 ml. of concentrated sulphuric acid, specific gravity 1·84, to 25 ml. of water; the cool solution is added a little at a time to 20 g. of specially prepared cuprous oxide contained in a mortar, and the mixture is well ground to obtain the solid in fine suspension. 25 Grams of pure β-naphthol is added and incorporated in the mixture by grinding; the final mixture is filtered through glass wool or through a sintered-glass funnel, and at once transferred to the absorption pipette. The reagent must be maintained above 15° C. and protected from the atmosphere; the β-naphthol separates out at a lower temperature, and the mixture slowly oxidises if exposed to the atmosphere.

The cuprous oxide is prepared as follows. 100 Grams of cupric acetate are added to 1 litre of distilled water contained in a 2-litre flask, and the mixture heated until the acetate is dissolved. The solution is filtered, heated to the boiling point, treated with a solution of 60 g. of glucose in 400 ml. of water, the boiling continued until the blue colour fades somewhat, and the mixture allowed to stand until the red cuprous oxide separates out. The cuprous oxide is washed several times with water by decantation, transferred to a filter, washed once with alcohol, and finally dried in a vacuum desiccator.

The cuprous sulphate-β-naphthol reagent absorbs carbon monoxide completely (1 ml. absorbs ca. 5 ml. of CO), but not hydrogen or methane; it is, however, rather slow in action, and absorption may take up to 30 minutes. The gas should be washed with potassium hydroxide solution after contact with the reagent, since traces of acid fumes are liable to be produced.

E. Hydrogen. Hydrogen is usually determined, together with methane, etc., by combustion (Section X, 8). However, in some cases it may be desirable to determine the gas by absorption.
The chief absorbent is palladium. If hydrogen is brought into contact with palladium in the presence of oxygen, the hydrogen is removed partly by absorption and partly by catalytic combustion. Two-thirds of the contraction is equal to the volume of hydrogen present. The method is far from accurate, since any carbon monoxide and methane present may be partly oxidised too. If palladinised asbestos at 100°C is used, for example, in the Orsat apparatus (Section X, 69), the percentage of carbon monoxide and methane burnt will be small, and an approximate value for the hydrogen content may be obtained; in technical analysis this value is corrected by determining the carbon dioxide simultaneously produced and adding this value to the initial contraction observed—a procedure which is open to many objections. The most satisfactory results are obtainable with a fractional-combustion "pipette" (see Section X, 60).

X, 8. Determination by explosion and combustion methods. The most important gases determined by combustion methods are hydrogen, carbon monoxide, and saturated hydrocarbons (methane CH₄, ethane C₂H₆, etc.). The combustion of these gases with excess of oxygen supplies three results, from which it is possible to determine the amount of gas burned and, in simple cases, its identity. The observations which can be made are:

(i) Contraction in volume, \( v_1 \).
(ii) Volume of carbon dioxide produced, \( v_2 \) (determined by absorption in alkali after the combustion).
(iii) Volume of oxygen consumed, \( v_3 \) (determined by absorption after the removal of the carbon dioxide).

In the following table the volume changes for a number of simple gases are shown; these refer to one volume of the combustible gas.

<table>
<thead>
<tr>
<th>Gases</th>
<th>( v_1 )</th>
<th>( v_2 )</th>
<th>( v_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen, H₂</td>
<td>3/2</td>
<td>0</td>
<td>1/2</td>
</tr>
<tr>
<td>Carbon monoxide, CO</td>
<td>1/2</td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>Methane, CH₄</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Ethane, C₂H₆</td>
<td>5/2</td>
<td>2</td>
<td>7/2</td>
</tr>
<tr>
<td>Paraffin, CₙH₂ₙ₊₂</td>
<td>((n + 3)/2)</td>
<td>(n)</td>
<td>((3n + 1)/2)</td>
</tr>
<tr>
<td>Ethylene, C₂H₄</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Olefine, CₙH₂ₙ₊₂</td>
<td>((n/2 - 1))</td>
<td>(n)</td>
<td>3n/2</td>
</tr>
</tbody>
</table>

The various equations from which the above table is derived are obvious, and include the following for the commonly encountered gases:

\[
2H₂ + O₂ \rightarrow 2H₂O \\
2CO + O₂ \rightarrow 2CO₂ \\
CH₄ + 2O₂ \rightarrow CO₂ + 2H₂O
\]

Methods of affecting the combustion. A. Explosion. After the removal of such gases as are determined by absorption, excess of air or oxygen is added to the residue and the gas transferred to the explosion vessel, which is usually fitted with a platinum-wire spark gap; the spark is produced by an induction coil or by a magneto. The Hempel explosion pipette is shown in Fig. X, 6, 7. It consists of a thick-walled
Gas Analysis

explosion bulb A and the levelling-vessel B, which are connected by means of thick-walled rubber tubing ("pressure" tubing); the latter is securely wired on. Two fine platinum wires are fused into the explosion pipette, the ends of the wires being about 2 mm. apart. The pipette is filled with mercury. The gas to be determined, together with excess of air or oxygen, is transferred to the bulb A, the mixture brought approximately to atmospheric pressure, and the stopcock D closed. The rubber tube attached to the extremity of E is next closed with a pinch-clamp, and the rubber tube closed by a suitable glass-rod plug (which acts as a safety valve). The pipette is shaken to ensure complete mixture of the gases, a safety screen of thick plate glass (preferably of the "Triplex" variety) placed in front of the pipette, and a few sparks passed (or until the gas is seen to explode). The tap D is immediately opened, the gas in the pipette transferred without delay to the burette, and measured at once if the burette is filled with mercury or after 2 minutes if the burette contains water. The technique for explosion in a Bone-Wheeler or similar apparatus is self-evident from the above description.

The chief source of error or failure in explosion analysis is an incorrect proportion of the combustible gas in the explosive mixture. If the proportion is too low, explosion does not take place or is incomplete; if it is too high and nitrogen is present, oxides of nitrogen are produced, giving excessive contractions and erroneous carbon dioxide figures. For hydrogen, the hydrogen content must be between 10 and 20 per cent; for methane, the corresponding limits are 6·0 and 8·3 per cent; for mixtures containing these gases, proportionately intermediate figures apply. The results for carbon monoxide by the explosion method (20–28 per cent) are not always satisfactory.

B. Slow combustion. Catalytic combustion with platinum. In the presence of oxygen, all combustible gases are oxidised in contact with platinum wire at about 980° C.; hydrogen and carbon monoxide are oxidised at a much lower temperature. The usual method of carrying out the combustion is by means of an electrically heated platinum wire. A slow-combustion pipette, due to Dennis (1899), is shown in Fig. X, 6, 8. It is really a Hempel pipette for solid absorbents (Fig. X, 6, 3) into the neck of which a two-holed rubber stopper is inserted which carries two glass tubes reaching to within 2 cm. of the top of the pipette. Stout iron (or nichrome) wires, 2·5 cm. in diameter, are mounted inside the tubes and reach nearly to the top; the upper ends of the wires carry small iron screws to which a platinum-wire spiral is attached, and the current passing through the spiral is controlled by a rheostat. The pipette and levelling-tube contain mercury. In use, a known volume (excess) of oxygen is passed into the pipette, followed by a known volume of the gas to be burned. With non-explosive gas mixtures, a current is passed through the platinum spiral, which is maintained at the requisite temperature with the aid of a rheostat, for 1 or 2 minutes. For hydrogen and carbon monoxide, 1 minute's treatment at a red heat is sufficient, but for methane, which is difficult to burn, 2 minutes at a bright yellow heat is usually required. After combustion, the current is turned off, the pipette allowed to cool, and the gas residue passed back into the burette and measured. The reader should be able to adapt the above experimental details for the Ambler and Bone-Wheeler type of apparatus.
An improved combustion pipette, due to Weaver and Ledig (1920) and to Shepherd (1931), is shown in Fig. X, 8, 1. It is made of Pyrex glass, has a volume of approximately 150 ml., and is used with mercury as the confining liquid; the lower end is attached by means of rubber tubing to a levelling-bulb. This is incorporated in Shepherd's modification of the Orsat apparatus (see Section X, 60). About 20 cm. of wire (90% Pt and 10% Ir alloy) of 0.16–0.17 cm. diameter is employed in the construction of the coil; the side arms, through which the wire passes, are sealed with Dekhotinsky cement.

For mixtures which are liable to explode, and also to reduce the danger of explosion in any combustion process, the combustion pipette of Ambler (1931)—Fig. X, 8, 2—is a valuable improvement upon the ordinary design. Oxygen is bubbled through the lower capillary tube side limb, thus enabling the rate of inflow to be seen and readily adjusted; in this way the gaseous mixture, already present in the pipette, may be burned in a controlled stream of oxygen.

Combustion with copper oxide. Copper oxide at 270–295° C. oxidises carbon monoxide and hydrogen rapidly and completely, methane and other hydrocarbons being unaffected. This is an example of fractional combustion and is utilised for separating these gases. The oxygen is supplied by the copper oxide; if oxygen is present, however, it acts as a catalyst and is not reduced.* Fractional combustion cannot be used in the presence of unsaturated hydrocarbons.

X, 9. Exercises in gas analysis.—The exact nature of these will depend upon the apparatus and gaseous mixtures which are available, upon the particular interests of the teacher (and of the student), and upon local conditions. The following are suggested as suitable for

* For further details, see Lunge and Ambler, *Technical Gas Analysis*, 1934, p. 141. The method is widely employed for the determination of hydrogen, and also of carbon monoxide if saturated hydrocarbons are absent.
classes of moderate size: they are likely to be useful in all laboratories as an introduction to gas analysis.

1. Determination of oxygen in air. A Winckler–Hempel burette, preferably filled with mercury and surrounded by a water-jacket, and a Hempel pipette, filled with phosphorus or with sodium hyposulphite solution, may be used.

2. Analysis of coal gas by means of the Bunte burette. Determination of carbon dioxide with potassium hydroxide solution, heavy hydrocarbons with bromine water, oxygen with sodium hyposulphite solution, and carbon monoxide with ammoniacal cuprous chloride solution (for order of absorption, see Section X, 7).


The term "gas-volumetric analysis" is applied to those processes in which a liquid or solid substance is determined by utilising some reaction in which it takes place with the quantitative liberation of a gas. Such processes are not, strictly speaking, gas analysis, but since they involve technique and principles which are commonly encountered in gas analysis, a few of the more important methods of this class will be described.

**X, 10. The Lunge nitrometer.**—This apparatus was introduced by G. Lunge in 1885 for the analysis of nitrous vitriol (crude sulphuric acid with dissolved oxides of nitrogen from the Chamber Process), but is of wide application in gas-volumetric analysis. A diagrammatic representation is given in Fig. X, 10, 1 (a). It consists of a 50-ml. burette A, fitted at the top with a three-way tap and cup-shaped funnel B, and communicating at the bottom, by means of thick-walled rubber tubing, with a levelling-tube C of the same diameter. To increase the accuracy, the volume may be increased by expanding the upper part of A into a 50-100-ml. bulb, only the lower part being graduated (see B in Fig. X, 4, 1).

For the analysis of nitrates, nitrites, and nitrous vitriol, the simple apparatus shown in Fig. X, 10, 1 (a) is employed. For other gas-volumetric determinations, a reaction vessel, such as is shown (enlarged) in Fig. X, 10, 1 (b), is attached at D by means of a short length of "pressure" tubing, secured with copper-wire ligatures; the inner tube of the reaction vessel is generally fused to the bottom, and the vessel is closed with a one-holed rubber bung. In these determinations it will, of course, be necessary to correct the final volume of the gas to N.T.P.; this may be avoided by the use of the Lunge gas volumeter, which has been described in Section X, 4.

The apparatus is filled with mercury, and should always stand on a "mercury" tray.

**X, 11. Determination of nitrates.**—Discussion. If a solution of a nitrate (or a nitrite) is shaken with mercury and an excess of concentrated sulphuric acid, all the nitrogen is set free as nitric oxide:

\[ 2\text{HNO}_3 + 3\text{H}_2\text{SO}_4 + 6\text{Hg} = 2\text{NO} + 4\text{H}_2\text{O} + 3\text{Hg}_2\text{SO}_4 \]
The weight of the nitrate can be computed from the volume of the nitric oxide.

**Procedure.** For practice in this determination, the student may determine the percentage of $\text{NO}_3$ in A.R. potassium nitrate. See that both arms of the nitrometer are completely filled with mercury. Weigh out accurately about 0.12 g. of potassium nitrate into the cup of the nitrometer. Dissolve in about 0.5 ml. of water, and draw the solution into the nitrometer by lowering the levelling-tube and carefully opening the stopcock. *No air must be allowed to enter.* Wash round the cup with 3 or 4 drops of water, and introduce the latter also. Then place 20 ml. of concentrated sulphuric acid in the cup, and allow this to enter. Wrap the bulb in a cloth, hold the tap securely and shake the contents of the nitrometer vigorously for a few minutes, when the reaction will take place and nitric oxide will be evolved. Continue the shaking until no more gas is liberated. The measurement of the volume of the nitric oxide may be effected in either of two ways; method (b) is the more accurate.

**Method (a).** Allow the apparatus to stand for at least an hour so as to acquire the room temperature. It is now necessary to measure the volume of the gas at atmospheric pressure. Adjust the height of the levelling-tube to be so much higher than that in the graduated limb as is necessary to compensate for the volume of acid in the latter: 1 mm. of mercury is equivalent to 0.5 mm. of acid. When the adjustment is made, clamp the tube in the appropriate position. Test the correctness of the adjustment by placing a few drops of liquid in the nitrometer cup; upon very cautiously opening the tap, the liquid should be neither drawn in nor forced out. Care must be taken not to warm the gas by handling the measuring-tube. Read the volume of the gas, the temperature, and the barometric pressure, and correct the volume to N.T.P.

**Method (b).** Transfer the nitric oxide to the graduated tube (filled with mercury) of a Lunge gas volumeter (Fig. 4, 1) as follows. Connect the nitrometer to the volumeter by means of as short a piece of rubber tubing as possible, joining the two side tubes, and secure with wire ligatures. Displace the air in the rubber tube by suitably manipulating the three-way taps and raising the levelling-tube of the volumeter. Drive most of the gas from the nitrometer into the volumeter until the upper level of the acid in the nitrometer is in the constricted portion just below the tap. Close both taps and shake the nitrometer once more. When the acid level is in the above position, it is possible to observe the evolution of a further small volume of the gas should such still be taking place. If all reaction has ceased, place a few ml. of concentrated sulphuric acid in the cup of the volumeter and allow 1 or 2 drops to enter; this ensures that the gas is dry when measured. Then open both taps and drive the remainder of the nitric oxide from the nitrometer into the side tube. As soon as the level of the acid rises to the tap, turn the latter so as to communicate with the cup of the nitrometer and force all the acid into the cup. When the mercury below the acid has risen to the tap, turn the latter back and continue to drive the gas in the side tube into the volumeter by means of the mercury, leaving the acid in the cup of the nitrometer. In this way the

* For a discussion of the errors in this determination, see Lunge and Ambler, *Technical Gas Analysis*, 1934, p. 373.
acid does not come into contact with the rubber connexion, which it would attack, thus liberating further quantities of gas. Read the volume of the gas at atmospheric pressure, and also the temperature. No correction need be made for water-vapour pressure, since the reaction takes place over concentrated sulphuric acid. Reduce the volume to N.T.P., and from your result calculate the percentage of NO₂ in KNO₃.

Assume 1 ml. of NO = 0.000625 g. N₂ = 0.002768 g. NO₃.*

Note. Two or three consecutive determinations may be carried out without washing the mercury. After each series of determinations, the mercury should be emptied out from both nitrometer and volumeter, and placed in the Mercury Residues bottle. The whole apparatus should then be washed out first with nitric acid, then with water and finally with a little acetone, and dried by passing a stream of air through it. The impure mercury should be washed thoroughly with water and filtered (see Section X, 3).

X, 12. Determination of hydrogen peroxide.—Discussion. This is an example of a determination by means of a nitrometer (or volumeter) with a special decomposition vessel. When hydrogen peroxide solution is treated with excess of acidified potassium permanganate solution, oxygen is evolved:

\[ 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O}_2 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2 \]

It is evident that half of the oxygen evolved is derived from the hydrogen peroxide and the other half from the potassium permanganate. Conversely, by using hydrogen peroxide solution in excess and a measured volume of potassium permanganate solution, the gas-volumetric method may be employed for the standardisation of permanganate solutions.

The reaction is applicable to other oxidising agents, such as bleaching powder, manganese dioxide, lead dioxide, chromates, etc. If any of these substances, in solution or in suspension, and hydrogen peroxide are mixed in the presence of sulphuric acid, the reagent which is not in excess gives up the whole of its available oxygen, and this is increased by an equal quantity of oxygen from the other reagent:

\[ \text{XO} + \text{H}_2\text{O}_2 = \text{X} + \text{H}_2\text{O} + \text{O}_2 \]

The oxygen so produced is measured directly as gas. Several examples will be given in the following Sections.

Procedure. Dilute 10 ml. of "20-volume" hydrogen peroxide to 40 ml. with distilled water. Measure out accurately 4 ml. of this diluted solution from a burette into the outer portion of the reaction vessel, Fig. X, 10, 1 (b), and acidify with an equal volume of dilute sulphuric acid. Fill the inner vessel with a concentrated solution of potassium permanganate. The decomposition vessel is connected either to a simple Lunge nitrometer (Fig. X, 10, 1 (a)) or to a Lunge gas volumeter (Fig. X, 4, 1); in either case the measuring-tube is filled with mercury. Mix the two liquids, taking care to hold the decomposition bottle so that its contents will not be warmed by the heat of the hand, and shake for 1 minute. Whilst gas is evolved, the pressure

* The control or compensating tube should not be used in this experiment in order to avoid contamination of the mercury in it.
should be reduced in the measuring-tube by lowering the levelling-tube. After the decomposition is complete (excess of permanganate must be present), place the bottle in a beaker of water and allow it to attain the temperature of the room. The subsequent procedure will depend on whether the simple nitrometer or the volumeter is used.

With the Lunge nitrometer, adjust the mercury levels, and read the volume of the oxygen. Note the temperature and barometric pressure, and reduce the volume to N.T.P.

With the Lunge gas volumeter (see Section X, 4), adjust the pressure to atmospheric, and isolate the gas in the burette. As the conditions of the gas in the decomposition vessel are now the same as they were at the commencement of the experiment, the volume of the gas in the burette is equal to the volume of gas liberated during the reaction. To reduce this volume to N.T.P., the control or compensating tube is employed. If a certain pressure is applied to the gas in the control tube so that its volume is reduced to 100 ml., it has been reduced to its volume at N.T.P. If the same pressure be applied to any other volume of gas under the same conditions as the gas in the control tube, it will also be reduced to N.T.P. (see Section X, 4). The actual adjustment is carried out as follows. Keeping the menisci of the mercury in the burette and control tube level, raise the levelling-tube until the meniscus in the control tube is exactly at the 100-ml. mark. The reading of the meniscus in the burette then gives the volume of gas reduced to N.T.P.

From the volume thus obtained, calculate the strength of the hydrogen peroxide solution in volumes of available oxygen per unit volume of the original solution, and also its concentration.

\[
1 \text{ ml. of } O_2 \text{ at N.T.P.} = 0.001518 \text{ g. } H_2O_2
\]

X, 13. Evaluation of pyrolusite.—Discussion. Manganese dioxide reacts with hydrogen peroxide in the presence of dilute sulphuric acid in accordance with the following equation:

\[
\text{MnO}_2 + H_2O_2 + H_2SO_4 = \text{MnSO}_4 + O_2 + 2H_2O
\]

1 ml. of \(O_2\) at N.T.P. = 0.003885 g. \(\text{MnO}_2\)

Pyrolusite may contain carbonate: the decomposition flask may therefore be left unstoppered for about 5 minutes or until all the carbonate is decomposed.

Procedure. Weigh out accurately about 0.2 g. of very finely ground pyrolusite * and introduce, together with about 10 ml of dilute sulphuric acid, into the outer compartment of the decomposition vessel (Fig. X, 10, 1 (b)). Place 15–25 ml of “10-volume” hydrogen peroxide into the inner tube. When no more gas is evolved from the outer compartment connect the flask to the gas burette in the usual manner, and bring the hydrogen peroxide solution into contact with the pyrolusite. Shake the flask for 2 minutes, at the end of which time the decomposition should be complete. No black particles of pyrolusite should remain in the flask. Measure the volume of oxygen evolved, and from the volume at N.T.P. calculate the \(\text{MnO}_2\) content of the mineral.

* Ridsdale's "Pyrolusite, No. 18" (one of the Analyzed Samples for Students) is suitable for this determination.
X. 14. Determination of the available chlorine in bleaching powder.—

Discussion. The reaction with acidified hydrogen peroxide is:

\[ \text{Ca(OCl)}_2 + 2\text{H}_2\text{O}_2 = \text{CaCl}_2 + 2\text{H}_2\text{O} + 2\text{O}_2 \]

i.e., 1 ml. of \( \text{O}_2 \) at N.T.P. = 0.003167 g. of available chlorine.

Procedure. Place 25 ml. of the well-mixed bleaching powder suspension (Section III, 111, Procedure A) into the outer compartment and 6 ml. of approximately “5-volume” hydrogen peroxide into the inner tube. Carry out the determination in the usual manner. Calculate the percentage of available chlorine in the sample of bleaching powder.

X. 15. Evaluation of zinc dust.—Zinc is frequently used as a reducing agent, and its value for this purpose may be determined by measuring the volume of hydrogen evolved when a weighed sample is treated with excess of dilute acid.

Weigh out accurately about 0.1 g. of the zinc dust into the outer compartment, and place 25 ml. of 1:3 sulphuric acid in the inner tube. Carry out the determination in the usual manner. From the volume of hydrogen evolved, reduced to N.T.P., calculate the percentage of zinc in the sample of zinc dust.

X. 16. Determination of ammonium salts.—Discussion. Ammonium salts are decomposed by sodium hypobromite solution with the evolution of nitrogen:

\[ 2\text{NH}_3 + 3\text{NaOBr} = 3\text{NaBr} + 3\text{H}_2\text{O} + \text{N}_2 \]

It is found, however, that only 97.5 per cent of the nitrogen is evolved. For practice in this determination, the student may either assume this factor and use it to determine the percentage of \( \text{NH}_3 \) in an ammonium salt (e.g., ammonium chloride) or he may employ a pure ammonium salt (e.g., A.R. ammonium chloride) and re-determine this factor.

Urea reacts similarly:

\[ \text{CO(NH}_3\text{)}_2 + 3\text{NaOBr} = \text{CO}_2 + 3\text{NaBr} + 2\text{H}_2\text{O} + \text{N}_2 \]

but here only 91.5 per cent of the nitrogen is evolved (the carbon dioxide is absorbed by the excess of sodium hydroxide in the sodium hypobromite solution). Similar exercises may be carried out with urea.

Procedure. Weigh out accurately about 0.25 g. of the ammonium salt (or about 0.12 g. of urea), dissolve in about 20 ml. of water, and place in the outer portion of the decomposition vessel (Fig. X, 10, 1(b)). Prepare a sodium hypobromite solution by dissolving 16 g. of sodium hydroxide in 40 ml. of water and add 4.0 ml. of bromine, measured in a small graduated cylinder. Fill the inner tube with the freshly prepared sodium hypobromite solution. Connect up the apparatus to a burette filled with mercury as in Section X, 11; shake the vessel gently to complete the evolution of nitrogen. Determine the volume of nitrogen at N.T.P. Use this result either to determine the purity of the initial substance, assuming the factors given in the discussion (1 ml. of \( \text{N}_2 \) at N.T.P. = 0.001559 g. \( \text{NH}_3 = 0.002929 \) g. urea) or determine the factor on the assumption that the initial compound (ammonium salt or urea) is pure.
X, 17.

SELECTED BIBLIOGRAPHY

CHAPTER XI

MICRO-GRAVIMETRIC AND MICRO-VOLUMETRIC ANALYSIS

XI, 1. General Discussion.—Macro-gravimetric analysis usually involves the accurate weighing of 0·1–0·5 g. of material, and macro-volumetric analysis is concerned with the precise measurement of 10–50 ml. of reagent. To secure the same order of accuracy in the final result when working with smaller quantities of materials, say of the order of one-tenth or one-hundredth of the above quantities, the mere scaling down of existing macro-chemical techniques described in Chapters III and IV is not always satisfactory. Special techniques have been developed for small-scale analysis which yield results of the same order of accuracy as those obtainable by macro methods; it is the purpose of the present chapter to provide a short introduction to the subject.

In the first place the terms semi-micro-analysis and micro-analysis require some explanation. Semi-micro-analysis is concerned with the manipulation of 10–100 mg. of material, whilst micro-analysis deals with 1–10 mg. of material; semi-micro-analysis has been termed centigram analysis, and micro-analysis is sometimes called milligram analysis. There is clearly no sharp line of demarcation between the two, although the broad significance of the two terms is now well established. In practice, semi-micro-analysis is generally carried out with the aid of a balance sensitive to 0·01 mg., whilst for micro-analysis a balance sensitive to 0·001 mg. (1γ) is employed. Most of the apparatus required for semi-micro-analysis is available commercially and, apart from the balance, is comparatively inexpensive. This apparatus will be described below; much of it can be employed for micro-analysis by obvious modifications of the technique, once that for semi-micro-analysis has been mastered. The training of large classes of students in micro-methods is, under the normal conditions existing in the average college or university laboratory, more conveniently carried out by experiments on the semi-micro-scale; the essential differences between macro- and micro-techniques will thus be appreciated and the broad features of the new techniques acquired. If the facilities are available (micro-balances reading to 0·001 mg., etc.), micro-analysis (milligram analysis) should be carried out.

XI, 2. Micro-balances.—A typical semimicro-balance, sensitive to 0·01 mg., has been described in Section II, 9F. A micro-balance (Oertling, No. 63. PA/PB), maximum load 20 g. and direct reading to 0·001 mg. (1 microgram = 1γ), is illustrated in Fig. XI, 2, 1. The beam, which carries a 5-mg. rider, is serrated into 100 parts: movement of the rider along the beam from one notch to the next represents a difference in weight of 0·1 mg. The pointer carries a tiny, finely divided graticule (200 divisions), and a magnified reflection of this is shown on an illuminated ground-glass screen at the top of the balance case; 0·1 mg. swings the pointer approximately 100 divisions, thus enabling readings to be made to 0·001 mg.
It will be evident that for accurate weightings to 1 microgram, the balance must be properly sited. The following points must be taken into consideration when setting up a micro-balance.

1. The balance should preferably be located in a separate room and be supported upon a stone slab mounted upon supports about 2 ft. 6 in. high. The latter should, if possible, be of stone or brick and not be connected with the walls of the balance room. Ideally, the supports should be built up from the level of the foundations. To damp out vibrations still further, strips of lead and, if available, “sorbo” rubber may be placed between the stone slab and its supports.

2. The temperature of the balance room should remain constant to within ± 1°C. It has been stated that a temperature change of 1–2°C will cause a shift of several micrograms in the zero reading. Draughts must be avoided at all times. The balance must be shielded from the direct rays of the sun. Artificial light sources, e.g., symmetrically placed lamps, should be at least 3 ft. away.

3. The humidity of the atmosphere should be kept as constant as possible. The relative humidity should not be below 50–60 per cent. A lower moisture content may permit the accumulation of electrostatic charges on the metal parts of the balance.

In quantitative analysis it is necessary to know only the weight of the
sample and the weight of the reaction products. It is standard practice in microchemical analysis to counterpoise all weighing vessels: the counterpoises are made, wherever possible, of the same volume and shape as the vessel being weighed. The buoyancy corrections are thus almost eliminated, and only a few small weights (0.01–0.1 g.) need be used; calibration corrections are consequently reduced to a minimum. For weighing crucibles, boats, etc., small glass bottles (Fig. XI, 2, 2) preferably provided with ground-glass stoppers and containing fine lead shot, are frequently employed. The preliminary weighing may be made on a macro-balance. The object is placed on the left-hand pan, and the empty tare flask and a 0.1 g. weight on the right-hand pan. Medium-sized lead shot are carefully added until a rough balance is obtained; the 0.1 g. weight is then removed and further balancing within a few mg. is carried out with the finest lead shot. The weights and counterpoises (the latter distinctly marked by etching with hydrofluoric acid) are kept permanently inside the micro-balance on specially constructed glass stands or upon clean microscope slides.

All objects to be weighed must acquire the temperature of the balance case. After they have attained the laboratory temperature in a desiccator or upon a copper or metal block under a glass cover, the objects are placed for 5–15 minutes, depending upon their size, in the neighbourhood of the balance and finally for 5–10 minutes inside the balance case. The objects are never touched with the hand, but always with forceps (which may be rubber tipped), wire clamps, chamois leather, etc. Glass and porcelain vessels are first wiped with a moist chamois leather and then gently with a piece of dry chamois leather; vigorous rubbing of the surface must be avoided, as this may produce an electrostatic charge and thus cause difficulties in weighing. This treatment is designed to remove the uneven film of moisture and microscopic traces of dust or grease. The same technique for wiping the glass or porcelain apparatus must be rigorously followed at all times; the procedure suggested leads to a reproducible moisture film. If the glass counterpoises are treated in the same manner, the effect of any variation in conditions during a weighing is eliminated or reduced to negligible proportions. It is also recommended that a pair of thin chamois-leather gloves be worn in the balance room in order to protect apparatus from the moisture of the hand.

**XI, 3. Miscellaneous apparatus for micro-analysis.**—A brief account will be given of certain items of equipment which are available commercially for semimicro-(and micro-) analysis.

**A. Wash bottles.** Two types in common use are shown in Fig. XI, 3, 1. Form (a) is a graduated cylinder of 50 ml. capacity, and the two parts of the wash bottle are held together at the standard ground-glass joint by means of two wire springs attached to the glass hooks; the mouthpiece is provided with a saliva trap for protecting the contents from contamination. A light metal stand is usually supplied to hold the bottle in a vertical position. Form (b) is similar but ungraduated; it is constructed from a 125- or 250-ml Pyrex flat-bottomed flask.

**B. Desiccators.** A useful desiccator for micro-analysis, due to Sasohek (1937), is shown in Fig. XI, 3, 2. A round aluminium block of
62 mm. diameter and 45 mm. in height has on its upper surface a concentric ring 5 mm. in height and 6 mm. wide; a 50-ml flat-bottomed crystallising dish of 56 mm. outer diameter and 38 mm. in height serves as a cover. The centre of the metal block has a flat-bottomed cavity 35 mm. wide and 33 mm. deep, which serves as a convenient receptacle *inter alia* for crucibles in which precipitates have been ignited. The rim of this cavity is 5 mm. below the concentric ring and supports a concave copper block of 39 mm. diameter and 12 mm. thickness, which serves as a support and an efficient cooling device. The above dimensions are those given by Saschek, and will serve as a guide for those wishing to construct the desiccator; they are not critical. A commercial form of this desiccator is available;* it is an aluminium desiccator and is provided with a cooling block and glass top. The metal base ensures more rapid cooling. The inside diameter is 34.5 mm., and the inside overall height is 64 mm. The depth of the apparatus is sufficient to permit its use with filter-stick and micro-beaker determinations as well as with the micro cooling block.

A 3-in. desiccator in Phoenix glass † (Fig. XI, 3, 3) is marketed either for use at atmospheric pressure (a) or for use under diminished pressure (b). The vacuum desiccator is fitted with a combined B14 ground-glass joint and stopcock. An aluminium, copper, or nickel-plated copper block

---

* For example, from Fisher Scientific Co., Pittsburgh, Pa.
may be placed inside the desiccator to promote rapid cooling. The vacuum desiccator has the widest application in micro-analysis. It is charged with an appropriate drying agent—anhydrous calcium sulphate, anhydrous calcium chloride, anhydride, or phosphoric oxide. The air entering the desiccator during the re-establishment of atmospheric pressure should be dried with the same drying agent. Since the sample is small, drying is, as a rule, quickly accomplished under reduced pressure. For substances which must be dried at higher temperatures but at normal pressure, a thermostatically controlled electric drying oven may be used.

Drying under reduced pressure in a current of dry air, either at the laboratory temperature or more usually at higher temperatures, may be carried out rapidly and efficiently by means of the Pregl micro-desiccator illustrated in Fig. XI, 3, 4. It consists of a glass tube 24–

\[ \text{Fig. XI, 3, 3.} \]

25 cm. long and 1 cm. diameter, constricted at the centre to a fine capillary of about 3 cm. length. One-half of the tube serves to hold the drying agent, which is kept in position by plugs of pure cotton wool at each end; the opening is closed by a rubber stopper through which a fine capillary passes and expands into a bulb filled with cotton wool; it is advisable to connect the latter to a bubble counter for the purpose of indicating a stoppage in the air current. The other half of the tube serves to hold the boat, crucible, and the like; this section of the tube is closed by a rubber stopper which carries a drying tube filled with a suitable desiccant and has, at its far end, a short length of capillary
tubing for connexion to the pump. When in use, the micro-desiccator is held in a Pregl drying block (Fig. XI, 4, 9) by means of two corks, which are flattened on one side so that the micro-desiccator may lie on the bench without rolling. By drawing a gentle current of air over the surface of the substance which is being heated, very rapid and thorough drying may be achieved.

For the rapid drying of somewhat larger apparatus, particularly filter-sticks and micro-beakers, the Benedetti-Pichler drier shown in Fig. XI, 3, 5, may be used. The tube is heated in a drying block B, which is a somewhat enlarged version of the Pregl apparatus (regenerating block, Fig. XI, 4, 9). The suction tube $S$ of ca. 4 mm. external diameter has a total length of 35–40 cm., and is 5–10 cm. longer than the drying tube proper. A 6-cm. length of 6-mm. tubing, followed by a short length of 2 mm. diameter, is sealed at one end; the wide portion forms a gas-tight joint with the stem of the drying tube by means of a short length of rubber tubing at M. The two corks C (flattened at one side so that the desiccator may rest securely on a sheet of clean paper on the bench) serve to hold the drying tube $T$ in position in the drying block; $F$ is charged with anhydrous calcium chloride, held in position between plugs of glass or cotton wool, to dry the air entering the apparatus. The experimental details for drying a filter-stick (Section XI, 4A) and its associated beaker will now be given.

The drying block is heated to the required temperature and the burner is regulated so that this temperature is maintained. The guard tube $F$ is removed and the tube $S$ is pushed into the drying tube $T$ until the end $N$ projects beyond the tube. Without being removed from the micro-beaker, the filter-stick is connected to the end $N$ by a short length of rubber valve tubing; the tube $S$ is now drawn back into the drying tube $T$ until the narrow-bore tube $S$ into the tube $T$: the filter-stick, whilst being

![Fig. XI, 3, 5.](image)
retained in the micro-beaker, is disconnected at \( N \). The pump is now turned off, the tube \( S \) is drawn back so as to form an air-tight seal at \( M \), and the guard tube \( F \) is inserted in order to prevent dust from entering the drying chamber \( T \). The end of the filter-stick which was connected to \( N \) is carefully cleaned with a linen cloth and, whilst retaining the filter-stick in the beaker, the outside of the beaker is wiped with moist and then with a dry chamois leather as detailed in Section XI, 2. The beaker and filter-stick are then placed in a desiccator (e.g., Fig. XI, 3, 2). After leaving near the balance case for 10 minutes, the beaker is transferred to the balance pan by means of forceps (Fig. XI, 4, 2a); if the frame (Fig. XI, 4, 2b) is used, the filter-stick may remain in the beaker. It is recommended that the tare consist of a beaker of similar size and that rods of soft glass (4 mm. and 1 mm. diameter, cleaned with moist and dry chamois leather) held by means of a piece of chamois leather or with forceps be added until the total weight of the tare is slightly less than that of the beaker and filter-stick; the difference in weight should preferably be about 0.5 g. for micro-analysis, but may be appreciably more for semimicro work. Finally, the doors of the balance are opened and the weighing is performed after 10 minutes. If it is desired to check the constancy in weight of the beaker and filter-stick, the beaker is filled with distilled water, the water is drawn off through the filter-stick, and the drying and weighing procedures are repeated.

C. Beakers. The following beakers are available commercially: Pyrex, low form with pour-out lip, 5, 10, 15, 20, and 30 ml.; Pyrex, round bottom, 5 and 10 ml.; Hysil, with or without lip, 1, 5, 10, 15, and 20 ml.

D. Flasks. The following flasks may be purchased: Pyrex, round-bottomed, 5, 10, and 25 ml.; Hysil, round-bottomed, 5, 10, 15, 20, 25, and 30 ml.; Pyrex or Hysil conical (Erlenmeyer) flasks, 5, 10, 15, and 25 ml.; Pyrex or Hysil filter-flasks with side tube, 25, 50, and 125 ml.

E. Evaporating basins or dishes. The following evaporating basins are suitable for micro-chemical analysis: deep form with lip, Royal Worcester, 13 ml., Coors porcelain, 10, 22, and 35 ml.; flat form with lip, Royal Worcester, 10 and 25 ml.

F. Crucibles. Micro-crucibles of approximate capacities 1, 3, 6, 8, 11, and 15 ml. in porcelain and in platinum may be purchased. Micro-crucibles for the collection of precipitates have been designed by Nebauer: the original type was 14 mm. high, 12 mm. wide at the top, and 10 mm. at the base. Such crucibles, when made of platinum, have a filtering-rod of compressed platinum-iridium sponge; when in porcelain, the base is of unglazed material. Each crucible is provided with a lid and also with a small capsule to cover the base; it should not be weighed without both of these. The dimensions have been modified, but the name Nebauer crucible has been retained. Micro-filter-crucibles, with saucer (capsule) and lid, provided with porous bottoms are standard commercial products: Royal Worcester, 1 ml. (height 15 mm., diameter at bottom 12 mm., diameter at top 15 mm.) and 3 ml. (22 x 14 x 10 mm.); Selas micro, 1·2 ml. (height 16 mm., diameter at bottom 12 mm.) and 2·6 ml. (23 x 12 mm.); Selas semi-micro, 5·5 ml. (31 x 16 mm.) and 7 ml. (37 x 16 mm.).

G. Burners. The diminutive form of the Bunsen burner, the so-called arsenic burner, is useful in semi-micro-work. Micro-burners of
excellent design are marketed by most dealers and/or manufacturers of scientific apparatus.

H. Water-baths. Micro-beakers and similar glass apparatus are never heated directly with a flame. The device (a) (Fig. XI, 3, 6) may be used for beakers; the metal ring rests on top of the beaker in which water is boiled. The device (b) is shown inside the associated 250-ml. Pyrex conical flask. The deep indentations, symmetrically placed, serve to support the micro-vessel.

I. Drying blocks. For drying substances, crucibles, etc., at temperatures of 100–200° C. at atmospheric pressure, the drying block shown in Fig. XI, 3, 7 may be employed. The solid metal block is either of aluminium or nickel-plated copper, has a concave surface, and is about 50 mm. in diameter; the block is heated by a micro-burner. A small electric crucible or muffle furnace is a valuable addition to micro-chemical equipment.*

J. Weighing-bottles. Various types of weighing-bottles employed in micro-chemical analysis are shown in Fig. XI, 3, 8 (these are not drawn to scale). Type (a) is the conventional form of weighing-bottle with

* A muffle-crucible furnace with built-in controls and pyrometer, well adapted for micro-chemical work, is manufactured by A. Gallenkamp and Co., Ltd., 17-29 Sun Street, London, E.C.2. Excellent crucible furnaces are also manufactured by Wild-Barrfield Electric Furnaces, Ltd., Eleofurn Works, Watford By-pass, Bushey.
external ground-glass cap; it is usually about 8 mm. high and 7–8 mm.
wide. Form (b) is a Pregl weighing-tube, 35 mm. long and of about
4 mm. diameter; the aluminium handle prevents appreciable warm-
ing of the tube. Type (c) is similar to (b), but is provided with an ex-
ternal ground-glass cap. Types (d) and (e) are long-handled weighing-
tubes (tube, 20 × 5 mm.; handle, 10 cm. long); these are useful for
weighing out a solid substance which is afterwards transferred to another
vessel, such as a conical flask. Type (f) is a micro weighing-bottle
(“weighing piggy”); it is generally employed for weighing out hygro-
scopic substances in a platinum or porcelain boat.
K. Centrifuges. Centrifuges are generally employed to separate a suspended solid from a liquid. An electrically-driven centrifuge, capable of giving speeds up to 3,000 revolutions per minute, is recommended for quantitative analysis. A full discussion of the theory and also of the applications of the centrifuge to qualitative inorganic analysis has been given elsewhere* by the author. It may, however, be desirable to discuss here the general precautions to be taken in the use of the centrifuge. These include:

1. The masses at the centrifuge head must always be balanced (to within 0.1 g.) before starting the centrifuge.
2. Centrifuge tubes should not be filled to more than 2.5 cm. from the rims of the tubes.
3. The cover must be placed on the shield before starting and it must not be removed before the centrifuge has come to rest.
4. All electrically-driven centrifuges are fitted with variable resistances. They should be started off at low speeds of rotation and gradually raised to the maximum required as indicated upon the revolution counter. At the end of the appropriate period the speed of rotation must be reduced gradually, since violent changes of speed of revolution tend to disturb the precipitate.
5. The liquid may be separated from the solid by decantation. The tube is inverted gradually and the liquid allowed to flow out at moderate speed, and the angle of inversion is maintained consistent with the volume of liquid remaining in the tube. The centrifuge tube is then inverted over a pad of filter paper and the residual liquid permitted to drain from the walls of the tube. Any liquid adhering to the rim of the tube is removed with filter paper. Alternatively, the mother liquor may be removed with the aid of a dropper pipette.
6. The precipitate must usually be purified by washing. This may be done by holding the centrifuge tube loosely in one hand and gently tapping the bottom of the tube with the fingers of the other hand so as to splash the precipitate up the sides of the tube. A known volume of wash liquid is then added from a calibrated pipette, care being taken that the sides of the tube are washed thoroughly. The bottom of the tube is flicked gently with the fingers to ensure intimate contact between the precipitate and the wash-liquid. The suspension is then centrifuged again. It is usually considered necessary to repeat the washing and centrifuging twice for the complete removal of the excess of the original precipitating reagent.

XI, 4. Apparatus for quantitative filtration.—The most widely used method for quantitative filtration in gravimetric analysis utilises the filter-stick. Micro filter-beakers, filter-tubes, and crucibles also find application for the same purpose. A description of all of these follows.

A. Filter sticks. In any attempt to reduce the scale of macrogravimetric determinations, a major source of error lies in the transference of precipitates from the beaker (or precipitation vessel) to the filter. The error may be eliminated altogether by the use of a filter-stick, first developed by F. Emich. The filter-stick is used for upward filtration.

Quantitative Inorganic Analysis

in a manner which will become evident upon inspection of Fig. XI, 4, 1. A filter-stick is always associated with a particular beaker or crucible; they are kept together in a special little rack and weighed together before and after the determination.

Pyrex round-bottomed beakers of 5 and 10 ml. capacity are marketed; they are usually supported in a metal stand (Fig. XI, 4, 2, a). The micro-beaker and filter-stick are conveniently supported on a frame (Fig. XI, 4, 2, b) on the pan of the balance. This may be constructed from aluminium wire of 0·5 mm. diameter; the weight of the frame should not exceed 1 g., and its base should be about 3 cm. square. The beaker and filter-stick are laid across the parts labelled B and F.
Micro-gravimetric and Micro-volumetric Analysis

respectively; the ends $A$ are flattened so that the frame may be readily picked up with the forceps. The frame is carefully cleaned and kept inside the balance case. The forceps (Fig. XI, 4, 3, a), shaped to grasp the cylindrical surface of the micro-beaker, are useful in transferring the beaker to the balance. The filter-stick may be handled with the forceps shown in Fig. XI, 4, 3, b; the slightly conical grooves are made to fit around cylindrical rods.

The commercial forms of micro-filter-sticks are made of Pyrex glass and of porcelain. The Pyrex filter-stick carries a 10-mm. sintered-glass disc. Porcelain filter-sticks have a porous disc fused at the lower end: in the Royal Worcester micro-filter-stick the porous plate has a diameter of 10 mm. and the tube is 50 mm. long. The Selas Corporation market a micro-filter-stick ($9 \times 57$ mm.) and a semimicro-filter-stick ($20 \times 85$ mm.).

Before use, the filter-stick and associated beaker (or crucible) are cleaned by filling the beaker with chromic acid mixture or with concentrated nitric acid, inserting the filter-stick into the beaker and heating on a water-bath. After about 10 minutes most of the acid is removed from the beaker by means of a pipette fitted with a rubber teat, and the beaker is filled with water. The diluted acid is removed by suction through the filter-stick; the beaker is filled several times with distilled water, and is similarly emptied by suction. The filter-stick and beaker are now dried, preferably in a Benedetti-Pichler drier (Fig. XI, 3, 5) at the same temperature as will be used subsequently in drying the precipitate, wiped, and weighed against a counterpoise of similar shape.

The substance to be analysed is weighed directly into the beaker (or crucible) and dissolved in a suitable solvent. [The filter-stick is kept outside the beaker until precipitation is complete.] The precipitation reaction is then carried out in the normal way. When precipitation is complete, the filter-stick may be inserted into the beaker (or crucible) and used as a stirring-rod. The precipitate is allowed to settle, all the supernatant liquid is sucked off through the filter-stick by attaching the latter with rubber tubing to either of the receivers depicted in Fig. XI, 4, 1; these are held in a small clamp attached to a stand (compare Fig. XI, 4, 2) to ensure stability. This operation must be carried out carefully using as little suction as possible; the rate of filtration can be easily controlled with the aid of the stopcock. The residual precipitate must be washed several times by successive portions of the wash liquid, which should be introduced from a wash...
bottle or pipette down the sides of the micro-beaker or micro-crucible and filter-stick. Finally, after sucking the residue as dry as possible, the precipitation vessel, with the filter-stick inside it, is wiped externally, placed in an appropriate drying apparatus (Benedetti-Pichler drier or thermostatically controlled electric drying oven) and heated for the requisite time. [Pyrex filter-sticks should not be heated above 180° C.] The apparatus is finally removed, allowed to cool for 10 minutes in a metal block desiccator, wiped carefully with moist and then dry chamois leather (Section XI, 2), transferred to a micro- or semimicro-balance, and weighed after 5–10 minutes.

The Miller micro-immersion filter or filter-stick (1939), Fig. XI, 4, 4, c, employs a filter-paper disc of about 5 mm. thickness, and is of particular value for the filtration of gelatinous precipitates such as hydrated silica, ferric and aluminium hydroxides. The filter-disc is conveniently cut from a Whatman “accelerator” by means of a sharp cork borer.

It is constructed in the following manner. Two pieces of Pyrex tubing are required, namely, a 12-mm. length of capillary tubing of 3·5 mm. external diameter and 1 mm. bore, cut off square, and a 150-mm. length of tubing of 1 mm. wall into which the capillary fits closely. The longer tube is drawn out at one end to form a capillary of 2·5 mm. external diameter and 70 mm. length, and the thick capillary tube is pushed in at the other end as far as it will go (Fig. XI, 4, 4, a). The pair of tubes is then steadily rotated and heated at Z in a small and not too hot blowpipe flame so as to fuse together the two pieces of glass with the minimum of deformation. The heating is gradually extended towards Y until the whole of the capillary tube is sealed in without deforming the flat end at Y; thereafter the size of the flame is increased a little, the capillary heated more strongly towards X, and the tube, after slight blowing, is drawn out to give the appearance shown in (b). The whole is then annealed. Finally, the tube is cut sharply at Z, and the piece of wider tubing removed, leaving not more than 2 mm. projecting from the capillary. If the break is irregular the tube is carefully ground flat and fire-polished without causing the glass to collapse. The final form is shown in (c).

B. Filter beakers. This device (Fig. XI, 4, 5), due to E. Schwarz-Bergkampf (1926), incorporates the filter-stick and beaker in one vessel. The commercial apparatus is of Pyrex glass, about 27 mm. in diameter and with a sintered-glass filter-disc (10 mm. diameter) sealed into the outlet neck. It is first used as a beaker in which the precipitation is carried out and then as a filter by which the precipitate is retained. If desired, the filtrate may pass into a similar beaker.
(Fig. XI, 4, 6), possibly for a further step in a separation. The filter-beakers are, of course, weighed accurately with the usual precautions before and after use. An interesting application of the filter-stick and the filter-beaker will be evident from Fig. XI, 4, 7.

C. Filter-tubes. A micro-filter-tube is shown in Fig. XI, 4, 8, a; it is of Pyrex glass with a sintered-glass disc 10 mm. in diameter and has a capacity of 3–4 ml. The filter-tube is generally used to handle precipitates of 5–30 mg. in volumes of liquid of 15–35 ml., or in larger volumes. The mode of use will be apparent from Fig. XI, 4, 8, b; the siphon tube has a bore of 2–3 mm., and the filter-flask is of 250 ml. capacity. A small test-tube may be placed inside the latter if the filtrate is required. The liquid and the precipitate in the test-tube are drawn over by gentle suction on to the filter, as are also the washings. To remove traces of precipitate a snipe feather set in a capillary handle * is used as a “policeman.” If the sintered-glass disc is not

* A small snipe feather is cemented into a capillary tube about 12 cm. long and 2 mm. external diameter; it should be impossible for liquid to enter the glass capillary. Freshly mounted feathers should be washed successively in benzene, alcohol, dilute soap solution, and distilled water. The mounted snipe feather should be stored in a closed test-tube, and must always be washed with distilled water before use.
sufficiently retentive, particularly for fine precipitates, a thin layer of asbestos is superimposed upon the fritted-glass disc by pouring a thin suspension of fine asbestos through it. If it is desired to measure the volume of the filtrate directly, the arrangement of Fig. XI, d, 8, c, may be employed.

Before use the filter-tube is boiled for 15 minutes in dilute nitric acid (1 : 1), then for the same time with distilled water, rinsed six times with distilled water and finally with pure ethyl alcohol. The filter-tube is removed, wiped with a clean linen cloth, and placed inside a Pregl drying block (Fig. XI, 4, 9). The latter consists of a split aluminum or copper block about 8 cm. long with two holes, one 13 mm. and the other 8 mm. in diameter; the lower block is drilled to accommodate a thermometer. The whole is mounted on a rigid base and is heated by a micro-burner. The filter-tube is dried directly in one of the channels, usually that of 13 mm. diameter. A glass tube containing a plug of pure cotton wool to act as an air-filter is placed in the wide end of the filter-tube, and the stem is inserted into a short length of rubber tubing which is connected by a glass tube and rubber tubing to a water-pump. A slow stream of air is aspirated through the apparatus as drying proceeds; the main body of the tube should be heated to 110°C. for not less than 15 minutes. [Alternatively, the Benedetti-Pichler drier, Fig. XI, 3, 5, may be used.] When dry, the filter-tube is disconnected, wiped, and weighed after 15 minutes. In use, the filter-tube is fitted to the siphoning system (Fig. XI, d, 8, b or c) and gentle suction applied: a test-tube or centrifuge tube is best employed as the reaction vessel. The whole apparatus must be supported firmly. When filtration is complete, the filter-tube is detached, dried, wiped, and weighed.

D. Micro-crucibles. A small porous-porcelain filter-crucible (Neubauer crucible, Section XI, 3F) is attached to a glass tube of the same outside diameter as the bottom of the crucible by means of a short rubber sleeve (Fig. XI, 4, 10). The glass tube is fitted by means of a
rubber stopper into a 250-ml. filter-flask as in Fig. XI, 4, 8, b. Filtra-
tion may be carried out with the aid of gentle suction from a water-
pump or by suction with the mouth through a 50-cm. length of rubber
 tubing attached to the side arm of the filter-flask. The
 siphon technique, described under Filter-tubes, is not
 always successful, especially when dealing with fine pre-
cipitates. The precipitate may be transferred from the
 precipitation vessel to the micro-crucible by means of
 a rubber-capped dropping pipette; the latter may be 8 cm.
 long, 5 mm. in diameter, and narrows sharply to a capill-
 ary of 1 mm. bore and 3 cm. in length. After the trans-
 fer of the precipitate and of the wash liquid, the rubber
 cap is removed and the pipette is rinsed with distilled water
 and alcohol.

In practice, it is found that most of the operations re-
 quiring the use of micro-crucibles can be carried out with
 a filter-stick constructed of appropriate material to with-
 stand the necessary temperature. Thus barium sulphate
 may be precipitated in the presence of agar (Section IV, 6); the re-
sulting crystalline precipitate is readily handled by the filter-stick
 technique.

XI, 5. Apparatus for micro-volumetric analysis.—Small quantities of
 liquids or substances may be titrated either with very dilute standard
 solutions or with small volumes of standard solutions of concentrations
 such as are employed in macro-analysis. The use of very dilute
 standard solutions is usually limited by the indefinite end points
 and by the solubility effects obtained under such conditions. Micro-
titrations are therefore generally carried out with small volumes (e.g.,
 1–10 ml.) of solutions of the usual strengths (e.g., 0·01–0·1N). Thus it is
 more accurate to titrate with 0·01N solutions from a 2-ml. micro-
burette than to use 0·001N solutions from a 25-ml. burette. If the
 stability of the indicator permits, it is often convenient to incorporate
 it in the standard solution. The various apparatus employed for
 semi-micro (centigram, i.e., 1–10 cg. of sample) procedures will now be
 described together with selected apparatus for micro (milligram, i.e.,
 1–10 mg. of sample) procedures: emphasis will, however, be laid on
 semi-micro-apparatus. From the viewpoint of the student’s initial
 training in micro-titrimetry, centigram procedures are to be preferred,
 particularly as a good semimicro-balance suffices, and comparatively
 inexpensive, commercially available apparatus may be used.

A. Volumetric flasks. Volumetric flasks are employed to prepare a
 definite volume of solution from a given weight of material. If sufficient
 of the material is available, especially if it is likely to be very hetero-
geneous, it is preferable to dissolve a relatively large sample in a large
 volumetric flask, and to employ a small aliquot portion for the analysis.
 If, however, only a small weight of the substance is given for the analysis,
 volumetric flasks of capacities of 1–25 ml. must be used. Ground-
 stoppered Pyrex volumetric flasks of 1 and 2 ml. capacity (test-tube
 shape) and 5, 10, and 25 ml. capacity (standard form) may be purchased.
 It is important that the graduation mark be so placed that adequate
 mixing is possible; care must also be taken that liquid is not trapped
 by, or leaks past, the stopper. The micro-volumetric flasks shown in
 Fig. XI, 5, I have been designed to reduce these possible errors to a
minimum. In type (a) the upper part has three to five times the capacity of that of the calibrated part; mixing is facile, but there is a tendency for the flask to tip over easily and, in consequence, it must be held in a suitable support. Type (b) can be held in a standard test-tube rack. Type (c) is useful for multiple operations, e.g., it can be used for wet digestion, and the reaction product may then be made up to volume.

B. Burettes. Semi-micro-burettes may be 1–10 ml. in capacity and graduated in 0.01-, 0.02-, or 0.05-ml. divisions. Recently semi-micro-burettes (5 ml. calibrated to 0.01 ml. and 10 ml. in 0.02 ml.) * with detachable platinum tips have been marketed: regular size of drops of 0.01 ml. are thus obtained, and this must be regarded as a real advance in burette construction. Burettes with glass stopcocks have a maximum precision of 0.01 ml. Two burettes,† with filling reservoirs, are depicted in Figs. XI, 6, 2, and XI, 6, 3, respectively. The former has a capacity of 5 ml. in 0.01-ml. divisions, whilst the reservoir has a volume of 50 ml. The latter is available in capacities of 1, 2, 5, and 10 ml., and is provided with two interchangeable outlet tips, one for calibration and the other for delivering 100–110 drops per ml.

Burettes with automatic zero adjustments, similar to those shown in Fig. II, 25, 4, find extensive application in semimicro-volumetric analysis. These deliver 1, 2, 5, or 10 ml., and are graduated in 0.01- or 0.02-ml. divisions; they are supported in a bottle of Pyrex or Jena glass containing the standard solution. The solution is delivered by air pressure to the top of the burette through a tube which, after filling, acts as a siphon and brings the level of the liquid in the burette automatically to zero. For alkaline solutions, rubber tubing should be used to connect the burette to its jet outlet, and either a pinchcock or, better, a glass bead inside the rubber tube is utilised instead of a

* Supplied by Kimble Glass Division, Owens-Illinois Glass Co., Toledo 1, Ohio, U.S.A.
† Supplied inter alia by the Fisher Scientific Co., Pittsburgh, Pa., U.S.A.
Micro-gravimetric and Micro-volumetric Analysis

Glass stopcock. The solutions are protected from atmospheric carbon dioxide by a small tube charged with soda lime.

Numerous types of micro-burettes which will deliver 0.5-1 ml. with an accuracy of 0.001 ml. have been described in the literature. A simple type, due to E. Schilow (1926), is shown in Fig. XI, 5, 4. A pressure-controlling device is employed in conjunction with a vertical burette made from a 1-ml. pipette subdivided into 100 (preferably 200) parts. The bulbs (upper, 10 ml.; lower, 25 ml. capacity) contain a heavy liquid of density 1.5-3; 50 per cent barium bromide solution is satisfactory. One bulb may be fixed and the other mounted on a stand with a rack-and-pinion motion in the vertical direction; this arrangement is desirable if mercury is used in the bulb. With the liquid in the bulbs at the same level, the tip of the burette is dipped into a standard solution and the burette is filled into equilibrium is attained, pressure $H$ equals pressure $H'$. When the burette is taken out of the solution, bulb $B$ may be raised slightly without causing the liquid to leave the burette; this is due to surface forces at the capillary jet.* Discharge takes place immediately if the tip of the burette is brought into contact with a wet surface. In the titration of a solution the tip of the burette is kept above its surface, and bulb $B$ is slowly raised. As the end point is approached, bulb $B$

* For a detailed discussion, see A. A. Benedetti-Pichler, Microtechnique of Inorganic Analysis, 1942, p. 234 (John Wiley; Chapman and Hall).
is left in a fixed position, and when the spontaneous discharge from the burette ceases, further minute quantities of liquid are added by bringing the solution in the titration vessel into contact at short intervals with the tip of the burette until the end point is reached, or no further change occurs in the burette reading; in the latter case $B$ is raised slightly and the process is repeated.

A similar device (Fig. XI, 5, 6) is employed for filling micro- and semimicro-pipettes. The pipette is attached to the pressure-controlling bulbs by means of rubber tubing. The pipette is then immersed in the liquid, bulb $B$ is lowered until the level of the liquid is slightly above the calibration mark, following which the liquid is removed. The capillary tip of the pipette is then placed against the wall of the vessel and bulb $B$ is carefully raised until the liquid level just reaches the calibration mark; if too much liquid has been expelled, the liquid can be adjusted to the mark merely by immersing the tip of the pipette in the liquid.

C. Pipettes. Pipettes of small capacity similar to those employed in macro-volumetric analysis and with volumes of the order of 1 ml. are marketed or can easily be constructed from glass tubing. They must be used only with solutions having a similar viscosity to that of the liquid employed to calibrate them (i.e., usually water). Such small pipettes are conveniently filled either by means of the apparatus illustrated in Fig. XI, 5, 6 or with the aid of that shown in Fig. XI, 5, 6, $a$. In the latter the glass tube is connected at $A$ to a rubber bulb or, by means of rubber tubing and a T-piece incorporating a glass tap, to the pump. A short length of rubber tubing $C$ of about 3 mm. bore fits over the wide end of the glass tube and the tapering portion near the bulb of the pipette. The pipette is filled with liquid 2–3 mm. above the calibration mark (the opening $B$ is closed during this process); it is then removed from the suction device, the outside of the pipette is wiped dry with filter-paper whilst held almost horizontally, and the liquid is adjusted to the mark by touching the tip with filter-paper. To empty the pipette it is held vertically and the tip made to touch the surface of the delivered liquid. The considerable amount of liquid which is finally held in the delivery tube by capillary attraction is expelled by closing the upper end of the pipette and warming the bulb by touching it with the fingers: the liquid should be expelled slowly, and is removed from the tip by touching either the surface of the liquid or the wet wall of the container. Alternatively, the device of Fig. XI, 5, 6, $a$, may be used; gentle pressure by a rubber bulb is exerted at $A$, and the opening $B$ is closed. The same procedure must be followed when the pipette is calibrated. The usual precautions are taken, including the use of distilled water at the temperature of the balance room, handling of the pipette with forceps or with several layers of chamois leather to prevent transfer of the heat from the hands.
Micro-gravimetric and Micro-volumetric Analysis

to the apparatus, and a glass-stoppered micro-weighing-bottle and counterpoise.

Small graduated pipettes of 0.5 and 1 ml. capacity are marketed; these are usually graduated in 0.1- or 0.01-ml. divisions and are emptied by means of a small rubber bulb or teat. They are useful for measuring out small volumes of liquid. Pipettes delivering between two marks possess the advantage that errors due to variations in the volume of retained liquid or to accidental damage to the tip are eliminated. The Van Slyke pipette (Fig. XI, 5, 6, b) is of this form with the addition of

![Fig. XI, 5, b.](image)

a high-quality glass stopcock; the latter should have a capillary bore in line with the capillary tubes.

Figs. XI, 5, 6, c and d, depict "wash-out" pipettes; these are filled as previously described (the suction device is shown in c), although type d can usually be filled by holding it in an inclined position in the liquid by taking advantage of the surface-tension effects. The pipette after emptying, by the application of slight pressure if necessary, is rinsed with 3-4 portions (each of approximately one quarter of the capacity of the pipette) of water or wash liquid introduced through the mouthpiece of the pipette. This will almost double the volume of solution used, and may constitute a disadvantage of the "wash-out" pipette. The pipette must be washed and dried before it is used again. A "wash-out" pipette is calibrated either by weighing the pipette empty and then filled with water or by titrating a volume of standard alkali solution delivered by the pipette with standard acid.

Micro-transfer pipettes without calibration marks are especially
Quantitative Inorganic Analysis

suited for small volumes from 0.1 ml. upwards; the zero point, which is the tip of the upper capillary, is adjusted automatically. The pipette, which may have a total length of about 3 cm., is shown in Fig. XI, 5, 7, which includes a convenient filling apparatus (Briscoe and Holt, 1950; compare Fig. XI, 5, 5). A small glass cap A is closed by a two-holed rubber stopper of about 5 mm. thickness; one hole supports the pipette, the other hole holds the wide bent tube (6-7 mm. bore) which is fitted through a rubber stopper into the small bottle C. A small hole D is blown in the wall of the glass tube; the latter is closed by a rubber teat or a small rubber bulb. The pipette is filled by compressing the rubber teat or bulb, closing the air inlet at D, and then releasing whilst the pipette is held beneath the surface of the liquid; the excess of liquid flows from the pipette into A and drains into the bottle C. The flow of liquid is immediately checked by simultaneously opening the air-inlet D and withdrawing the pipette tip from the liquid. The pipette remains completely filled to the tip of the capillary. The liquid in the pipette is delivered by applying pressure with the rubber bulb whilst the air inlet D is closed until the upper capillary is emptied; D is now opened and the liquid is allowed to flow out with the capillary tip touching the side of the vessel: after allowing 10 seconds for drainage, D is closed and a slight pressure is applied with the rubber bulb in order to expel the liquid remaining in the lower capillary.

The "Exelo" safety syringe pipettes,* constructed in borosilicate glass, are particularly useful for semimicro- and micro-volumetric analysis. Fig. XI, 5, 8 a, illustrates a graduated pipette fitted with a

standard ground glass joint and an all-glass syringe; models are also available in which the syringe is fused directly to the pipette. A variation, which possesses certain advantages, is shown in Fig. XI, 5, 8, 9: here the fitting of the syringe to the pipette is reversed, the barrel of the syringe being employed to draw the liquid into the pipette; the piston is hollow and forms an integral part of the pipette. All capacities from 0·001 ml. to 50 ml. are available as one-mark and as graduated pipettes.

D. Titration vessels. Semimicro-titrations may be carried out in small tubes, crucibles, beakers, or flasks. Stirring may be effected by a stream of air or nitrogen introduced through a capillary tube, or magnetically by means of an iron-filled capillary tube actuated by a rotating electromagnet. A small mechanical stirrer supporting a very fine stirring-rod, which is afterwards rinsed by running two drops of water from a dropper pipette along the length of the rod and into the titration vessel, may often be used. The titration vessel may also be held with its axis about 45° from the vertical and rotated a number of times.

The titration vessel should be steamed out before every titration. The device depicted in Fig. XI, 5, 9, which fits into a 500-ml. or 1-litre round-bottomed flask, may be employed. The side tube at the bottom of the funnel may be connected to a length of rubber tubing so that the condensed steam drains into a sink.

XI, 6. Some simple micro-gravimetric determinations.—In order to attain experience with some of the apparatus described in the previous Sections, the experimental details for a few simple semimicro determinations (centigram procedures) will be given: the student should have no difficulty in adapting these to the micro-scale (milligram procedures). For a more detailed treatment of the subject reference should be made to the treatises on micro-chemical analysis listed in the Bibliography at the end of this chapter.

A. Determination of magnesium as the ammonium phosphate hexahydrate. Procedure. Weigh a micro-beaker with its Pyrex or porcelain filter-stick on a semimicro-balance: take the usual precautions with regard to counterpoise, preparing the surface of the beaker by wiping with moist followed by dry chamois leather, etc. Select a crystal of A.R. magnesium sulphate weighing 20–30 mg., drop it into the micro-beaker from the tip of a small spatula, and re-weigh. Place the filter-stick in its special stand (compare Fig. XI, 4, 2, 6). Dissolve the sample in 1–2 ml. of water, add 0·8–1·0 ml. of 15 per cent ammonium chloride solution and heat in a boiling water-bath (compare Fig. XI, 3, 6) for 5 minutes. Remove the beaker from the water-bath and add from a calibrated dropper pipette 0·4–0·5 ml. of 2N-ammonia solution, followed by a slight excess (0·8–1·0 ml.) of 10 per cent disodium hydro-
Quantitative Inorganic Analysis

836

...gen phosphate solution. Allow the precipitate to stand for 4–5 hours. Filter with the aid of the filter-stick, wash the precipitate with several portions of 2N-ammonia solution (ca. 8 ml. in all), and finally with several portions (total volume, 4–5 ml.) of anhydrous methyl alcohol. Dry at room temperature in a Benedetti-Pichler apparatus (Fig. XI, 3 5). After 15 minutes, remove the beaker and filter-stick, and weigh it in the usual manner.

Calculate the percentage of magnesium in the sample of magnesium sulphate.

B. Determination of chloride as silver chloride. Procedure. Dry a small quantity of A.R. potassium chloride at 120° C. and allow to cool in a desiccator. Weigh a micro-beaker with its Pyrex or porcelain filter-stick. Weigh out accurately into the micro-beaker 20–30 mg. of the potassium chloride, dissolve it in about 2 ml. of water, and add a few drops of dilute nitric acid (1:4). Heat on a water-bath and add 0.1N-silver nitrate solution dropwise until precipitation is complete. Continue the heating for a further 15 minutes, remove the beaker from the water-bath, and allow to stand for 15 minutes. Filter and wash the precipitate with 2 ml. of 0.01–0.02N-nitric acid, and finally with 2 ml. of hot water. Dry the precipitate for 5 minutes in a Benedetti-Pichler drying block at 130–140° C., and weigh on the semimicro-balance.

Calculate the percentage of chlorine in the sample of potassium chloride.

In order to secure practice in the use of a filter-tube, repeat the above determination, but transfer the precipitated silver chloride quantitatively to a test-tube and thence to a weighed filter-tube (compare Fig. XI, 4, 8). Dry the filter-tube and precipitate in a Benedetti-Pichler drier at 130–140° C. Weigh, after leaving in a metal rack near the balance for 15 minutes.

C. Determination of aluminium as the 8-hydroxyquinolate. Procedure. Use a solution of A.R. aluminium ammonium sulphate containing about 1 mg. of Al per ml.: the exact aluminium concentration is calculated from the weight of ammonium alum employed in preparing the solution. By means of a semimicro-burette transfer 2.00 ml. of this solution to a micro-beaker, previously weighed with its glass or porcelain filter-stick. Add about 2 ml. of water, followed by 2.5 ml. of a 2 per cent solution of oxine in 2N-acetic acid. Heat on a water-bath for 2–3 minutes, then add 2N-ammonium acetate solution dropwise until a permanent cloudiness is produced. Heat for a further 2–3 minutes to assist the initial coagulation of the precipitate and add 1 ml. more of the ammonium acetate solution. Continue the heating on a boiling water-bath for 10 minutes, by which time the precipitate should have become crystalline. Remove from the water-bath, filter, and wash five times with 0.5-ml. portions of hot water: the final washings should be colourless. Dry the filter-stick and beaker at 140° C. for about 30 minutes. After wiping the beaker with chamois leather and allowing to stand for 10–15 minutes, weigh the beaker and filter-stick on the semimicro-balance.

Calculate the weight of aluminium in the volume of solution employed from the weight of aluminium oxinate obtained, and compare this value with that computed from the known strength of the stock solution.
D. Determination of nickel as the dimethylglyoxime complex. **Procedure.**

Weigh out accurately 20-30 mg. of pure nickel ammonium sulphate into a micro-beaker (previously weighed empty with its filter-stick), dissolve it in 3-4 ml. of water, and add 2-3 drops of dilute hydrochloric acid (1:1). Add a slight excess of a 1 per cent solution of dimethylglyoxime in alcohol, warm the beaker on a water-bath to about 70° C., and introduce dilute ammonia solution dropwise until a slight excess is present (odour). Digest on the water-bath for 10 minutes, allow to cool, and filter in conjunction with the filter-stick.

Wash the precipitate first with cold water and then twice with 20 per cent ethyl alcohol. Dry the precipitate at 110-120° C. in a Benedetti-Pichler block, cool, and weigh.

Calculate the percentage of nickel in the sample of nickel ammonium sulphate.

E. Determination of calcium as calcium oxalate monohydrate. **Procedure.**

Weigh out accurately 10-20 mg. of dry A.R. calcium carbonate into a micro-beaker. Add about 2 ml. of water and cover with a hollow glass bulb similar to that shown in Fig. XI, 6, 1. Lift the glass bulb just sufficiently to permit the insertion of a capillary pipette, add dilute hydrochloric acid (1:1) dropwise down the side of the beaker until all the solid has reacted. Warm the beaker on a water-bath, with the bulb covering the mouth, for 5 minutes to expel carbon dioxide. Raise the bulb slightly and rinse it with about 0-5 ml. of distilled water from a wash bottle, taking care that all the rinsings are collected in the beaker; remove the glass bulb. Add a micro-drop of methyl-red indicator, followed by a slight excess (1-5-3-0 ml. in all) of 3 per cent oxalic acid solution. Transfer the beaker to a boiling water-bath and add dilute ammonia solution (1:5) dropwise until the colour of the solution changes to yellow. Heat for a further 5 minutes, and allow to stand for 1 hour. Decant the clear solution through the filter-stick so that as little of it as possible is left with the precipitate in the micro-beaker. In a similar manner wash the precipitate with three 1-ml. portions of cold 0-2 per cent ammonium oxalate solution, and finally twice with 1-ml. portions of cold water. The main portion of the precipitate is allowed to enter the filter-stick during the last washing. Dry in a Benedetti-Pichler block at 100-105° C. for 10 minutes, and weigh as usual.

Calculate the percentage of calcium in the sample of calcium carbonate.

**Note.** Owing to the tendency of the precipitate to clog the filter, washing by decantation is recommended. If a Miller micro-immersion filter (Fig. XI, 4, 4) is employed, this difficulty does not arise.

**XI, 7. Some simple micro-volumetric determinations.**—All micro-volumetric apparatus should be calibrated before use if the highest precision is to be obtained; the apparatus must, of course, be clean before calibration is attempted. The method of calibration should, in general, imitate the conditions under which the apparatus is to be used. Burettes may also be calibrated by titration, e.g., standard hydrochloric acid may be placed in the burette and the acid titrated with carefully prepared standard solutions of alkali of different strengths. Small
conical flasks may be used in semimicro-titrimetric analysis: mixing of the solutions can be readily attained by swirling between additions of reagent. Another procedure, suitable for most titration vessels, is to pass air or an inert gas, such as nitrogen, through the solution by means of a fine capillary jet when the regular stream of bubbles results in adequate mixing.

Care should be taken in the addition of the correct quantity of indicator. A glass-stoppered dropping-bottle of about 50 ml. capacity may be used as the container for the indicator solution; the capillary of the glass stopper should be drawn out to a solid glass rod of about 1 mm. thickness. The glass rod is dipped into the indicator solution, and some of it is transferred to the titration vessel by touching the inner wall: the indicator is mixed with the solution to be titrated by tilting the titration vessel.

Practice in semimicro-volumetric determinations can be obtained by fairly obvious modifications of the macro-procedures described in Chapter III. The notes given below should assist the reader in securing the necessary experience.

A. Preparation of 0.01N-hydrochloric acid. 0.1N-hydrochloric acid is first prepared from the constant-boiling-point acid (Section III, 3); 100 ml. of this solution is diluted with boiled-out distilled water to 1 litre in a volumetric flask. It may be standardised, if desired, against 10–20 mg. of pure anhydrous sodium carbonate, accurately weighed and dissolved in about 10 ml. of water, using bromophenol blue as indicator (Section III, 4).

B. Preparation of 0.01N-potassium bi-iodate. 3.8994 G. of pure potassium bi-iodate (Section III, 6, G) are dissolved in warm distilled water, and made up to volume with boiled-out distilled water in a 1-litre volumetric flask.

C. Preparation of 0.01N-sodium hydroxide. 0.1N carbonate-free sodium hydroxide is prepared as detailed in Section III, 5, and the solution is diluted with boiled-out distilled water in a volumetric flask. It may be standardised with 0.01N-hydrochloric acid or with 0.01N-potassium bi-iodate.

D. Preparation of 0.01N-sodium thiosulphate. A ca. 0.01N-sodium thiosulphate solution is prepared by dissolving 2.48 g. of A.R. sodium thiosulphate pentahydrate in distilled water, 0.1 ml. of chloroform is added and the solution is made up to the mark with boiled-out distilled water in a litre volumetric flask. The thiosulphate solution may be standardised as follows. About 0.8 ml. of 0.01N-potassium bi-iodate solution is accurately measured with a semimicro-burette and run into a 50- or 100-ml. glass-stoppered conical flask. Three ml. of 10 per cent sulphuric acid and 2 ml. of 4 per cent potassium iodide solution are added, and, after standing for 2–3 minutes, the titration with the sodium thiosulphate solution is commenced. Before the iodine colour has completely disappeared, the solution is diluted with 10 ml. of distilled water, 0.05 ml. of 1 per cent starch solution is added, and the titration is continued to the disappearance of the blue colour. Alternatively, a 0.01N solution of potassium iodate (Section III, 102) may be used for the standardisation.

E. Standardisation of 0.01N-sodium thiosulphate with pure copper. Procedure. Clean the surface of a pure copper wire (electrolytic) and weigh out accurately about 10 mg. into a small conical flask. Treat the
metal with 0.7–0.8 ml. of 3N-nitric acid; cover the flask with a glass bulb (Fig. XI, 6, 1). Heat on a water-bath until the metal is completely dissolved, then introduce 2 ml. of 2 per cent urea solution and continue the heating on a water-bath for 5 minutes. Rinse the glass bulb with 1–2 ml. of water, taking care that all the washings are collected in the flask. Add dilute ammonia solution (1:1) dropwise to the cold solution until a slight permanent, blue-green precipitate of cupric hydroxide just forms. Avoid such an excess of ammonia solution as to give the blue colour of the cuprammonium ion, since this will lead to an unsatisfactory end point in the subsequent titration. Treat the resulting neutral solution with 0.4 ml. of dilute acetic acid (1:1), cool and add 1 ml. of 10 per cent potassium iodide solution. After 1 minute titrate the liberated iodine with the sodium thiosulphate solution until the colour of the iodine is almost discharged, and introduce 0.1 ml. of starch solution from a measuring pipette. Continue the titration until the blue colour commences to fade, add 0.7–0.8 ml. of 10 per cent potassium thiocyanate solution, and complete the titration until one drop of the thiosulphate solution discharges the blue colour.

Calculate the normality of the sodium thiosulphate solution (compare Section III, 102, D).

F. Titration of ferrous iron with ceric sulphate solution. Procedure. A 0.1N-ceric sulphate solution is prepared (Section III, 74) and diluted to a concentration of 0.01N. The latter may be standardised with 0.01N-ferrous ammonium sulphate solution and a micro-drop of o-phenanthroline ferrous sulphate (ferroin) solution as indicator. A ferrous solution of unknown strength may then be titrated with the 0.01N-ceric sulphate solution on the semimicro scale.
XI, 8. SELECTED BIBLIOGRAPHY ON MICRO-GRAVIMETRIC AND MICRO-VOLUMETRIC ANALYSIS

## APPENDIX

### A.1. INTERNATIONAL ATOMIC WEIGHTS, 1949

Published by The Journal of the American Chemical Society

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol No.</th>
<th>Atomic Weight.*</th>
<th>Element</th>
<th>Symbol No.</th>
<th>Atomic Weight.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinium</td>
<td>Ac</td>
<td>89 227</td>
<td>Neptunium</td>
<td>Np</td>
<td>93 237</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>13 135</td>
<td>Neon</td>
<td>Ne</td>
<td>10 20-183</td>
</tr>
<tr>
<td>Americium</td>
<td>Am</td>
<td>95 [241]</td>
<td>Nickel</td>
<td>Ni</td>
<td>28 58-09</td>
</tr>
<tr>
<td>Antimony</td>
<td>Sb</td>
<td>51 121-76</td>
<td>Niobium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>18 39-94</td>
<td>(Columbia)</td>
<td>Nb</td>
<td>41 92-91</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>33 74-91</td>
<td>Nitrogen</td>
<td>N</td>
<td>7 14-068</td>
</tr>
<tr>
<td>Astetine</td>
<td>At</td>
<td>85 [210]</td>
<td>Osmium</td>
<td>Os</td>
<td>76 186-2</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>56 137-68</td>
<td>Oxygen</td>
<td>O</td>
<td>8 16-0000</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>4 9-03</td>
<td>Palladium</td>
<td>Pd</td>
<td>46 106-7</td>
</tr>
<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>83 200-00</td>
<td>Phosphorus</td>
<td>P</td>
<td>15 30-98</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>5 10-82</td>
<td>Platinum</td>
<td>Pt</td>
<td>78 195-23</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br</td>
<td>35 79-918</td>
<td>Plutonium</td>
<td>Pu</td>
<td>94 [239]</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>48 113-41</td>
<td>Polonium</td>
<td>Po</td>
<td>84 210</td>
</tr>
<tr>
<td>Cesium</td>
<td>Cs</td>
<td>55 132-01</td>
<td>Potassium</td>
<td>K</td>
<td>19 39-066</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca</td>
<td>20 40-08</td>
<td>Prasodymium</td>
<td>Pr</td>
<td>59 140-92</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>6 12-010</td>
<td>Promethium</td>
<td>Pm</td>
<td>61 [147]</td>
</tr>
<tr>
<td>Cerium</td>
<td>Ce</td>
<td>58 140-13</td>
<td>Protactinium</td>
<td>Pa</td>
<td>91 231</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>17 35-477</td>
<td>Radium</td>
<td>Ra</td>
<td>88 226-05</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>24 52-01</td>
<td>Radon</td>
<td>Rn</td>
<td>86 222</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>27 58-94</td>
<td>Rheinum</td>
<td>Re</td>
<td>75 136-31</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>29 63-04</td>
<td>Rhodium</td>
<td>Rh</td>
<td>46 102-91</td>
</tr>
<tr>
<td>Curium</td>
<td>Cm</td>
<td>96 [242]</td>
<td>Rubidium</td>
<td>Rb</td>
<td>37 85-64</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>Dy</td>
<td>66 162-46</td>
<td>Ruthenium</td>
<td>Ru</td>
<td>44 101-7</td>
</tr>
<tr>
<td>Erbium</td>
<td>Er</td>
<td>68 167-2</td>
<td>Samarium</td>
<td>Sm</td>
<td>62 150-43</td>
</tr>
<tr>
<td>Europium</td>
<td>Eu</td>
<td>63 162-0</td>
<td>Scandium</td>
<td>Sc</td>
<td>21 45-10</td>
</tr>
<tr>
<td>Fluorine</td>
<td>F</td>
<td>9 19-00</td>
<td>Selenium</td>
<td>Se</td>
<td>34 79-08</td>
</tr>
<tr>
<td>Francium</td>
<td>Fr</td>
<td>87 [223]</td>
<td>Silicon</td>
<td>Si</td>
<td>14 23-06</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>Gd</td>
<td>64 156-9</td>
<td>Silver</td>
<td>Ag</td>
<td>47 107-860</td>
</tr>
<tr>
<td>Gallium</td>
<td>Ga</td>
<td>31 69-72</td>
<td>Sodium</td>
<td>Na</td>
<td>11 22-97</td>
</tr>
<tr>
<td>Germanium</td>
<td>Ge</td>
<td>32 72-60</td>
<td>Strontium</td>
<td>Sr</td>
<td>38 87-63</td>
</tr>
<tr>
<td>Gold</td>
<td>Au</td>
<td>79 197-2</td>
<td>Sulphur</td>
<td>S</td>
<td>16 32-066</td>
</tr>
<tr>
<td>Hafnium</td>
<td>Hf</td>
<td>72 178-6</td>
<td>Thorium</td>
<td>Th</td>
<td>70 232-12</td>
</tr>
<tr>
<td>Holmium</td>
<td>Ho</td>
<td>67 164-04</td>
<td>Technetium</td>
<td>Te</td>
<td>43 [199]</td>
</tr>
<tr>
<td>Holmium</td>
<td>He</td>
<td>2 40-08</td>
<td>Tellurium</td>
<td>Te</td>
<td>52 127-61</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1 1-0080</td>
<td>Terbium</td>
<td>Tb</td>
<td>65 159-2</td>
</tr>
<tr>
<td>Indium</td>
<td>In</td>
<td>49 114-76</td>
<td>Thallium</td>
<td>Tl</td>
<td>81 204-39</td>
</tr>
<tr>
<td>Iodine</td>
<td>I</td>
<td>53 126-92</td>
<td>Thorium</td>
<td>Th</td>
<td>70 232-12</td>
</tr>
<tr>
<td>Iridium</td>
<td>Ir</td>
<td>77 193-1</td>
<td>Thallium</td>
<td>Tm</td>
<td>69 164-4</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>26 58-85</td>
<td>Tin</td>
<td>Sn</td>
<td>60 116-70</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>26 58-85</td>
<td>Titanium</td>
<td>Ti</td>
<td>22 47-90</td>
</tr>
<tr>
<td>Krypton</td>
<td>Kr</td>
<td>36 83-7</td>
<td>Tungsten</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lanthanum</td>
<td>La</td>
<td>57 138-02</td>
<td>(Wolfram)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>82 207-21</td>
<td>(Wolfram)</td>
<td>W</td>
<td>74 153-92</td>
</tr>
<tr>
<td>Lithium</td>
<td>Li</td>
<td>3 6-04</td>
<td>Uranium</td>
<td>U</td>
<td>92 238-07</td>
</tr>
<tr>
<td>Lutetium</td>
<td>Lu</td>
<td>71 174-99</td>
<td>Vanadium</td>
<td>V</td>
<td>23 50-85</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg</td>
<td>12 24-32</td>
<td>Xenon</td>
<td>Xe</td>
<td>64 131-3</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>25 54-93</td>
<td>Ytterbium</td>
<td>Yb</td>
<td>70 173-74</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>80 200-61</td>
<td>Yttrium</td>
<td>Y</td>
<td>39 88-92</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Mo</td>
<td>42 95-95</td>
<td>Zinc</td>
<td>Zn</td>
<td>30 65-38</td>
</tr>
<tr>
<td>Neodymium</td>
<td>Nd</td>
<td>60 144-27</td>
<td>Zirconium</td>
<td>Zr</td>
<td>40 91-22</td>
</tr>
</tbody>
</table>

* A value given in brackets denotes the mass number of the most stable known isotope.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pb</strong></td>
<td>PbSO₄</td>
<td>0.68325</td>
<td>1.84488</td>
</tr>
<tr>
<td></td>
<td>PbCrO₄</td>
<td>0.64108</td>
<td>1.64691</td>
</tr>
<tr>
<td></td>
<td>PbMoO₄</td>
<td>0.60529</td>
<td>1.76197</td>
</tr>
<tr>
<td></td>
<td>Pb(C₆H₄O₂N₂)</td>
<td>0.37108</td>
<td>1.67052</td>
</tr>
<tr>
<td></td>
<td>PbO₃</td>
<td>0.88823</td>
<td>1.63763</td>
</tr>
<tr>
<td><strong>Ag</strong></td>
<td>AgCl</td>
<td>0.75263</td>
<td>1.67653</td>
</tr>
<tr>
<td></td>
<td>HgS</td>
<td>0.86221</td>
<td>1.93361</td>
</tr>
<tr>
<td></td>
<td>Hg(Zn(CNS)₄)</td>
<td>0.40259</td>
<td>1.60486</td>
</tr>
<tr>
<td></td>
<td>[Cu(C₂H₄N₂)₄][HgI₄]</td>
<td>0.22458</td>
<td>1.53105</td>
</tr>
<tr>
<td></td>
<td>Hg₆(IO₄)₄</td>
<td>0.69219</td>
<td>1.54027</td>
</tr>
<tr>
<td><strong>Bi</strong></td>
<td>BiOI</td>
<td>0.59388</td>
<td>1.77370</td>
</tr>
<tr>
<td></td>
<td>Bi(C₂H₆O₂₅)</td>
<td>0.62937</td>
<td>1.79809</td>
</tr>
<tr>
<td></td>
<td>Bi₂O₅</td>
<td>0.89700</td>
<td>1.95279</td>
</tr>
<tr>
<td></td>
<td>Bi(C₂H₄ON)₃</td>
<td>0.32583</td>
<td>1.51209</td>
</tr>
<tr>
<td></td>
<td>BiPO₄</td>
<td>0.68755</td>
<td>1.83730</td>
</tr>
<tr>
<td><strong>Cd</strong></td>
<td>CdMoO₄</td>
<td>0.41273</td>
<td>1.61566</td>
</tr>
<tr>
<td></td>
<td>[(C₆H₄N)₄]H₂CdI₄</td>
<td>0.11464</td>
<td>1.05934</td>
</tr>
<tr>
<td></td>
<td>Cd(C₂H₄N₂)₆</td>
<td>0.24612</td>
<td>1.73011</td>
</tr>
<tr>
<td></td>
<td><a href="CNS">Cd(C₂H₄N)₄</a>₂</td>
<td>0.30305</td>
<td>1.46330</td>
</tr>
<tr>
<td></td>
<td>Cd(C₂H₄N₂)₆</td>
<td>0.22022</td>
<td>1.40572</td>
</tr>
<tr>
<td></td>
<td>CdNH₄PO₄·H₂O</td>
<td>0.42669</td>
<td>1.03011</td>
</tr>
<tr>
<td></td>
<td>Cd₂P₂O₇</td>
<td>0.56377</td>
<td>1.75110</td>
</tr>
<tr>
<td><strong>Cu</strong></td>
<td>Cu₂(CNS)₃</td>
<td>0.52257</td>
<td>1.71814</td>
</tr>
<tr>
<td></td>
<td>Cu(C₂H₄N₂)O₅</td>
<td>0.22011</td>
<td>1.53264</td>
</tr>
<tr>
<td></td>
<td>Cu(C₂H₆O₂₅)</td>
<td>0.18933</td>
<td>1.27715</td>
</tr>
<tr>
<td></td>
<td>Cu(C₂H₆O₂₅)       H₂O</td>
<td>0.14926</td>
<td>1.17394</td>
</tr>
<tr>
<td></td>
<td><a href="CNS">Cu(C₂H₄N)₄</a>₂</td>
<td>0.18112</td>
<td>1.27444</td>
</tr>
<tr>
<td></td>
<td><a href="HgI%E2%82%84">Cu(C₂H₆N₂)₆</a></td>
<td>0.07128</td>
<td>0.85285</td>
</tr>
<tr>
<td><strong>As</strong></td>
<td>As₂S₃</td>
<td>0.50603</td>
<td>1.78463</td>
</tr>
<tr>
<td></td>
<td>Mg(NH₂)₃AsO₄·6H₂O</td>
<td>0.55287</td>
<td>1.41309</td>
</tr>
<tr>
<td></td>
<td>Mg₂As₂O₇</td>
<td>0.48258</td>
<td>1.63356</td>
</tr>
<tr>
<td></td>
<td>U₂O₅</td>
<td>0.26683</td>
<td>1.42624</td>
</tr>
<tr>
<td><strong>Sb</strong></td>
<td>Sb₄S₃</td>
<td>0.71657</td>
<td>1.85544</td>
</tr>
<tr>
<td></td>
<td>Sb₂O₅</td>
<td>0.79189</td>
<td>1.88666</td>
</tr>
<tr>
<td></td>
<td>Sb₂C₂H₄O₈</td>
<td>0.65759</td>
<td>1.69669</td>
</tr>
<tr>
<td><strong>Sn</strong></td>
<td>SnO₂</td>
<td>0.78766</td>
<td>1.89634</td>
</tr>
<tr>
<td><strong>Mo</strong></td>
<td>PbMoO₄</td>
<td>0.26133</td>
<td>1.41719</td>
</tr>
<tr>
<td></td>
<td>MoO₂</td>
<td>0.60655</td>
<td>1.82383</td>
</tr>
<tr>
<td></td>
<td>MoO₂·(C₂H₄ON)₄</td>
<td>0.23681</td>
<td>1.36209</td>
</tr>
<tr>
<td><strong>Te</strong></td>
<td>TeO₂</td>
<td>0.70061</td>
<td>1.90282</td>
</tr>
<tr>
<td><strong>Pd</strong></td>
<td>Pd(C₂H₄O₂N₂)₂</td>
<td>0.31669</td>
<td>1.50064</td>
</tr>
<tr>
<td></td>
<td>Pd(C₂H₄O₂N₂)₂</td>
<td>0.27429</td>
<td>1.43821</td>
</tr>
<tr>
<td><strong>Al</strong></td>
<td>Al₂O₃</td>
<td>0.59013</td>
<td>1.72375</td>
</tr>
<tr>
<td></td>
<td>Al(C₂H₄ON)₆</td>
<td>0.65871</td>
<td>1.79068</td>
</tr>
<tr>
<td><strong>Be</strong></td>
<td>BeO</td>
<td>0.38051</td>
<td>1.56692</td>
</tr>
</tbody>
</table>

* For discussion on chemical factors, see Section IV, 3
## CHEMICAL FACTORS—Continued

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>CrO₃</td>
<td>0.68425</td>
<td>1.83572</td>
</tr>
<tr>
<td></td>
<td>BaCrO₄</td>
<td>0.20527</td>
<td>1.31233</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe₂O₃</td>
<td>0.69940</td>
<td>1.84472</td>
</tr>
<tr>
<td></td>
<td>Fe(C₆H₅O₇N₃)₃</td>
<td>0.11393</td>
<td>1.05835</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(C₆H₅O₇N₃)₃</td>
<td>0.20314</td>
<td>1.30780</td>
</tr>
<tr>
<td></td>
<td>Ni(C₆H₅O₇N₃)₂</td>
<td>0.17734</td>
<td>1.24881</td>
</tr>
<tr>
<td></td>
<td>Ni(C₂₆H₃₃O₇N₃)₂</td>
<td>0.11947</td>
<td>1.07727</td>
</tr>
<tr>
<td></td>
<td>Ni(C₂₆H₃₃O₇N₃)₄</td>
<td>0.10928</td>
<td>1.03844</td>
</tr>
<tr>
<td></td>
<td>Ni(C₂₆H₃₃O₇N₃)₆</td>
<td>0.22466</td>
<td>1.36511</td>
</tr>
<tr>
<td>Cu</td>
<td>CoSO₄</td>
<td>0.38023</td>
<td>1.58005</td>
</tr>
<tr>
<td></td>
<td>Co₂(C₆H₅O₇N₃)₃</td>
<td>0.17706</td>
<td>1.25032</td>
</tr>
<tr>
<td></td>
<td>Co₃O₄</td>
<td>0.73424</td>
<td>1.86884</td>
</tr>
<tr>
<td></td>
<td>[Co(C₆H₃N)₄]₀₄(CNS)₉</td>
<td>0.11892</td>
<td>1.07990</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn(NH₄)PO₄</td>
<td>0.38043</td>
<td>1.58405</td>
</tr>
<tr>
<td></td>
<td>Zn₂P₂O₇</td>
<td>0.42912</td>
<td>1.63257</td>
</tr>
<tr>
<td></td>
<td>Zn₃S</td>
<td>0.67098</td>
<td>1.82671</td>
</tr>
<tr>
<td></td>
<td>Zn(C₂₆H₃₃O₇N₃)₃</td>
<td>0.15286</td>
<td>1.28609</td>
</tr>
<tr>
<td></td>
<td>Zn(C₂₆H₃₃O₇N₃)₄</td>
<td>0.19495</td>
<td>1.28431</td>
</tr>
<tr>
<td></td>
<td>Zn(C₂₆H₃₃O₇N₃)₅</td>
<td>0.19364</td>
<td>1.28309</td>
</tr>
<tr>
<td></td>
<td>Zn(C₂₆H₃₃O₇N₃)₆</td>
<td>0.17102</td>
<td>1.23930</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn₃P₂O₇</td>
<td>0.38708</td>
<td>1.53780</td>
</tr>
<tr>
<td>U</td>
<td>UO₃</td>
<td>0.84922</td>
<td>1.92841</td>
</tr>
<tr>
<td>UO₂</td>
<td>U₂O₃</td>
<td>0.96200</td>
<td>1.99318</td>
</tr>
<tr>
<td></td>
<td>UO₂(C₆H₅O₇N₃)₃C₆H₅ON</td>
<td>0.33840</td>
<td>1.62943</td>
</tr>
<tr>
<td>Th</td>
<td>ThO₂</td>
<td>0.87884</td>
<td>1.64391</td>
</tr>
<tr>
<td>Ce</td>
<td>Ce₂O₃</td>
<td>0.81409</td>
<td>1.69106</td>
</tr>
<tr>
<td>Ti</td>
<td>TiO(C₆H₅O₇N₃)₃</td>
<td>0.13601</td>
<td>1.13356</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>0.59550</td>
<td>1.77779</td>
</tr>
<tr>
<td>Zr</td>
<td>Zr₂P₂O₇</td>
<td>0.34391</td>
<td>1.53645</td>
</tr>
<tr>
<td></td>
<td>Zr₂O₇</td>
<td>0.74030</td>
<td>1.80941</td>
</tr>
<tr>
<td></td>
<td>Zr₂(SeO₄)₂</td>
<td>0.28430</td>
<td>1.42209</td>
</tr>
<tr>
<td>Tl</td>
<td>Tl₂CrO₄</td>
<td>0.77994</td>
<td>1.69150</td>
</tr>
<tr>
<td></td>
<td>Tl₂[Co(NO₃)₄]₂</td>
<td>0.64669</td>
<td>1.81070</td>
</tr>
<tr>
<td>Ca</td>
<td>CaCl₂·H₂O</td>
<td>0.27430</td>
<td>1.43822</td>
</tr>
<tr>
<td></td>
<td>CaCl₂</td>
<td>0.40044</td>
<td>1.60254</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>0.71469</td>
<td>1.85412</td>
</tr>
<tr>
<td></td>
<td>CaMoO₄</td>
<td>0.20037</td>
<td>1.30183</td>
</tr>
<tr>
<td></td>
<td>CaWO₄</td>
<td>0.13917</td>
<td>1.14554</td>
</tr>
<tr>
<td>Sr</td>
<td>SrSO₄</td>
<td>0.47705</td>
<td>1.67567</td>
</tr>
<tr>
<td></td>
<td>SrO</td>
<td>0.84560</td>
<td>1.92717</td>
</tr>
<tr>
<td>Ba</td>
<td>BaSO₄</td>
<td>0.58847</td>
<td>1.76972</td>
</tr>
<tr>
<td></td>
<td>BaCrO₄</td>
<td>0.54213</td>
<td>1.73411</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg(C₆H₅O₇N₃)₂·2H₂O</td>
<td>0.09976</td>
<td>2.84356</td>
</tr>
<tr>
<td></td>
<td>Mg(C₆H₅O₇N₃)₃</td>
<td>0.07780</td>
<td>2.89006</td>
</tr>
<tr>
<td></td>
<td>Mg(NH₄)PO₄·6H₂O</td>
<td>0.09009</td>
<td>2.99602</td>
</tr>
<tr>
<td></td>
<td>Mg₃PO₄</td>
<td>0.21851</td>
<td>1.33947</td>
</tr>
<tr>
<td></td>
<td>Mg(C₂₆H₃₃O₇N₃)₃</td>
<td>0.07139</td>
<td>2.85363</td>
</tr>
<tr>
<td>--------</td>
<td>--------</td>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>Na</td>
<td>Na₂SO₄</td>
<td>0.32376</td>
<td>1.61029</td>
</tr>
<tr>
<td></td>
<td>Na₂Zn(VO₄)₆(C₆H₆O₆)₆·6H₂O</td>
<td>0.01495</td>
<td>2.17475</td>
</tr>
<tr>
<td></td>
<td>NaMg(UB₅O₈)(C₆H₆O₆)₆·5H₂O</td>
<td>0.01527</td>
<td>2.18390</td>
</tr>
<tr>
<td>K</td>
<td>K₃[PtCl₄]</td>
<td>0.16083</td>
<td>2.20637</td>
</tr>
<tr>
<td></td>
<td>KClO₄</td>
<td>0.28217</td>
<td>1.65052</td>
</tr>
<tr>
<td></td>
<td>K₂SO₄</td>
<td>0.44888</td>
<td>1.66213</td>
</tr>
<tr>
<td></td>
<td>K₂Na₂[Co(NO₃)₆]·H₂O</td>
<td>0.17215</td>
<td>1.23891</td>
</tr>
<tr>
<td></td>
<td>KClO₄</td>
<td>0.16999</td>
<td>1.23041</td>
</tr>
<tr>
<td>Li</td>
<td>Li₂SO₄</td>
<td>0.12255</td>
<td>1.10123</td>
</tr>
<tr>
<td></td>
<td>LiCl</td>
<td>0.16399</td>
<td>1.21402</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>(NH₄)₆[PtCl₄]</td>
<td>0.08125</td>
<td>2.20983</td>
</tr>
<tr>
<td>W</td>
<td>WO₃</td>
<td>0.79303</td>
<td>1.89929</td>
</tr>
<tr>
<td></td>
<td>WO₃(C₆H₆ON)₂</td>
<td>0.36477</td>
<td>1.56202</td>
</tr>
<tr>
<td></td>
<td>BaWO₄</td>
<td>0.47737</td>
<td>1.67865</td>
</tr>
<tr>
<td>Ge</td>
<td>GeO₂</td>
<td>0.53148</td>
<td>1.72549</td>
</tr>
<tr>
<td></td>
<td>GeO₃</td>
<td>1.51022</td>
<td>1.76470</td>
</tr>
<tr>
<td></td>
<td>GeO₄</td>
<td>2.17475</td>
<td>1.70510</td>
</tr>
<tr>
<td></td>
<td>GeO₅</td>
<td>2.18390</td>
<td>1.67865</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>AgCl</td>
<td>0.24737</td>
<td>1.39334</td>
</tr>
<tr>
<td>Br⁻</td>
<td>AgBr</td>
<td>0.42565</td>
<td>1.02965</td>
</tr>
<tr>
<td>I⁻</td>
<td>AgI</td>
<td>0.64055</td>
<td>1.73283</td>
</tr>
<tr>
<td></td>
<td>PdI₄</td>
<td>0.70405</td>
<td>1.84761</td>
</tr>
<tr>
<td>CNS⁻</td>
<td>AgCNS</td>
<td>0.34096</td>
<td>1.54402</td>
</tr>
<tr>
<td></td>
<td>Cu₂(CNS)₂</td>
<td>0.47744</td>
<td>1.67865</td>
</tr>
<tr>
<td></td>
<td>BaSO₄</td>
<td>0.24882</td>
<td>1.30580</td>
</tr>
<tr>
<td>CN⁻</td>
<td>AgCN</td>
<td>0.19413</td>
<td>1.28850</td>
</tr>
<tr>
<td>F⁻</td>
<td>PbClF</td>
<td>0.07261</td>
<td>2.86100</td>
</tr>
<tr>
<td></td>
<td>CuF₃</td>
<td>0.48568</td>
<td>1.88724</td>
</tr>
<tr>
<td></td>
<td>(C₆H₆Sn)₃SnF</td>
<td>0.05149</td>
<td>2.71173</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>AgClO₄</td>
<td>0.58224</td>
<td>1.70510</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>AgCl</td>
<td>0.63877</td>
<td>1.84128</td>
</tr>
<tr>
<td></td>
<td>KCIO₄</td>
<td>0.71783</td>
<td>1.86692</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>BaSO₄</td>
<td>0.41163</td>
<td>1.61440</td>
</tr>
<tr>
<td>S</td>
<td>BaSO₄</td>
<td>0.13735</td>
<td>1.13783</td>
</tr>
<tr>
<td>SO₃²⁻</td>
<td>BaSO₄</td>
<td>0.34299</td>
<td>1.53528</td>
</tr>
<tr>
<td>S₄O₆²⁻</td>
<td>BaSO₄</td>
<td>0.24017</td>
<td>1.38052</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>MgNH₄PO₄·6H₂O</td>
<td>0.38698</td>
<td>1.58769</td>
</tr>
<tr>
<td></td>
<td>Mg₃P₂O₇</td>
<td>0.86387</td>
<td>1.93114</td>
</tr>
<tr>
<td></td>
<td>(NH₄)₆[PMo₁₂O₄₀]</td>
<td>0.05062</td>
<td>2.70428</td>
</tr>
<tr>
<td></td>
<td>P₂O₅·2MoO₃</td>
<td>0.05281</td>
<td>2.72275</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>H₃P₃O₁₀</td>
<td>0.10442</td>
<td>1.22896</td>
</tr>
<tr>
<td></td>
<td>Mg₂(HP₂O₇)₆·4H₂O</td>
<td>0.32250</td>
<td>1.61390</td>
</tr>
<tr>
<td></td>
<td>Mg₃P₂O₇</td>
<td>0.71869</td>
<td>1.86654</td>
</tr>
</tbody>
</table>
Appendix

CHEMICAL FACTORS—Continued

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{PO}_4$</td>
<td>$\text{H}_2\text{Cl}_2$</td>
<td>0.06884</td>
<td>2.83781</td>
</tr>
<tr>
<td></td>
<td>$\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$</td>
<td>0.26483</td>
<td>1.42297</td>
</tr>
<tr>
<td></td>
<td>$\text{Mg}_3\text{P}_2\text{O}_7$</td>
<td>0.58401</td>
<td>1.76642</td>
</tr>
<tr>
<td>$\text{C}_6\text{O}_4$</td>
<td>$\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$</td>
<td>0.60238</td>
<td>1.77987</td>
</tr>
<tr>
<td></td>
<td>$\text{CaCO}_3$</td>
<td>0.87941</td>
<td>1.94419</td>
</tr>
<tr>
<td></td>
<td>$\text{CaO}$</td>
<td>1.06954</td>
<td>0.10577</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>$\text{SiO}_2$</td>
<td>1.26640</td>
<td>0.10257</td>
</tr>
<tr>
<td>$\text{SiF}_6$</td>
<td>$\text{SiO}_2$</td>
<td>2.36530</td>
<td>0.37389</td>
</tr>
<tr>
<td>$\text{NO}_3$</td>
<td>$\text{C}_2\text{H}_5\text{N}_4\text{HNO}_3$</td>
<td>0.16519</td>
<td>1.21799</td>
</tr>
</tbody>
</table>

A. 3. THE LITERATURE OF ANALYTICAL CHEMISTRY

The following list is not intended to be exhaustive*; it indicates books and journals which may well form the nucleus of a library for inorganic analysis. Many of these books have already been listed in the Selected Bibliographies at the end of the various Chapters. A number of comparatively elementary works on general analysis are included as illustrative of a somewhat different treatment of the subject and also because they contain references to the scientific literature.

1. Theory of Analytical Chemistry


2. General Reference Works


3. Text-books


* A more detailed list of books is to be found in B. A. Soule, *Library Guide for the Chemist* (McGraw-Hill, 1938).
Quantitative Inorganic Analysis


4. Volumetric Analysis


5. Electro-analysis


6. Colorimetric Analysis


7. Gas Analysis


Appendix

8. Electrometric Methods including Polarography


9. Organic Reagents


10. Micro-analysis
J. Wiley: Chapman and Hall.

11. Qualitative Inorganic Analysis

12. Metallurgical Analysis

13. Ore Analysis
Appendix

14. Water Analysis


15. Reagents


*Specifications for Analytical Reagents.* Recommended by the Committee on Analytical Reagents of the American Chemical Society. American Chemical Society, Washington, D.C., 1951.


16. General Industrial Analysis


17. Agricultural Analysis, Food Analysis, etc.


18. Apparatus, etc.

Much valuable information concerning apparatus is to be found in the catalogues of various manufacturers. A selected list is given below:


Quantitative Inorganic Analysis

Townson and Mercer, Ltd., Croydon, Surrey.
E. R. Sargent and Company, 4647 W. Foster Avenue, Chicago 30, Illinois.
Central Scientific Company, 1700 Irving Park Road, Chicago 13, Illinois.
Will Corporation, Rochester 3, N.Y.
Wilkens-Anderson Co., 4525 W. Division Street, Chicago 51, Illinois.

Some firms publish booklets from time to time in which recent improvements in laboratory apparatus and technique are described, for example: Bulletin and Laboratory Notes (Baird and Tatlock (London), Ltd.).
The Laboratory (Fisher Scientific Co.).

19. Chemical and Physical Constants


20. Journals

A list of the most important Journals in which the results of original research in analytical chemistry are published is given below. Many memoirs on chemical analysis appear in numerous other scientific journals; abstracts of these may be found in the British Chemical Abstracts published by the Bureau of Chemical Abstracts, London, or in Chemical Abstracts published by the American Chemical Society. Valuable summaries appear in the Annual Reports on the Progress of Chemistry published by the Chemical Society, London. An Annual Review of Analytical Chemistry (commenced 1949), covering the various branches of Fundamental Analysis and also Applications of Analytical Developments, appears in the January and February issues of Analytical Chemistry, published by the American Chemical Society. This provides an excellent means of keeping in touch with recent developments.

The Analyst.
Industrial and Engineering Chemistry, Analytical Edition. (The name was changed on January 1st, 1947, to Analytical Chemistry.)
### Appendix

*Annales de Chimie analytique et de Chimie appliquée et Revue de Chimie analytique réunies.*  
*Zeitschrift für analytischen Chemie.*  
*Journal of the Chemical Society.*  
*Journal of the Society of Chemical Industry.*  
*(The name was changed on January 1st, 1951, to Journal of Applied Chemistry.)*  
*Journal of the American Chemical Society.*  
*Bulletin de la Société chimique de France.*  
*Berichte der Deutschen chemischen Gesellschaft.*  
*Recueil des Travaux chimiques des Pays-Bas et de la Belgique.*  
*Journal of Research of the National Bureau of Standards.*  
*Analytica Chimica Acta.*  
*Mikrochemie vereinigt mit Mikrochimica Acta.*  
*Chemist-Analyst.*

**A. 4.**

**DENSITIES OF ACIDS AT 20° C.**

*(Densities and Percentages by Weight are based on weights in vacuo and the percentage by weight refers to the formula given.)*

<table>
<thead>
<tr>
<th>Per Cent by Weight</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$SO$_4$</td>
</tr>
<tr>
<td>1</td>
<td>1.0051</td>
</tr>
<tr>
<td>2</td>
<td>1.0118</td>
</tr>
<tr>
<td>3</td>
<td>1.0184</td>
</tr>
<tr>
<td>4</td>
<td>1.0250</td>
</tr>
<tr>
<td>5</td>
<td>1.0317</td>
</tr>
<tr>
<td>6</td>
<td>1.0385</td>
</tr>
<tr>
<td>7</td>
<td>1.0463</td>
</tr>
<tr>
<td>8</td>
<td>1.0522</td>
</tr>
<tr>
<td>9</td>
<td>1.0591</td>
</tr>
<tr>
<td>10</td>
<td>1.0651</td>
</tr>
<tr>
<td>11</td>
<td>1.0731</td>
</tr>
<tr>
<td>12</td>
<td>1.0802</td>
</tr>
<tr>
<td>13</td>
<td>1.0874</td>
</tr>
<tr>
<td>14</td>
<td>1.0947</td>
</tr>
<tr>
<td>15</td>
<td>1.1020</td>
</tr>
<tr>
<td>16</td>
<td>1.1094</td>
</tr>
<tr>
<td>17</td>
<td>1.1159</td>
</tr>
<tr>
<td>18</td>
<td>1.1263</td>
</tr>
<tr>
<td>19</td>
<td>1.1361</td>
</tr>
<tr>
<td>20</td>
<td>1.1394</td>
</tr>
<tr>
<td>21</td>
<td>1.1371</td>
</tr>
<tr>
<td>22</td>
<td>1.1458</td>
</tr>
<tr>
<td>23</td>
<td>1.1526</td>
</tr>
<tr>
<td>24</td>
<td>1.1674</td>
</tr>
<tr>
<td>25</td>
<td>1.1733</td>
</tr>
<tr>
<td>26</td>
<td>1.1802</td>
</tr>
<tr>
<td>27</td>
<td>1.1842</td>
</tr>
<tr>
<td>28</td>
<td>1.2023</td>
</tr>
<tr>
<td>29</td>
<td>1.2101</td>
</tr>
<tr>
<td>30</td>
<td>1.2115</td>
</tr>
<tr>
<td>31</td>
<td>1.2207</td>
</tr>
<tr>
<td>32</td>
<td>1.2249</td>
</tr>
<tr>
<td>33</td>
<td>1.2343</td>
</tr>
<tr>
<td>34</td>
<td>1.2515</td>
</tr>
<tr>
<td>35</td>
<td>1.2599</td>
</tr>
<tr>
<td>36</td>
<td>1.2684</td>
</tr>
<tr>
<td>37</td>
<td>1.2769</td>
</tr>
<tr>
<td>38</td>
<td>1.2855</td>
</tr>
<tr>
<td>39</td>
<td>1.2941</td>
</tr>
<tr>
<td>40</td>
<td>1.3028</td>
</tr>
</tbody>
</table>
### Quantitative Inorganic Analysis

#### Densities of Acids at 20° C.—Continued

<table>
<thead>
<tr>
<th>Per Cent by Weight</th>
<th>Density</th>
<th>Density</th>
<th>Density</th>
<th>Density</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂SO₄</td>
<td>HNO₃</td>
<td>H₂C₂H₄O₂</td>
<td>H₂PO₄</td>
<td>HCl</td>
</tr>
<tr>
<td>41</td>
<td>1.3116</td>
<td>1.2627</td>
<td>1.0408</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>42</td>
<td>1.3205</td>
<td>1.2591</td>
<td>1.0507</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>43</td>
<td>1.3294</td>
<td>1.2655</td>
<td>1.0610</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>44</td>
<td>1.3384</td>
<td>1.2719</td>
<td>1.0625</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>45</td>
<td>1.3476</td>
<td>1.2783</td>
<td>1.0634</td>
<td>1.293</td>
<td>—</td>
</tr>
<tr>
<td>46</td>
<td>1.3569</td>
<td>1.2847</td>
<td>1.0642</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>47</td>
<td>1.3663</td>
<td>1.2911</td>
<td>1.0651</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>48</td>
<td>1.3759</td>
<td>1.2975</td>
<td>1.0659</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>49</td>
<td>1.3854</td>
<td>1.3040</td>
<td>1.0667</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>1.3951</td>
<td>1.3100</td>
<td>1.0675</td>
<td>1.335</td>
<td>—</td>
</tr>
<tr>
<td>51</td>
<td>1.4049</td>
<td>1.3160</td>
<td>1.0682</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>52</td>
<td>1.4148</td>
<td>1.3219</td>
<td>1.0690</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>53</td>
<td>1.4248</td>
<td>1.3278</td>
<td>1.0697</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>54</td>
<td>1.4350</td>
<td>1.3336</td>
<td>1.0694</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>55</td>
<td>1.4453</td>
<td>1.3393</td>
<td>1.0691</td>
<td>1.370</td>
<td>—</td>
</tr>
<tr>
<td>56</td>
<td>1.4557</td>
<td>1.3449</td>
<td>1.0688</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>57</td>
<td>1.4662</td>
<td>1.3506</td>
<td>1.0684</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>58</td>
<td>1.4768</td>
<td>1.3560</td>
<td>1.0681</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>59</td>
<td>1.4876</td>
<td>1.3614</td>
<td>1.0677</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>60</td>
<td>1.4983</td>
<td>1.3667</td>
<td>1.0642</td>
<td>1.426</td>
<td>—</td>
</tr>
<tr>
<td>61</td>
<td>1.5091</td>
<td>1.3719</td>
<td>1.0648</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>62</td>
<td>1.5200</td>
<td>1.3769</td>
<td>1.0663</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>63</td>
<td>1.5310</td>
<td>1.3818</td>
<td>1.0673</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>64</td>
<td>1.5421</td>
<td>1.3866</td>
<td>1.0672</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>65</td>
<td>1.5533</td>
<td>1.3913</td>
<td>1.0671</td>
<td>1.475</td>
<td>—</td>
</tr>
<tr>
<td>66</td>
<td>1.5646</td>
<td>1.3959</td>
<td>1.0681</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>67</td>
<td>1.5760</td>
<td>1.4004</td>
<td>1.0687</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>68</td>
<td>1.5874</td>
<td>1.4049</td>
<td>1.0693</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>69</td>
<td>1.5988</td>
<td>1.4091</td>
<td>1.0699</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>70</td>
<td>1.6010</td>
<td>1.4134</td>
<td>1.0705</td>
<td>1.526</td>
<td>—</td>
</tr>
<tr>
<td>71</td>
<td>1.6071</td>
<td>1.4176</td>
<td>1.0689</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>72</td>
<td>1.6138</td>
<td>1.4218</td>
<td>1.0690</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>73</td>
<td>1.6195</td>
<td>1.4258</td>
<td>1.0693</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>74</td>
<td>1.6253</td>
<td>1.4298</td>
<td>1.0694</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>75</td>
<td>1.6311</td>
<td>1.4337</td>
<td>1.0692</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>76</td>
<td>1.6370</td>
<td>1.4375</td>
<td>1.0693</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>77</td>
<td>1.6427</td>
<td>1.4413</td>
<td>1.0698</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>78</td>
<td>1.6483</td>
<td>1.4453</td>
<td>1.0700</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>79</td>
<td>1.6538</td>
<td>1.4486</td>
<td>1.0700</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>80</td>
<td>1.6592</td>
<td>1.4521</td>
<td>1.0700</td>
<td>1.633</td>
<td>—</td>
</tr>
<tr>
<td>81</td>
<td>1.6646</td>
<td>1.4555</td>
<td>1.0699</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>82</td>
<td>1.6691</td>
<td>1.4589</td>
<td>1.0698</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>83</td>
<td>1.6734</td>
<td>1.4623</td>
<td>1.0696</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>84</td>
<td>1.6769</td>
<td>1.4655</td>
<td>1.0693</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>85</td>
<td>1.6806</td>
<td>1.4686</td>
<td>1.0693</td>
<td>1.630</td>
<td>—</td>
</tr>
<tr>
<td>86</td>
<td>1.6842</td>
<td>1.4716</td>
<td>1.0685</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>87</td>
<td>1.6877</td>
<td>1.4746</td>
<td>1.0680</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>88</td>
<td>1.6912</td>
<td>1.4773</td>
<td>1.0675</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>89</td>
<td>1.6947</td>
<td>1.4800</td>
<td>1.0668</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>90</td>
<td>1.6982</td>
<td>1.4826</td>
<td>1.0661</td>
<td>1.748</td>
<td>—</td>
</tr>
<tr>
<td>91</td>
<td>1.7015</td>
<td>1.4850</td>
<td>1.0652</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>92</td>
<td>1.7048</td>
<td>1.4873</td>
<td>1.0643</td>
<td>1.770</td>
<td>—</td>
</tr>
<tr>
<td>93</td>
<td>1.7099</td>
<td>1.4902</td>
<td>1.0632</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>94</td>
<td>1.7132</td>
<td>1.4932</td>
<td>1.0638</td>
<td>1.794</td>
<td>—</td>
</tr>
<tr>
<td>95</td>
<td>1.7176</td>
<td>1.4963</td>
<td>1.0632</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>96</td>
<td>1.7222</td>
<td>1.4992</td>
<td>1.0643</td>
<td>1.770</td>
<td>—</td>
</tr>
<tr>
<td>97</td>
<td>1.7259</td>
<td>1.5022</td>
<td>1.0638</td>
<td>1.819</td>
<td>—</td>
</tr>
<tr>
<td>98</td>
<td>1.7287</td>
<td>1.5050</td>
<td>1.0640</td>
<td>1.844</td>
<td>—</td>
</tr>
<tr>
<td>99</td>
<td>1.7313</td>
<td>1.5079</td>
<td>1.0649</td>
<td>1.844</td>
<td>—</td>
</tr>
<tr>
<td>100</td>
<td>1.7339</td>
<td>1.5108</td>
<td>1.0652</td>
<td>1.870</td>
<td>—</td>
</tr>
</tbody>
</table>
A. 5. **DENSITIES OF ALKALINE SOLUTIONS AT 20° C.**

(Densities and percentages by weight are based on weights in vacuo and the percentage by weight refers to the formula given.)

<table>
<thead>
<tr>
<th>Per Cent by Weight</th>
<th>Density</th>
<th>Per Cent by Weight</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH</td>
<td>NaOH</td>
<td>NH₃</td>
<td>KOH</td>
</tr>
<tr>
<td>1</td>
<td>1.0083</td>
<td>1.0095</td>
<td>0.9939</td>
</tr>
<tr>
<td>2</td>
<td>1.0175</td>
<td>1.0207</td>
<td>0.9811</td>
</tr>
<tr>
<td>3</td>
<td>1.0267</td>
<td>1.0318</td>
<td>0.9730</td>
</tr>
<tr>
<td>4</td>
<td>1.0359</td>
<td>1.0428</td>
<td>0.9651</td>
</tr>
<tr>
<td>5</td>
<td>1.0452</td>
<td>1.0538</td>
<td>0.9612</td>
</tr>
<tr>
<td>6</td>
<td>1.0544</td>
<td>1.0648</td>
<td>0.9573</td>
</tr>
<tr>
<td>7</td>
<td>1.0637</td>
<td>1.0758</td>
<td>0.9534</td>
</tr>
<tr>
<td>8</td>
<td>1.0730</td>
<td>1.0869</td>
<td>0.9495</td>
</tr>
<tr>
<td>9</td>
<td>1.0824</td>
<td>1.0979</td>
<td>0.9456</td>
</tr>
<tr>
<td>10</td>
<td>1.0918</td>
<td>1.1089</td>
<td>0.9417</td>
</tr>
<tr>
<td>11</td>
<td>1.1013</td>
<td>1.1199</td>
<td>0.9378</td>
</tr>
<tr>
<td>12</td>
<td>1.1108</td>
<td>1.1309</td>
<td>0.9339</td>
</tr>
<tr>
<td>13</td>
<td>1.1203</td>
<td>1.1419</td>
<td>0.9290</td>
</tr>
<tr>
<td>14</td>
<td>1.1299</td>
<td>1.1529</td>
<td>0.9251</td>
</tr>
<tr>
<td>15</td>
<td>1.1395</td>
<td>1.1639</td>
<td>0.9212</td>
</tr>
<tr>
<td>16</td>
<td>1.1493</td>
<td>1.1751</td>
<td>0.9173</td>
</tr>
<tr>
<td>17</td>
<td>1.1590</td>
<td>1.1862</td>
<td>0.9134</td>
</tr>
<tr>
<td>18</td>
<td>1.1688</td>
<td>1.1973</td>
<td>0.9095</td>
</tr>
<tr>
<td>19</td>
<td>1.1786</td>
<td>1.2084</td>
<td>0.9056</td>
</tr>
<tr>
<td>20</td>
<td>1.1884</td>
<td>1.2191</td>
<td>0.9017</td>
</tr>
<tr>
<td>21</td>
<td>1.1982</td>
<td>1.2298</td>
<td>0.8978</td>
</tr>
<tr>
<td>22</td>
<td>1.2080</td>
<td>1.2404</td>
<td>0.8939</td>
</tr>
<tr>
<td>23</td>
<td>1.2184</td>
<td>1.2511</td>
<td>0.8899</td>
</tr>
<tr>
<td>24</td>
<td>1.2286</td>
<td>1.2618</td>
<td>0.8859</td>
</tr>
<tr>
<td>25</td>
<td>1.2387</td>
<td>1.2724</td>
<td>0.8819</td>
</tr>
</tbody>
</table>

A. 6. **DATA ON THE STRENGTH OF AQUEOUS SOLUTIONS OF THE COMMON ACIDS AND OF AMMONIUM HYDROXIDE**

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Approximate.</th>
<th>Per Cent by Weight</th>
<th>Specific Gravity</th>
<th>Normality</th>
<th>Vol. Required to Make 1 Litre of Approx. N Solution (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>35</td>
<td>1.18</td>
<td>11.3</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>Nitric acid</td>
<td>70</td>
<td>1.42</td>
<td>10.0</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>96</td>
<td>1.84</td>
<td>10.0</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Perchloric acid</td>
<td>70</td>
<td>1.66</td>
<td>11.6</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>46</td>
<td>1.75</td>
<td>10.5</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>85</td>
<td>1.69</td>
<td>11.1</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>99.5</td>
<td>1.05</td>
<td>17.4</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>27(NH₃)</td>
<td>0.90</td>
<td>14.3</td>
<td>71</td>
<td></td>
</tr>
</tbody>
</table>
A. 7. SAMPLES AND SOLUTIONS FOR ELEMENTARY ANALYSIS

There are two main methods which may be used for the supply of samples for analysis by elementary students, i.e., for students who are just beginning the study of quantitative analysis. These are:

1. The use of pure (e.g., A.R.) substances of known composition. This method has been largely adopted in the present treatise, and in the author's experience has given excellent results. It has been urged that the use of known amounts of material does not give the student practice in discovering for himself the quantity of precipitant to be used and solving similar simple problems which arise in analysis. This is true, but the writer feels that in the early stages of training it is far more important that the student should first acquire the experimental technique of quantitative analysis. The analysis of comparatively simple "unknown" solutions and solids is better reserved for a later stage, when they will present comparatively little difficulty. However, many teachers prefer that quantitative exercises should be performed with solids or solutions of "unknown" composition. These are discussed below.

2. The use of standard solutions prepared from A.R. solids. A series of solutions, each containing one element or radical to be determined, is prepared of such concentration that, say, 20–30 ml. will provide a convenient quantity for analysis. For small classes the portion for analysis is measured out with a graduated pipette; for large classes it is convenient to store the stock solution in a bottle with a burette permanently attached (Fig. II, 25, 1; the burette may also be of the automatic-filling type as in Fig. II, 25, 2). For each solution the instructor should draw a large-scale graph in which the volume of solution is plotted against the quantity of the component present; this graph will provide a rapid means for checking the accuracy of the students' results.

Details of a few typical solutions are given below; others may be prepared similarly.

**Aluminium**: 70 g. of A.R. ammonium aluminium sulphate \((\text{NH}_4)_2\text{SO}_4\cdot\text{Al}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O}\) per litre.

**Ammonium**: (i) 15 g. of A.R. ferrous ammonium sulphate \(\text{FeSO}_4\cdot(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O}\) per litre.
  (ii) 4 g. of A.R. ammonium chloride \(\text{NH}_4\text{Cl}\) per litre.

**Barium**: 12 g. of A.R. barium chloride \(\text{BaCl}_2\cdot2\text{H}_2\text{O}\) per litre.

**Bromide**: 8 g. of A.R. potassium bromide \(\text{KBr}\) per litre.

**Calcium**: 20 g. of A.R. calcium carbonate \(\text{CaCO}_3\) dissolved in a little dilute hydrochloric acid and diluted to 1 litre.

**Carbonate**: 30 g. of A.R. sodium carbonate \(\text{Na}_2\text{CO}_3\) per litre.

**Chloride**: 8 g. of A.R. potassium chloride \(\text{KCl}\) per litre.

**Chromium**: 20 g. of A.R. potassium dichromate \(\text{K}_2\text{Cr}_2\text{O}_7\) per litre.
Appendix

Cobalt: 8 g. of A.R. cobalt ammonium sulphate \( \text{CoSO}_4(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O} \) per litre.

Copper: 30 g. of A.R. copper sulphate \( \text{CuSO}_4\cdot5\text{H}_2\text{O} \) per litre.

Iodide: 7 g. of A.R. potassium iodide KI per litre.

Iron: (i) 50 g. of A.R. ferric ammonium sulphate \( \text{Fe}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4\cdot24\text{H}_2\text{O} \) per litre.
   (ii) 40 g. of A.R. ferrous ammonium sulphate \( \text{FeSO}_4(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O} \) per litre.

Lead: 12 g. of A.R. lead nitrate \( \text{Pb(NO}_3)_2 \) per litre (a little nitric acid should be present).

Magnesium: 25 g. of A.R. magnesium sulphate \( \text{MgSO}_4\cdot7\text{H}_2\text{O} \) per litre.

Manganese: 10 g. of A.R. potassium permanganate \( \text{KMnO}_4 \) per litre.

Mercury: 10 g. of A.R. mercuric chloride \( \text{HgCl}_2 \) per litre.

Nickel: 7 g. of A.R. nickel ammonium sulphate \( \text{NiSO}_4(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O} \) per litre.

Phosphate: 1·2 g. of A.R. microcosmic salt \( \text{Na(NH}_4\text{)HPO}_4\cdot4\text{H}_2\text{O} \) per litre (for the molybdate method).

Potassium: 7 g. of A.R. potassium chloride \( \text{KCl} \) per litre.

Silver: 14 g. of A.R. silver nitrate \( \text{AgNO}_3 \) per litre.

Sulphate: 7 g. of A.R. potassium sulphate \( \text{K}_2\text{SO}_4 \) per litre.

Zinc: (i) 30 g. of A.R. zinc sulphate \( \text{ZnSO}_4\cdot7\text{H}_2\text{O} \) per litre.
   (ii) 40 g. of pure zinc ammonium sulphate \( \text{ZnSO}_4(\text{NH}_4)_2\text{SO}_4\cdot6\text{H}_2\text{O} \)
   (see Section IV, 34A) per litre.

A, 8.

ANALYSED SAMPLES

ANALYSED SAMPLES FOR STUDENTS IN METALLURGICAL ANALYSIS*

These are comparatively inexpensive analysed samples, and are particularly useful for the training of students in quantitative analysis; a sheet giving the proportions of the various components determined is supplied. The use of many of these ("Ridsdale's Samples") is suggested in the present volume.

* Supplied by Bureau of Analysed Samples, Ltd., 234 Marton Road, Middlesbrough, Yorks., England.
### Quantitative Inorganic Analysis

**Analysed Samples for Students in Metallurgical Analysis**—Continued

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name</th>
<th>Constituents Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ferrous</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Mild carbon steel</td>
<td>Cd. C,* P</td>
</tr>
<tr>
<td>0a, 1b</td>
<td>Mild carbon steel</td>
<td>Cd. C, Si, S, P, Mn</td>
</tr>
<tr>
<td>2a</td>
<td>Medium carbon steel</td>
<td>Cd. C, Si, S, P, Mn</td>
</tr>
<tr>
<td>3a, 21</td>
<td>High carbon steel</td>
<td>Cd. C, Si, S, P, Mn</td>
</tr>
<tr>
<td>22a</td>
<td>Nickel steel</td>
<td>Ni</td>
</tr>
<tr>
<td>60b</td>
<td>Ni-Cr-Mo steel</td>
<td>Cd. C, Si, S, P, Mn, Ni, Cr, Mo</td>
</tr>
<tr>
<td>64a</td>
<td>High-speed steel</td>
<td>Cd. C, Si, S, P, Mn</td>
</tr>
<tr>
<td>4, 35</td>
<td>Cast iron</td>
<td>Cd. C, Si, S, P, Mn</td>
</tr>
<tr>
<td>12b</td>
<td>Foundry iron</td>
<td>Cd. C, Si, S, P, Mn</td>
</tr>
<tr>
<td>13b</td>
<td>Haematite iron</td>
<td>Cd. C, Si, S, P, Mn, Gr. C</td>
</tr>
<tr>
<td>33</td>
<td>Alloy cast iron</td>
<td>Total C, Si, S, P, Mn, Ni, Cr, Mo</td>
</tr>
<tr>
<td><strong>Non-Ferrous</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6e</td>
<td>Brass</td>
<td>Cu, Zn, Sn, Pb</td>
</tr>
<tr>
<td>6e</td>
<td>Gun-metal</td>
<td>Cu, Zn, Sn, Pb, Fe, P</td>
</tr>
<tr>
<td>7</td>
<td>Phosphor bronze</td>
<td>Cu, Zn, Sn, Pb, Fe, P, Sb</td>
</tr>
<tr>
<td>19</td>
<td>Cupro-nickel</td>
<td>Cu, Ni, Mn, P</td>
</tr>
<tr>
<td>10d</td>
<td>Manganese bronze</td>
<td>Cu, Zn, Fe, Mn, Al</td>
</tr>
<tr>
<td>20</td>
<td>Aluminium alloy</td>
<td>Cu, Zn, Ni, Mg, Fe, Al, Pb</td>
</tr>
<tr>
<td>32</td>
<td>Aluminium bronze</td>
<td>Cu, Al, Fe, Si, Sn</td>
</tr>
<tr>
<td>8b</td>
<td>White metal</td>
<td>Cu, Sn, Sb, Pb, Zn</td>
</tr>
<tr>
<td>11c</td>
<td>Solder</td>
<td>Sn, Sb</td>
</tr>
<tr>
<td><strong>Minerals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9b</td>
<td>Dolomite</td>
<td>CaCO₃, MgCO₃, Fe₂O₃, Al₂O₃, SiO₂, CaF₂, SiO₂</td>
</tr>
<tr>
<td>15d, 15b</td>
<td>Limestone</td>
<td>CaCO₃, MgCO₃, Fe₂O₃, Al₂O₃, SiO₂</td>
</tr>
<tr>
<td>14b, 14c</td>
<td>Fluor spar</td>
<td>Approximate analysis, S</td>
</tr>
<tr>
<td>16a</td>
<td>Coal (bituminous)</td>
<td>Approximate analysis, S</td>
</tr>
<tr>
<td>16b</td>
<td>Coal (anthracite)</td>
<td>Ca₂O, MgO, FeO, Al₂O₃, SiO₂, MnO₁, P₂O₅</td>
</tr>
<tr>
<td>31</td>
<td>Thomas's phosphate (basic slag)</td>
<td>CaO, MgO, Fe₂O₃, Al₂O₃, SiO₂, SO₃, Alkalis.</td>
</tr>
<tr>
<td>24a</td>
<td>Portland cement</td>
<td>Total P₂O₅, water-soluble P₂O₅</td>
</tr>
<tr>
<td>25</td>
<td>Superphosphate</td>
<td>Cu, Fe, S</td>
</tr>
<tr>
<td>26aG</td>
<td>Copper concentrates</td>
<td>Cu, Fe, S</td>
</tr>
<tr>
<td>44aG</td>
<td>Iron pyrites</td>
<td>K₂O, Na₂O, SiO₂, Fe, SiO₂</td>
</tr>
<tr>
<td>29c</td>
<td>Felspars (potoash)</td>
<td>MnO₂</td>
</tr>
<tr>
<td>17</td>
<td>Iron ore (red)</td>
<td>Mn, MnO₂</td>
</tr>
<tr>
<td>18</td>
<td>Manganese ore</td>
<td>Zn, S</td>
</tr>
<tr>
<td>18aG</td>
<td>Manganese ore</td>
<td>Zn, S, Pb, Cu, Fe, As</td>
</tr>
<tr>
<td>30aG</td>
<td>Zinc blende</td>
<td>Zn, S, Pb</td>
</tr>
<tr>
<td>41G</td>
<td>Zinc concentrates</td>
<td>Pb, S, Zn, Fe, Cu, As</td>
</tr>
<tr>
<td>41aG</td>
<td>Zinc concentrates</td>
<td>Pb, Zn, Ag, S</td>
</tr>
<tr>
<td>42G</td>
<td>Lead concentrates</td>
<td>Sn, As</td>
</tr>
<tr>
<td>42aG</td>
<td>Lead concentrates</td>
<td>Cu, Pb, Ag</td>
</tr>
<tr>
<td>43aG</td>
<td>Tin concentrates</td>
<td>Ni, Pb, Cu, Ag, As</td>
</tr>
<tr>
<td>46G</td>
<td>Cu-Pb matte</td>
<td>Mo, Cu</td>
</tr>
<tr>
<td>47G</td>
<td>Cu-Ni speiss</td>
<td>Cr₂O₃, MgO, SiO₂, Cr₂O₃, MgO, CaO, FeO</td>
</tr>
<tr>
<td>48aG</td>
<td>Molybdenum ore</td>
<td>BaSO₄</td>
</tr>
<tr>
<td>48bG</td>
<td>Chrome iron ore</td>
<td>V₂O₅</td>
</tr>
<tr>
<td>50G</td>
<td>Barytes</td>
<td>Cu</td>
</tr>
<tr>
<td>51G</td>
<td>Fused vanadium</td>
<td>WO₃</td>
</tr>
<tr>
<td>52G</td>
<td>Copper precipitate</td>
<td>TiO₂</td>
</tr>
</tbody>
</table>

* Cd. C = Combined Carbon.
† Gr. C = Graphitic Carbon.
### BRITISH CHEMICAL STANDARDS *

<table>
<thead>
<tr>
<th>Description</th>
<th>Special Features</th>
<th>Constituents Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ordinary Carbon Steels</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No. 150, Armco Iron</td>
<td>Standard for K,Cr,O</td>
<td>C, Si, S, P, Mn, As, Ni, Cu</td>
</tr>
<tr>
<td>No. 237, 0.1 % C</td>
<td>C and Mn standard</td>
<td>C, Mn</td>
</tr>
<tr>
<td>No. 162, 0.2 % S</td>
<td>Free cutting</td>
<td>C, Si, S, P, Mn</td>
</tr>
<tr>
<td>No. 218, 0.15 % C</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn</td>
</tr>
<tr>
<td>No. 232, 0.07 % S, 0.08 % P</td>
<td>Free cutting</td>
<td>C, Si, S, P, Mn</td>
</tr>
<tr>
<td>No. 235, 0.2 % C</td>
<td>C and Si standard</td>
<td>C, Si</td>
</tr>
<tr>
<td>No. 239, 0.3 % C</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn, Ni, Cr, Cu, Mo</td>
</tr>
<tr>
<td>No. 240, 0.4 % C</td>
<td>C, S and P standard</td>
<td>C, S, P</td>
</tr>
<tr>
<td>No. 150, 0.6 % C</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn</td>
</tr>
<tr>
<td>No. 221, 0.6 % C</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn, Ni, Cr, Cu</td>
</tr>
<tr>
<td>No. 161, 0.8 % C</td>
<td>C, S and Mn standard</td>
<td>C, S, Mn</td>
</tr>
<tr>
<td>No. 215, 0.9 % C</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn</td>
</tr>
<tr>
<td>No. 163, 1.2 % C</td>
<td>Complete analysis</td>
<td>C, Mn, Ni</td>
</tr>
<tr>
<td>No. 229, 0.6 % Si</td>
<td>Si standard</td>
<td>Si</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy Steels</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 222, Nickel steel</td>
<td>Ni only</td>
<td>Ni</td>
</tr>
<tr>
<td>No. 212, Lead steel</td>
<td>0.28 % Pb, free cutting</td>
<td>C, S, Si, P, Mn</td>
</tr>
<tr>
<td>No. 224, Cr-V steel</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn, Ni, Cr, V</td>
</tr>
<tr>
<td>No. 214, Mn-Mo steel</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn, Mo, Ni, Cr, Cu</td>
</tr>
<tr>
<td>No. 225, Ni-Cr-Mo steel</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn, Mo, Ni, Cr</td>
</tr>
<tr>
<td>No. 219, Ni-Cr-Mo steel</td>
<td>Complete analysis</td>
<td>C, Si, S, P, Mn, Mo, Ni, Cr, Cu</td>
</tr>
<tr>
<td>No. 241, Cr-V-W-Co-Mo</td>
<td>High-speed steel</td>
<td>C, Si, S, P, Mn, Mo, Ni, Cr, Cu</td>
</tr>
<tr>
<td>No. 250, 7 % W, 4 % Mo steel</td>
<td>High-speed steel</td>
<td>C, Si, S, P, Mn, Mo, Ni, Cr, V, Co, W</td>
</tr>
<tr>
<td>No. 235, 18 : 8 + Ti</td>
<td>Stainless</td>
<td>C, Si, S, P, Mn, Ni, Cr, Ti, W</td>
</tr>
<tr>
<td>No. 211, 18 % Cr</td>
<td>Rustless</td>
<td>C, S, Si, P, Mn, Mo, Ni, Cr</td>
</tr>
<tr>
<td>No. 233, 11 % Ni, 24 % Cr</td>
<td>Permanent magnet</td>
<td>Al, Cu, Co, Ti, Ni</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cast Irons</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 236, Haematite</td>
<td>Complete analysis</td>
<td>Si, S, P, Mn, Ti, Cd. C, Total C</td>
</tr>
<tr>
<td>No. 198, Haematite</td>
<td>Low P, titanianous</td>
<td>S, P, As, Cd. C, Total C</td>
</tr>
<tr>
<td>No. 170, Foundry</td>
<td>Si, P and Mn standard</td>
<td>Si, P, Mn</td>
</tr>
<tr>
<td>No. 234, High duty</td>
<td>Complete analysis, high S</td>
<td>Si, S, P, Mn, As, Ti, Cd. C, Total C</td>
</tr>
<tr>
<td>No. 206, High Si and P</td>
<td>Complete analysis</td>
<td>Si, S, P, Mn, As, Ni, Ti, V, Cd. C, Total C</td>
</tr>
<tr>
<td>No. 172, Alloy</td>
<td>Complete analysis, Ni-Cr-Mo</td>
<td>Si, S, P, Mn, Mo, Ni, Cr, Cd. C, Total C</td>
</tr>
<tr>
<td>No. 173, Austenitio</td>
<td>High Ni-Cr-Cu</td>
<td>Si, S, P, Mn, Ni, Cr, Cu, Total C</td>
</tr>
</tbody>
</table>

* Supplied by Bureau of Analysed Samples, 234 Marton Road, Middlesbrough, Yorks., England.
### Ferro Alloys

| No. 202, Ferro-tungsten | Tungsten, low C | W |
| No. 231, Ferro-molybdenum | Molybdenum, low C | Mo |
| No. 203, Ferro-chromium | Chromium, low C and S | Cr, S, Cd. C |
| No. 204, Ferro-chromium | Chromium, high C and S | Cr, S, Cd. C |
| No. 205, Ferro-vanadium | Vanadium standard only | V |
| No. 208, Ferro-manganese | Complete analysis | Si, S, P, Mn, As, Ni, Fe, Ti, Cr, Cd. C, Total C |
| No. 201, Ferro-titanium | Titanium, low C | Ti |

### Slag

| No. 174, Basic slag | P₂O₅ and part analysis | P₂O₅, SiO₂, CaO, MgO, Fe, Mn |
| No. 175, Iron ore | Complete analysis and volumetric standard | Fe, P, CuO, MgO, Alkalis, SiO₂, Al₂O₃, TiO₂, S, Cd, H₂O, CO₂ |
| No. 176, Manganese ore | Mn, O, SiO₂, P, Fe | Fe, P, Mn, O, SiO₂ |

### Ores

| No. 177, White metal | Complete analysis | Pb, Sb, Sn, Cu, Bi, As, Zn, Fe |
| No. 178, White metal brass | Complete analysis | Pb, Sb, Sn, Cu, Fe, As, Zn, Al |
| No. 180, Cupro-nickel alloy | Complete analysis | Cu, Fe, Mn, Ni, Mg, Si |
| No. 181, Aluminium alloy | Complete analysis | Pb, Cu, Fe, Zn, Ni, Mg, Sn, Al, Si |
| No. 182, Aluminium alloy | Complete analysis, high Si | Si, Fe, Al |
| No. 216, Aluminium alloy | General purpose | Si, Sn, Cu, Fe, Bi, Ti, Zn, Ni, Mg |
| No. 183, Bronze containing P | Complete analysis | Pb, Sb, Sn, Cu, Fe, As, Zn, Ni, P |
| No. 207, Bronze | Complete analysis | Pb, Sb, Sn, Cu, Fe, As, Zn, Ni, P, S |

### Non-Ferrous Alloys

| No. 251, Basic slag | P₂O₅ and part analysis | P₂O₅, SiO₂, CaO, MgO, Fe, Mn |

### Pure Standardised Reagents and Metals

| Benzoic acid, No. 190e | Purity 99.93% | M.p. 231.9° C. |
| Tm, No. 192b | Purity 99.96% | M.p. 327.9° C. |
| Zr, No. 194a | Purity 99.96% | M.p. 419.4° C. |
| Aluminium, No. 195a | Purity 99.94% | M.p. 669.2° C. |
| Aluminium, No. 198 | Purity 99.96% | M.p. 1083° C. |
| Molybdenum, No. 227 | Purity 99.9% | |

### Spectrographic Standards (Low-Alloy Steel Series)

A series of eight low-alloy steels in the form of ¼-in.-diameter rods is available for use as standards in spectrographic analysis; these contain different proportions of Si, Mn, Ni, Cr, Mo, V, and Cu (Nos. S.S. 1–8). The same series of low-alloy steels is also marketed in the form of turnings, British Chemical Standards, Nos. 251–258.
Elements and compounds of very high purity are marketed by Messrs. Johnson and Matthey: a detailed laboratory report accompanies each supply of material. The substances at present available include:

- Aluminium: metal, chloride, oxide, sulphate, and ammonium alum.
- Ammonium: chloride, nitrate, and sulphate.
- Antimony: metal, tetroxide, and trichloride.
- Arsenic: element and oxide.
- Barium: carbonate, chloride, and nitrate.
- Beryllium: metal, carbonate, chloride, nitrate, oxide, and sulphate.
- Bismuth: metal, chloride, nitrate, and oxide.
- Boron: boric acid.
- Cadmium: metal, chloride, nitrate, oxide, and sulphate.
- Caesium: carbonate, chloride, and dichromate.
- Calcium: carbonate and chloride.
- Carbon: rod.
- Cerium: oxide.
- Chromium: metal, chloride, and sesquioxide.
- Cobalt: metal, chloride, nitrate, oxide, and sulphate.
- Copper: metal, sulphate, chloride, and oxide.
- Dysprosium: oxide.
- Erbium: oxide.
- Europium: oxide.
- Gadolinium: oxide.
- Gallium: metal, chloride, nitrate, oxide, and sulphate.
- Germanium: metal, dioxide, and ammonium oxalate.
- Gold: metal, chloride, chlorauric acid, and ammonium chloraurate.
- Graphite: rod and powder.
- Hafnium: oxide and sulphate.
- Holmium: oxide.
- Indium: metal, chloride, nitrate, oxide, and sulphate.
- Iridium: metal, ammonium chloroiridate, and ammonium chloroiridite.
- Iron: metal, ferric chloride, ferrous sulphate, and ferric oxide.
- Lanthanum: oxide.
- Lead: metal, oxide, and nitrate.
- Lithium: carbonate, chloride, hydroxide, and nitrate.
- Lutecium: oxide.
- Magnesium: metal, chloride, nitrate, oxide, and sulphate.
- Manganese: metal, chloride, oxide, and sulphate.

* Supplied by Johnson, Matthey and Co. Ltd., Hatton Garden, London, E.C.1, England. For further details, see the booklet bearing the above title (No. 1760 of May 1950) issued by this Firm.

† Substances marked with an asterisk are in the form of solutions.
Quantitative Inorganic Analysis

Mercury: metal, chloride, nitrate, and oxide.
Molybdenum: metal, trioxide, and ammonium molybdate.
Neodymium: oxide.
Nickel: metal, chloride, nitrate,* oxide, and sulphate.
Niobium (columbium): metal, pentachloride, and pentoxide.
Osmium: metal, tetrachloride,* and ammonium chlorosmate.
Palladium: metal, ammonium chloropalladite, tetramminepalladous chloride and tetramminepalladous nitrate.
Platinum: metal, chloroplatinic acid,* ammonium chloroplatinate, and tetrammineplatinous chloride.
Potassium: bromide, carbonate, chloride, dihydrogen phosphate, and iodide.
Praseodymium: oxide.
Rhenium: metal, ammonium perrhenate, and potassium perrhenate.
Rhodium: metal, ammonium chlororhodite, and chloropentamminerhodium sulphate.
Rubidium: chloride.
Ruthenium: metal, ammonium chlororuthenate, and hydroxonitrosotetrammineruthenium chloride.
Samarium: oxide.
Scandium: oxide.
Selenium: element, selenium oxide, and selenious acid.
Silicon: element, dioxide, and tetrachloride.*
Silver: metal, chloride, nitrate, and oxide.
Sodium: bicarbonate, carbonate, chloride, and nitrate.
Strontium: carbonate, chloride,* and nitrate.
Tantalum: metal, pentachloride, and pentoxide.
Tellurium: element, dioxide, and tellurous acid.*
Terbium: oxide.
Thallium: metal, acetate,* carbonate, chloride, formate,* nitrate, sulphate, and oxide.
Thorium: chloride,* nitrate, and oxide.
Thulium: oxide.
Tin: metal, chloride, oxide, and ammonium chlorostannate.
Titanium: metal, oxide, and ammonium titanoyl xalate.
Tungsten: metal and trioxide.
Uranium: metal, chloride,* nitrate, and oxide.
Vanadium: metal, pentoxide, vanadyl chloride,* and ammonium meta-
vanadate.
Ytterbium: oxide.
Yttrium: oxide.
Zinc: metal, chloride, nitrate,* sulphate, and oxide.
Zirconium: metal, nitrate, oxide, oxychloride, and sulphate.
The following standards are at present available:

No. 1. — Sulphur (S = 0.027%).
No. 2. — Sulphur (S = 0.071%).
No. 3. — Phosphorus (P = 0.029%).
No. 5. — Carbon (C = 0.65%). Acid O.-H. steel.
No. 6. — Carbon (C = 0.10%). Basic O.-H. steel.
No. 8. — Carbon (C = 0.27%). Acid O.-H. steel.
No. 9. — Carbon (C = 1.00%). Acid O.-H. steel.
No. 11. — Manganese (Mn = 1.09%). Acid O.-H. steel.
No. 12. — Cast iron standard sample (Si = 2.22%, P = 1.14%, Mn = 0.50%, S = 0.075%).
No. 13. — Silicon (Si = 14.95%). Acid-resisting silicon iron.

**STANDARD SAMPLES ISSUED BY U.S. NATIONAL BUREAU OF STANDARDS**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>Constituents Determined.†</th>
</tr>
</thead>
<tbody>
<tr>
<td>8g</td>
<td>Bessemer, 0-1 C</td>
<td>C, Mn, P, S, Si, Cu, Ni</td>
</tr>
<tr>
<td>10e</td>
<td>Bessemer, 0-4 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo</td>
</tr>
<tr>
<td>22e</td>
<td>Bessemer, 0-6 C, aluminium-bearing</td>
<td>C, Mn, P, S, Si, Cu, Al</td>
</tr>
<tr>
<td>15d</td>
<td>B.O.H., 0-1 C</td>
<td>C, Mn, P, S, Cu, Ni, Cr</td>
</tr>
<tr>
<td>11f</td>
<td>B.O.H., 0-2 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo</td>
</tr>
<tr>
<td>12e</td>
<td>B.O.H., 0-4 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo</td>
</tr>
<tr>
<td>152</td>
<td>B.O.H., 0-5 C, 0-04 Sn</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo</td>
</tr>
<tr>
<td>13e</td>
<td>B.O.H., 0-6 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo</td>
</tr>
<tr>
<td>14e</td>
<td>B.O.H., 0-8 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Al</td>
</tr>
<tr>
<td>16e</td>
<td>B.O.H., 1-0 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr</td>
</tr>
<tr>
<td>19e</td>
<td>A.O.H., 0-2 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo, Sn</td>
</tr>
<tr>
<td>20e</td>
<td>A.O.H., 0-4 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo, Sn</td>
</tr>
<tr>
<td>21d</td>
<td>A.O.H., 0-6 C, 0-08 Sn</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo, Sn</td>
</tr>
<tr>
<td>34a</td>
<td>A.O.H., 0-8 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo</td>
</tr>
<tr>
<td>35a</td>
<td>A.O.H., 1-0 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Mo, V</td>
</tr>
<tr>
<td>51a</td>
<td>Electric furnace, 1-2 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Sn</td>
</tr>
<tr>
<td>66e</td>
<td>Basic electric, 0-8 C</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr</td>
</tr>
<tr>
<td>100a</td>
<td>Manganese</td>
<td>C, Mn, P, S, Si, Cu, Ni, Cr, Al</td>
</tr>
</tbody>
</table>

* These are issued jointly by the Iron and Steel Institute and the National Physical Laboratory, and are obtainable from the National Physical Laboratory, Metallurgy Department, Teddington, Middlesex, England.
† Obtainable from the U.S. Department of Commerce, Bureau of Standards, Washington, D.C., U.S.A.
‡ Metals present in quantities less than 0.01 per cent are not indicated. The data have been extracted from Supplement to National Bureau of Standards Circular 398, issued January 1, 1949.
### Standard Samples Issued by the U.S. National Bureau of Standards—Continued

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>Constituents Determined:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Stainless (Cr 14)</strong></td>
<td>C, Mn, P, Si, Cu, Ni, Cr, V, Mo, W, Co, Ti</td>
</tr>
<tr>
<td></td>
<td><strong>Cr 18-Ni 9 (carbon only)</strong></td>
<td>C, Mn, P, Si, Cu, Ni, Cr, V, Mo, W</td>
</tr>
<tr>
<td></td>
<td><strong>Ingot iron</strong></td>
<td>C, Mn, P, Si, Cu, Ni, Cr, V, Mo, W</td>
</tr>
<tr>
<td></td>
<td><strong>Chromium-nickel-molybdenum cast iron</strong></td>
<td>C, Gr, C, Mn, P, S, Si, Cu, Ni, Cr, V, Ti</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>Constituents Determined:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Total C, Gr, C, Mn, P, S, Si, Cu, Ni, Cr, V, Mo, Ti</strong></td>
<td>C, Mn, P, Si, Cu, Ni, Cr, V, Ti</td>
</tr>
</tbody>
</table>

---

*Gr. C = Graphitic Carbon.*
# Appendix

## Standard Samples Issued by the U.S. National Bureau of Standards—Continued

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>Constituents Determined.‡</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Steel-making Alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>Refined silicon</td>
<td>C, Mn, Si, Ti, Al, Ca, Fe, Cr</td>
</tr>
<tr>
<td>58</td>
<td>Ferrosilicon (75% Si)</td>
<td>C, Mn, P, S, Si, Ti, Al, Ca, Fe, Cr</td>
</tr>
<tr>
<td>59</td>
<td>Ferrosilicon (60% Si)</td>
<td>C, Mn, P, S, Si, Ti, Al, Ca, Fe, Cr</td>
</tr>
<tr>
<td>61a</td>
<td>Ferrovanadium (high carbon)</td>
<td>C, Mn, P, Si, V, Ti, Al, Cu, Fe, Cr</td>
</tr>
<tr>
<td>64a</td>
<td>Ferrochromium (high carbon)</td>
<td>C, Mn, P, Si, Cr, V, Al</td>
</tr>
<tr>
<td>66a</td>
<td>Spiegelisen</td>
<td>C, Mn, P, S, Si</td>
</tr>
<tr>
<td>67</td>
<td>Manganese metal</td>
<td>C, Mn, P, Si, Ni, Cr, V, Fe</td>
</tr>
<tr>
<td>68a</td>
<td>Ferromanganese</td>
<td>C, Mn, P, S, Si, Cr, V</td>
</tr>
<tr>
<td>71</td>
<td>Calcium molybdate</td>
<td>Mo = 35–36; Fe = 1·92; Ti = 0·06</td>
</tr>
<tr>
<td>75a</td>
<td>Ferrotungsten</td>
<td>W</td>
</tr>
<tr>
<td>80</td>
<td>Ferrophosphorus</td>
<td>P</td>
</tr>
<tr>
<td>119a</td>
<td>Ferrotitanium (low carbon)</td>
<td>C, Si, V, Ti, Al, Cr</td>
</tr>
<tr>
<td><strong>Non-ferrous Alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85a</td>
<td>Aluminium alloy, wrought</td>
<td>Cu, Mn, Si, Mg, Fe, Ti, Zn, Ga, Ni, Cr</td>
</tr>
<tr>
<td>86c</td>
<td>Aluminium-base casting alloy</td>
<td>Cu, Mn, Si, Mg, Fe, Ti, Zn, Pb, Ni, Cr</td>
</tr>
<tr>
<td>87</td>
<td>Aluminium–silicon alloy</td>
<td>Cu, Mn, Si, Mg, Fe, Ti, Zn, Pb, Sn, Ni, Cr</td>
</tr>
<tr>
<td>37d</td>
<td>Brass, sheet</td>
<td>Cu, Zn, Sn, Pb, Ni, Fe</td>
</tr>
<tr>
<td>164</td>
<td>Brass, aluminium</td>
<td>Cu, Zn, Al, Mn, Fe, Sn, Pb, Ni, Si</td>
</tr>
<tr>
<td>52b</td>
<td>Bronze, cast</td>
<td>Cu, Zn, Sn, Pb, Ni, Fe</td>
</tr>
<tr>
<td>62b</td>
<td>Bronze, manganese</td>
<td>Cu, Zn, Sn, Pb, Ni, Fe, Al, Mn</td>
</tr>
<tr>
<td>63b</td>
<td>Bronze, phosphorous</td>
<td>Cu, Zn, Sn, Pb, Ni, Fe, Al</td>
</tr>
<tr>
<td>158</td>
<td>Bronze, silicon</td>
<td>Cu, Si, Zn, Fe, Mn, Sn, Al</td>
</tr>
<tr>
<td>157</td>
<td>Nickel silver (Cu 72–Ni 18–Zn 10)</td>
<td>Cu, Zn, Pb, Ni, Fe, Mn</td>
</tr>
<tr>
<td>158b</td>
<td>Ounce metal (Cu 85–Pb 5–Sn 6–Zn 5)</td>
<td>Cu, Zn, Sn, Pb, Ni, Fe</td>
</tr>
<tr>
<td>53c</td>
<td>Lead-base bearing metal</td>
<td>Sn, Sb, Cu, Bi, As</td>
</tr>
<tr>
<td>127</td>
<td>Solder (Pb 65–Sn 35)</td>
<td>Sn, Sb, Bi, Cu, As</td>
</tr>
<tr>
<td>54a</td>
<td>Tin-base bearing metal</td>
<td>Pb, Sn, Sb, Bi, Cu, Fe, As, Ag, Ni</td>
</tr>
<tr>
<td>162</td>
<td>Monel type (Ni 66–Cu 29)</td>
<td>Ni, Cu, Mn, Si, Co, Fe, Cr, Al, Ti, C</td>
</tr>
<tr>
<td>161</td>
<td>Nickel-base casting alloy</td>
<td>Ni, Cu, Mn, Si, Co, Fe, Cr, C, P</td>
</tr>
<tr>
<td>94a</td>
<td>Zine-base die-casting alloy</td>
<td>Al, Cu, Mg, Fe, Mn</td>
</tr>
<tr>
<td>108</td>
<td>Zine spelter</td>
<td>Pb, Cd, Fe</td>
</tr>
<tr>
<td>109</td>
<td>Zine spelter</td>
<td>Impurities &lt;0·1%</td>
</tr>
<tr>
<td>110</td>
<td>Zine spelter</td>
<td>Pb, Cd, Fe</td>
</tr>
<tr>
<td>171</td>
<td>Magnesium-base alloy</td>
<td>Al, Zn, Mn, Si, Cu</td>
</tr>
<tr>
<td><strong>Ores</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69a</td>
<td>Bauxite</td>
<td>SiO₂, TiO₂, P, Al₂O₃, Fe, CaO, MgO</td>
</tr>
<tr>
<td>36</td>
<td>Iron ore, Crescent</td>
<td>SiO₂, P, Fe</td>
</tr>
<tr>
<td>29a</td>
<td>Iron ore, Magnetite</td>
<td>Total Mn, available oxygen</td>
</tr>
<tr>
<td>28a</td>
<td>Iron ore, Norrie</td>
<td>P₂O₅, MgO, F</td>
</tr>
<tr>
<td>27b</td>
<td>Iron ore, Sibley</td>
<td>P₂O₅, Fe₂O₃, Al₂O₃, CaO, MgO, F</td>
</tr>
<tr>
<td>28b</td>
<td>Manganese ore</td>
<td>Sn</td>
</tr>
<tr>
<td>56b</td>
<td>Phosphate rock (Tennessee)</td>
<td>Sn</td>
</tr>
<tr>
<td>120</td>
<td>Phosphate rock (Florida)</td>
<td>Zn</td>
</tr>
<tr>
<td>127</td>
<td>Tin ore (Bolivian concentrate)</td>
<td></td>
</tr>
</tbody>
</table>
## Quantitative Inorganic Analysis

### Standard Samples Issued by the U.S. National Bureau of Standards—Continued

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name</th>
<th>Constituents Determined†</th>
</tr>
</thead>
<tbody>
<tr>
<td>104</td>
<td>Burned magnesite</td>
<td>SiO₂, Fe₂O₃, Al₂O₃, TiO₂, MnO, CaO, MgO, Na₂O</td>
</tr>
<tr>
<td>76</td>
<td>Burned refractory (40 % Al₂O₃)</td>
<td>Al₂O₃, Fe₂O₃, SiO₂, TiO₂, ZrO₂</td>
</tr>
<tr>
<td>77</td>
<td>Burned refractory (60 % Al₂O₃)</td>
<td>Al₂O₃, Fe₂O₃, SiO₂, TiO₂, ZrO₂</td>
</tr>
<tr>
<td>78</td>
<td>Burned refractory (70 % Al₂O₃)</td>
<td>Cr₂O₃, SiO₂, FeO, Al₂O₃, CaO, MgO, TiO₂</td>
</tr>
<tr>
<td>103</td>
<td>Chrome refractory</td>
<td></td>
</tr>
<tr>
<td>97</td>
<td>Clay, flint</td>
<td>SiO₂, Al₂O₃, TiO₂, ZrO₂, Fe₂O₃, P₂O₅, V₂O₅, Cr₂O₃, K₂O</td>
</tr>
<tr>
<td>98</td>
<td>Clay, plastic</td>
<td>SiO₂, Al₂O₃, TiO₂, ZrO₂, Fe₂O₃, P₂O₅, V₂O₅, Cr₂O₃, K₂O</td>
</tr>
<tr>
<td>70</td>
<td>Feldspar, potash</td>
<td>K₂O, Na₂O, SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO</td>
</tr>
<tr>
<td>79</td>
<td>Feldspar, soda</td>
<td>K₂O, Na₂O, SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, TiO₂</td>
</tr>
<tr>
<td>77</td>
<td>Fluorspar</td>
<td>CaF₂, CO₂, SiO₂, Zn, Pb, S, Fe₂O₃, Al₂O₃, K₂O, Na₂O, MgO, BaO</td>
</tr>
<tr>
<td>92</td>
<td>Glass, low boron</td>
<td>SiO₂, Al₂O₃, Fe₂O₃, TiO₂, ZrO₂, MgO, K₂O, Na₂O, B₂O₃, As₂O₃, Cl</td>
</tr>
<tr>
<td>93</td>
<td>Glass, high boron</td>
<td>SiO₂, Al₂O₃, Fe₂O₃, MnO, TiO₂, CaO, BaO, MgO, K₂O, Na₂O, P₂O₅, As₂O₃, Cl</td>
</tr>
<tr>
<td>78</td>
<td>Glass, lead–barium</td>
<td>SiO₂, PbO, Al₂O₃, Fe₂O₃, MnO, TiO₂, CaO, BaO, MgO, K₂O, Na₂O, P₂O₅, As₂O₃, Cl, F</td>
</tr>
<tr>
<td>77</td>
<td>Glass, opal</td>
<td>SiO₂, PbO, Al₂O₃, Fe₂O₃, MnO, TiO₂, CaO, BaO, MgO, K₂O, Na₂O, P₂O₅, As₂O₃, Cl, F</td>
</tr>
<tr>
<td>79</td>
<td>Glass, soda–lime</td>
<td>SiO₂, Al₂O₃, Fe₂O₃, TiO₂, CaO, MgO, K₂O, Na₂O, B₂O₃, BaO</td>
</tr>
<tr>
<td>80</td>
<td>Glass, soda–lime (B₂O₃, BaO)</td>
<td>SiO₂, Al₂O₃, Fe₂O₃, TiO₂, CaO, BaO</td>
</tr>
<tr>
<td>128</td>
<td>Glass sand</td>
<td>Fe₂O₃, Al₂O₃, Fe₂O₃, ZrO₂, CaO, MgO</td>
</tr>
<tr>
<td>165</td>
<td>Glass sand (low iron)</td>
<td>Fe₂O₃, Al₂O₃, Fe₂O₃, TiO₂, MnO, CaO, SrO, MgO, Na₂O, K₂O, SO₃, S, P₂O₅, CO₂, C</td>
</tr>
<tr>
<td>1a</td>
<td>Limestone, argillaceous</td>
<td>SiO₂, Fe₂O₃, Al₂O₃, CaO, MgO, Na₂O, K₂O, SO₃, S, CO₂, C</td>
</tr>
<tr>
<td>88</td>
<td>Limestone, dolomitic</td>
<td>SiO₂, Fe₂O₃, Al₂O₃, CaO, MgO, Na₂O, K₂O, SO₃, S, CO₂, C</td>
</tr>
<tr>
<td>102</td>
<td>Silica brick</td>
<td>SiO₂, Fe₂O₃, Al₂O₃, TiO₂, CaO, MgO, Na₂O, K₂O, P₂O₅</td>
</tr>
<tr>
<td>112</td>
<td>Silicon carbide</td>
<td>SiO₂, Fe₂O₃, Al₂O₃, TiO₂, CaO, MgO, Na₂O, K₂O, P₂O₅</td>
</tr>
<tr>
<td>154</td>
<td>Titanium dioxide</td>
<td>TiO₂</td>
</tr>
</tbody>
</table>

### Spectrographic Standards

| 401–430 | Steels; 4-in. rods | The twenty steel samples cover varying proportions of Mn, Si, Cu, Ni, Cr, V, Mo, Al, Sn, and B; also 0.007% Co and 0.02% W |
| 601–604 | Aluminium alloys; discs two-and-a-half in. in diameter | The four alloys cover varying proportions of Cu, Mg, Si, Mn, Fe, Cr, and Ti; also 2.00% Ni and 0.02% Zn |
### Chemicals

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>Intended Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>84d</td>
<td>Acid potassium phthalate (purity by titration, 100-05%)</td>
<td>Acidimetric value</td>
</tr>
<tr>
<td>39f</td>
<td>Benzoic acid (purity by titration, 100-03%)</td>
<td>Acidimetric and calorimetric values</td>
</tr>
<tr>
<td>40e</td>
<td>Sodium oxalate (purity by titration, 99-06%)</td>
<td>Oxidimetric value</td>
</tr>
<tr>
<td>83a</td>
<td>Arsonic trioxide (purity by titration, 99-99%)</td>
<td>Oxidimetric value</td>
</tr>
<tr>
<td>136</td>
<td>Potassium dichromate (purity by titration, 100-00%)</td>
<td>Oxidimetric value</td>
</tr>
<tr>
<td>17</td>
<td>Sucrose or cane sugar (purity, 99-99%)</td>
<td>Calorimetric and saccharimetric values</td>
</tr>
<tr>
<td>41</td>
<td>Dextrose or glucose (purity, 99-99%)</td>
<td>Reducing value</td>
</tr>
</tbody>
</table>

### Microchemical Standards

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>Intended Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>Benzoic acid</td>
<td>For C and H determination</td>
</tr>
<tr>
<td>141</td>
<td>Acetanilide</td>
<td>For N, C, and H determination</td>
</tr>
<tr>
<td>142</td>
<td>Anisic acid</td>
<td>For methoxyl determination</td>
</tr>
<tr>
<td>143</td>
<td>Cystine</td>
<td>For S, C, H, and N determination</td>
</tr>
<tr>
<td>144</td>
<td>2-Chlorobenzoic acid</td>
<td>For Cl determination</td>
</tr>
<tr>
<td>145</td>
<td>2-Iodobenzoic acid</td>
<td>For I determination</td>
</tr>
<tr>
<td>146</td>
<td>Tri-naphthyl phosphate</td>
<td>For P determination</td>
</tr>
</tbody>
</table>

### pH Standards

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>pH (approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>185</td>
<td>Acid potassium phthalate</td>
<td>4-0</td>
</tr>
<tr>
<td>185Ia</td>
<td>Potassium dihydrogen phosphate</td>
<td>6-8 *</td>
</tr>
<tr>
<td>185IIa</td>
<td>Potassium hydrogen phosphate</td>
<td>9-2</td>
</tr>
</tbody>
</table>

### Melting-point Standards

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>118</td>
<td>Alumel wire, No. 8 gauge</td>
<td>659-7°C</td>
</tr>
<tr>
<td>119</td>
<td>Chromel wire, No. 8 gauge</td>
<td>1083-2°C</td>
</tr>
<tr>
<td>122</td>
<td>Lead</td>
<td>327-31°C</td>
</tr>
<tr>
<td>123</td>
<td>Tin</td>
<td>231-90°C</td>
</tr>
<tr>
<td>124</td>
<td>Zinc</td>
<td>419-50°C</td>
</tr>
</tbody>
</table>

### Turbidimetric and Fineness Standards

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>Fineness standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>47i</td>
<td>Cement</td>
<td>No. 200 sieve residue, 9-4%</td>
</tr>
<tr>
<td>114f</td>
<td>Cement</td>
<td>No. 325 sieve residue, 9-6%</td>
</tr>
</tbody>
</table>

### Thermoelectric Standards

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Name.</th>
<th>e.m.f. vs. NBS Pt No. 27, 0-1300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>118</td>
<td>Alumel wire, No. 8 gauge</td>
<td>e.m.f. vs. NBS Pt No. 27, 0-1300°C</td>
</tr>
<tr>
<td>119</td>
<td>Chromel wire, No. 8 gauge</td>
<td>e.m.f. vs. NBS Pt No. 27, 0-1300°C</td>
</tr>
</tbody>
</table>

* The two phosphates are to be used together in equal molar proportions.
## A.9. SOLUBILITIES OF SOME INORGANIC COMPOUNDS IN WATER AT VARIOUS TEMPERATURES

The Table gives the number of grams of the anhydrous substance which can be dissolved in 100 g. of water at the temperature (° C), indicated at the head of the column. Where the formula is followed by an asterisk, the value is expressed in grams of the anhydrous substance in 100 g. of the saturated solution at the temperature indicated.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Molecular Weight</th>
<th>0°</th>
<th>10°</th>
<th>20°</th>
<th>30°</th>
<th>40°</th>
<th>50°</th>
<th>60°</th>
<th>70°</th>
<th>80°</th>
<th>90°</th>
<th>100° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl₃,6H₂O</td>
<td>241.44</td>
<td>30.6</td>
<td>31.0</td>
<td>31.4</td>
<td>31.8</td>
<td>32.3</td>
<td>32.5</td>
<td>32.7</td>
<td>32.9</td>
<td>33.2</td>
<td>33.8</td>
<td>34.2</td>
</tr>
<tr>
<td>Al₃(PO₄)₃,18H₂O</td>
<td>618.48</td>
<td>23.0</td>
<td>25.1</td>
<td>26.7</td>
<td>28.8</td>
<td>31.0</td>
<td>34.3</td>
<td>37.2</td>
<td>40.2</td>
<td>44.7</td>
<td>47.1</td>
<td></td>
</tr>
<tr>
<td>Al₂(SO₄)₃,5H₂O</td>
<td>378.67</td>
<td>2.0</td>
<td>4.99</td>
<td>7.49</td>
<td>10.94</td>
<td>14.88</td>
<td>20.10</td>
<td>26.70</td>
<td>34.6</td>
<td>40.0</td>
<td>71.0</td>
<td>109.0</td>
</tr>
<tr>
<td>Al₂(SO₄)₃,6H₂O</td>
<td>948.78</td>
<td>3.0</td>
<td>4.0</td>
<td>5.0</td>
<td>6.4</td>
<td>8.1</td>
<td>11.7</td>
<td>16.0</td>
<td>21.8</td>
<td>26.0</td>
<td>66.3</td>
<td>71.3</td>
</tr>
<tr>
<td>Al₂(SO₄)₃,24H₂O</td>
<td>65.90</td>
<td>20.0</td>
<td>33.0</td>
<td>37.0</td>
<td>40.0</td>
<td>43.0</td>
<td>47.0</td>
<td>51.4</td>
<td>54.4</td>
<td>63.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>60.02</td>
<td>118.0</td>
<td>168.0</td>
<td>241.8</td>
<td>597.0</td>
<td>344.3</td>
<td>484.0</td>
<td>663.0</td>
<td>778.0</td>
<td>871.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂CO₃,6H₂O</td>
<td>142.19</td>
<td>2.3</td>
<td>3.1</td>
<td>4.26</td>
<td>5.74</td>
<td>7.75</td>
<td>9.74</td>
<td>12.25</td>
<td>15.10</td>
<td>18.30</td>
<td>21.84</td>
<td>25.73</td>
</tr>
<tr>
<td>(NH₄)₂CO₃</td>
<td>32.37</td>
<td>50.0</td>
<td>80.0</td>
<td>120.0</td>
<td>160.0</td>
<td>200.0</td>
<td>240.0</td>
<td>280.0</td>
<td>320.0</td>
<td>360.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>115.94</td>
<td>15.0</td>
<td>22.0</td>
<td>28.0</td>
<td>34.0</td>
<td>40.0</td>
<td>47.0</td>
<td>51.4</td>
<td>54.4</td>
<td>63.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>132.15</td>
<td>40.0</td>
<td>42.0</td>
<td>46.0</td>
<td>48.0</td>
<td>47.0</td>
<td>46.0</td>
<td>45.4</td>
<td>45.2</td>
<td>46.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄CN</td>
<td>37.15</td>
<td>54.5</td>
<td>59.0</td>
<td>63.0</td>
<td>67.0</td>
<td>67.0</td>
<td>67.0</td>
<td>67.0</td>
<td>67.0</td>
<td>67.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaBr₂,2H₂O</td>
<td>378.96</td>
<td>58.0</td>
<td>101.0</td>
<td>104.0</td>
<td>114.0</td>
<td>114.0</td>
<td>128.0</td>
<td>135.0</td>
<td>149</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaCl₂,2H₂O</td>
<td>244.30</td>
<td>31.0</td>
<td>33.0</td>
<td>35.0</td>
<td>35.0</td>
<td>34.0</td>
<td>34.0</td>
<td>34.0</td>
<td>34.0</td>
<td>34.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(OH)₂,3H₂O</td>
<td>315.90</td>
<td>1.67</td>
<td>2.48</td>
<td>3.89</td>
<td>5.79</td>
<td>8.22</td>
<td>10.4</td>
<td>14.6</td>
<td>19.1</td>
<td>24.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba(NO₃)₂</td>
<td>261.38</td>
<td>4.0</td>
<td>6.0</td>
<td>8.0</td>
<td>10.0</td>
<td>12.4</td>
<td>14.6</td>
<td>16.9</td>
<td>19.1</td>
<td>24.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCl₂,2H₂O</td>
<td>184.10</td>
<td>37.0</td>
<td>46.0</td>
<td>54.0</td>
<td>59.0</td>
<td>67.0</td>
<td>72.0</td>
<td>78.0</td>
<td>82.0</td>
<td>85.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaBr₂,2H₂O</td>
<td>309.01</td>
<td>125</td>
<td>132</td>
<td>143</td>
<td>213</td>
<td>273</td>
<td>295</td>
<td>312</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF₂</td>
<td>74.10</td>
<td>0.16</td>
<td>0.25</td>
<td>0.40</td>
<td>0.60</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td>Ca₂(OH)₂</td>
<td>172.13</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
<td>32.0</td>
</tr>
<tr>
<td>Ca₂SO₄,3H₂O</td>
<td>353.35</td>
<td>45.5</td>
<td>50.0</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
<td>55.0</td>
</tr>
<tr>
<td>Ca₂SO₄,9H₂O</td>
<td>460.50</td>
<td>14.3</td>
<td>17.4</td>
<td>20.7</td>
<td>25.0</td>
<td>29.5</td>
<td>33.0</td>
<td>37.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>242.69</td>
<td>17.4</td>
<td>20.7</td>
<td>25.0</td>
<td>29.5</td>
<td>33.0</td>
<td>37.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>278.02</td>
<td>17.4</td>
<td>20.7</td>
<td>25.0</td>
<td>29.5</td>
<td>33.0</td>
<td>37.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
<td>40.0</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂,2H₂O</td>
<td>392.16</td>
<td>12.5</td>
<td>15.0</td>
<td>17.5</td>
<td>20.0</td>
<td>22.5</td>
<td>25.0</td>
<td>27.5</td>
<td>30.0</td>
<td>32.5</td>
<td>35.0</td>
<td>37.5</td>
</tr>
<tr>
<td>CuCl₂,2H₂O</td>
<td>197.01</td>
<td>63.4</td>
<td>68.1</td>
<td>73.9</td>
<td>80.7</td>
<td>88.6</td>
<td>98.2</td>
<td>108.0</td>
<td>118.0</td>
<td>130.0</td>
<td>143.0</td>
<td>157.0</td>
</tr>
<tr>
<td>CuCl₂,2H₂O</td>
<td>321.23</td>
<td>60.0</td>
<td>57.6</td>
<td>55.0</td>
<td>51.1</td>
<td>46.2</td>
<td>41.9</td>
<td>37.6</td>
<td>33.4</td>
<td>29.2</td>
<td>25.0</td>
<td>18.0</td>
</tr>
<tr>
<td>CuCl₂,2H₂O</td>
<td>256.50</td>
<td>10.0</td>
<td>22.0</td>
<td>25.0</td>
<td>28.0</td>
<td>30.0</td>
<td>32.0</td>
<td>34.0</td>
<td>36.0</td>
<td>38.0</td>
<td>40.0</td>
<td>40.0</td>
</tr>
<tr>
<td>CuCl₂,2H₂O</td>
<td>306.04</td>
<td>11.0</td>
<td>14.0</td>
<td>17.0</td>
<td>20.0</td>
<td>23.0</td>
<td>26.0</td>
<td>29.0</td>
<td>32.0</td>
<td>35.0</td>
<td>38.0</td>
<td>41.0</td>
</tr>
<tr>
<td>CuCl₂,2H₂O</td>
<td>286.53</td>
<td>56.0</td>
<td>57.6</td>
<td>55.0</td>
<td>51.1</td>
<td>46.2</td>
<td>41.9</td>
<td>37.6</td>
<td>33.4</td>
<td>29.2</td>
<td>25.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Mn₃(PO₄)₂</td>
<td>231.45</td>
<td>27.3</td>
<td>25.0</td>
<td>22.0</td>
<td>19.0</td>
<td>16.0</td>
<td>13.0</td>
<td>10.0</td>
<td>7.0</td>
<td>4.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Mn₃(PO₄)₂</td>
<td>254.50</td>
<td>18.0</td>
<td>22.0</td>
<td>26.0</td>
<td>30.0</td>
<td>34.0</td>
<td>38.0</td>
<td>42.0</td>
<td>46.0</td>
<td>50.0</td>
<td>54.0</td>
<td>58.0</td>
</tr>
<tr>
<td>Mn₃(PO₄)₂</td>
<td>231.45</td>
<td>30.3</td>
<td>32.0</td>
<td>34.0</td>
<td>36.0</td>
<td>38.0</td>
<td>40.0</td>
<td>42.0</td>
<td>44.0</td>
<td>46.0</td>
<td>48.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Mn₃(PO₄)₂</td>
<td>254.50</td>
<td>18.0</td>
<td>22.0</td>
<td>26.0</td>
<td>30.0</td>
<td>34.0</td>
<td>38.0</td>
<td>42.0</td>
<td>46.0</td>
<td>50.0</td>
<td>54.0</td>
<td>58.0</td>
</tr>
<tr>
<td>Compound</td>
<td>Mass (g/mol)</td>
<td>Molar Mass (g/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------</td>
<td>--------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnSO₄·4H₂O</td>
<td>223.06</td>
<td>272.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂Br⁻ *</td>
<td>360.45</td>
<td>360.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgCl₂ *</td>
<td>271.53</td>
<td>271.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiBr₂·6H₂O *</td>
<td>326.63</td>
<td>326.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCl₂·6H₂O *</td>
<td>237.72</td>
<td>237.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni₂SO₄·6H₂O *</td>
<td>420.63</td>
<td>420.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiSO₄·7H₂O *</td>
<td>280.87</td>
<td>280.87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂CO₃ *</td>
<td>138.21</td>
<td>138.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂Cr₂O₇ *</td>
<td>119.92</td>
<td>119.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KBrO₃</td>
<td>167.01</td>
<td>167.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂[Fe(CN)₆]₃·3H₂O</td>
<td>422.43</td>
<td>422.43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCNS</td>
<td>97.19</td>
<td>97.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>74.56</td>
<td>74.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KClO₃ *</td>
<td>122.56</td>
<td>122.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KClO₄ *</td>
<td>138.50</td>
<td>138.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂Cr₄O₇ *</td>
<td>204.23</td>
<td>204.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>166.02</td>
<td>166.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KIO₃ *</td>
<td>214.02</td>
<td>214.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂SO₄ *</td>
<td>174.27</td>
<td>174.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KBSO₄ *</td>
<td>136.18</td>
<td>136.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgNO₃ *</td>
<td>169.89</td>
<td>169.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag₂SO₄ *</td>
<td>183.89</td>
<td>183.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBr·2H₂O *</td>
<td>138.66</td>
<td>138.66</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBrO₂ *</td>
<td>100.92</td>
<td>100.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃·H₂O·3H₂O *</td>
<td>136.09</td>
<td>136.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>84.02</td>
<td>84.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃·10H₂O *</td>
<td>286.17</td>
<td>286.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄·2H₂O *</td>
<td>134.02</td>
<td>134.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>58.45</td>
<td>58.45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂Cr₂O₇·3H₂O *</td>
<td>298.05</td>
<td>298.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>42.00</td>
<td>42.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃·H₂O</td>
<td>185.95</td>
<td>185.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O₃·H₂O·2 *</td>
<td>215.93</td>
<td>215.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaNO₃ *</td>
<td>85.01</td>
<td>85.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>40.01</td>
<td>40.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃·10H₂O *</td>
<td>322.23</td>
<td>322.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄·5H₂O *</td>
<td>248.21</td>
<td>248.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrCl₂·6H₂O</td>
<td>266.84</td>
<td>266.84</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
BUFFER SOLUTIONS

The exact significance of the pH of a solution has recently received special attention (see R. G. Bates, "Definitions of pH Scales," Chemical Reviews, 1948, 42, 1) and it would appear doubtful whether, with few exceptions, the values hitherto published for buffer solutions possess greater accuracy than 0-1 pH unit. The British Standards Institution (British Standard 1647: 1950, "pH Scales") recommend 0-05M-potassium hydrogen phthalate as the primary standard; the pH is 4-000 at 15° C., 4-005 at 25° C., and 4-026 at 38° C.† The following supplementary standards are recommended for the calibration of the glass electrode:

<table>
<thead>
<tr>
<th>Buffer Solution</th>
<th>12° C.</th>
<th>25° C.</th>
<th>38° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1M-KHC$_2$O$_4$, H$_2$C$_2$O$_4$,2H$_2$O</td>
<td>---</td>
<td>1-48</td>
<td>1-50</td>
</tr>
<tr>
<td>0-01M-HCl + 0-00M-KCl</td>
<td>---</td>
<td>2-07</td>
<td>2-08</td>
</tr>
<tr>
<td>0-1M-CH$_3$COOH + 0-1M-CH$_3$COONa</td>
<td>4-05</td>
<td>4-04</td>
<td>4-03</td>
</tr>
<tr>
<td>0-05M-K$_2$HPO$_4$ + 0-025M-Na$_2$HPO$_4$,12H$_2$O</td>
<td>---</td>
<td>8-85</td>
<td>8-84</td>
</tr>
<tr>
<td>0-05M-Na$_2$B$_4$O$_7$,10H$_2$O</td>
<td>---</td>
<td>9-18</td>
<td>9-07</td>
</tr>
</tbody>
</table>

* Prepared from pure acetic acid, diluted, and half neutralised with sodium hydroxide. It need hardly be emphasised that all the reagents employed in the preparation of buffer solutions should be of the highest purity, e.g., A.R. quality.

J. J. Lingane (1947) has recommended potassium hydrogen tartrate, saturated solution, which has a pH of 3-57 at 25° C.∗

1. Buffers suitable for precision standardisation of pH measurements (D. A. MacInnes, 1939)

<table>
<thead>
<tr>
<th>Buffer Solution</th>
<th>12° C.</th>
<th>25° C.</th>
<th>38° C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$COOH (0-01N), CH$_3$COONa (0-01N)</td>
<td>pH.</td>
<td>4-710</td>
<td>4-700</td>
</tr>
<tr>
<td>CH$_3$COOH (0-1N), CH$_3$COONa (0-1N)</td>
<td>pH.</td>
<td>4-650</td>
<td>4-640</td>
</tr>
<tr>
<td>Potassium acid phthalate (0-05M)</td>
<td>pH.</td>
<td>4-060</td>
<td>4-050</td>
</tr>
<tr>
<td>Potassium acid tartrate (0-03M) (D. I. Hitchcock and A. C. Taylor, 1937)</td>
<td>pH.</td>
<td>---</td>
<td>3-567</td>
</tr>
</tbody>
</table>

* The pH of a saturated solution of pure potassium hydrogen tartrate at 25° C. (0-034M) is 3-57. This value is not significantly affected by moderate dilution, and consequently the pH of a solution saturated at any temperature above 10° C. and then brought to 25° C. for measurement will give a pH within 0-02 unit of a solution saturated at 25° C. No special care is therefore necessary in preparing the saturated solution. The temperature coefficient is +0-0014 pH per degree at 25° C., and may be regarded as negligible for most practical purposes.

### Appendix

**2. pH Range: 0·65–5·20; 18° C.**  
(Walpole, 1914)

50 ml. N-sodium acetate + X ml. N-HCl made up to 250 ml.

<table>
<thead>
<tr>
<th>pH</th>
<th>X (ml.) HCl</th>
<th>pH</th>
<th>X (ml.) HCl</th>
<th>pH</th>
<th>X (ml.) HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·65</td>
<td>100</td>
<td>1·99</td>
<td>52·5</td>
<td>3·79</td>
<td>42·5</td>
</tr>
<tr>
<td>0·75</td>
<td>90</td>
<td>2·32</td>
<td>51·0</td>
<td>3·95</td>
<td>40·0</td>
</tr>
<tr>
<td>0·91</td>
<td>80</td>
<td>2·64</td>
<td>50·0</td>
<td>4·19</td>
<td>35·0</td>
</tr>
<tr>
<td>1·09</td>
<td>70</td>
<td>2·72</td>
<td>49·75</td>
<td>4·39</td>
<td>30·0</td>
</tr>
<tr>
<td>1·24</td>
<td>65</td>
<td>3·09</td>
<td>48·5</td>
<td>4·53</td>
<td>25·0</td>
</tr>
<tr>
<td>1·43</td>
<td>60</td>
<td>3·29</td>
<td>47·5</td>
<td>4·76</td>
<td>20·0</td>
</tr>
<tr>
<td>1·71</td>
<td>55</td>
<td>3·49</td>
<td>46·25</td>
<td>4·92</td>
<td>15·0</td>
</tr>
<tr>
<td>1·85</td>
<td>53·5</td>
<td>3·61</td>
<td>45·0</td>
<td>5·20</td>
<td>10·0</td>
</tr>
</tbody>
</table>

**3. pH range: 3·42–5·89; 18° C** (Walpole, 1914)

10-ml. mixtures of X ml. of 0·2N-acetic acid and Y ml. of 0·2N-sodium acetate.

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>9·5</td>
<td>0·5</td>
<td>3·42</td>
<td>4·0</td>
<td>0·0</td>
<td>4·80</td>
</tr>
<tr>
<td>9·0</td>
<td>1·0</td>
<td>3·72</td>
<td>3·0</td>
<td>1·0</td>
<td>4·99</td>
</tr>
<tr>
<td>8·0</td>
<td>2·0</td>
<td>4·05</td>
<td>2·0</td>
<td>2·0</td>
<td>5·23</td>
</tr>
<tr>
<td>7·0</td>
<td>3·0</td>
<td>4·27</td>
<td>1·5</td>
<td>3·0</td>
<td>5·37</td>
</tr>
<tr>
<td>6·0</td>
<td>4·0</td>
<td>4·45</td>
<td>1·0</td>
<td>4·0</td>
<td>5·57</td>
</tr>
<tr>
<td>5·0</td>
<td>5·0</td>
<td>4·63</td>
<td>0·5</td>
<td>5·0</td>
<td>5·89</td>
</tr>
</tbody>
</table>

**4. pH Range: 2·2–8·0** (McIlvaine, 1921)

20-ml. mixtures of X ml. of 0·2M-Na$_2$HPO$_4$ and Y ml. of 0·1M-citric acid.

<table>
<thead>
<tr>
<th>X (ml.) Na$_2$HPO$_4$</th>
<th>Y (ml.) Citric acid</th>
<th>pH</th>
<th>X (ml.) Na$_2$HPO$_4$</th>
<th>Y (ml.) Citric acid</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·40</td>
<td>19·60</td>
<td>2·2</td>
<td>10·72</td>
<td>9·28</td>
<td>5·2</td>
</tr>
<tr>
<td>1·24</td>
<td>18·76</td>
<td>2·4</td>
<td>11·15</td>
<td>8·85</td>
<td>5·4</td>
</tr>
<tr>
<td>2·18</td>
<td>17·82</td>
<td>2·6</td>
<td>11·60</td>
<td>8·40</td>
<td>5·6</td>
</tr>
<tr>
<td>3·17</td>
<td>16·83</td>
<td>2·8</td>
<td>12·09</td>
<td>7·91</td>
<td>5·8</td>
</tr>
<tr>
<td>4·11</td>
<td>15·89</td>
<td>3·0</td>
<td>12·63</td>
<td>7·37</td>
<td>6·0</td>
</tr>
<tr>
<td>4·04</td>
<td>15·06</td>
<td>3·2</td>
<td>13·22</td>
<td>6·78</td>
<td>6·2</td>
</tr>
<tr>
<td>5·70</td>
<td>14·30</td>
<td>3·4</td>
<td>13·85</td>
<td>6·15</td>
<td>6·4</td>
</tr>
<tr>
<td>4·44</td>
<td>13·56</td>
<td>3·6</td>
<td>14·45</td>
<td>5·45</td>
<td>6·6</td>
</tr>
<tr>
<td>7·10</td>
<td>12·90</td>
<td>3·8</td>
<td>15·45</td>
<td>4·55</td>
<td>6·8</td>
</tr>
<tr>
<td>7·21</td>
<td>12·29</td>
<td>4·0</td>
<td>16·47</td>
<td>4·53</td>
<td>7·0</td>
</tr>
<tr>
<td>8·28</td>
<td>11·72</td>
<td>4·2</td>
<td>17·39</td>
<td>3·52</td>
<td>7·2</td>
</tr>
<tr>
<td>8·82</td>
<td>11·18</td>
<td>4·4</td>
<td>18·17</td>
<td>2·61</td>
<td>7·4</td>
</tr>
<tr>
<td>9·35</td>
<td>10·65</td>
<td>4·6</td>
<td>18·73</td>
<td>1·83</td>
<td>7·6</td>
</tr>
<tr>
<td>9·86</td>
<td>10·14</td>
<td>4·8</td>
<td>19·15</td>
<td>0·85</td>
<td>7·8</td>
</tr>
<tr>
<td>10·30</td>
<td>9·70</td>
<td>5·0</td>
<td>19·45</td>
<td>0·55</td>
<td>8·0</td>
</tr>
</tbody>
</table>
Quantitative Inorganic Analysis

5. pH Range: 5.29-8.04; 15° C. (Sorensen, 1909-12)

10-Ml. mixtures of X ml. M/15-Na₂HPO₄ and Y ml. of M/15-KH₂PO₄.

<table>
<thead>
<tr>
<th>X (ml.) Na₂HPO₄</th>
<th>Y (ml.) KH₂PO₄</th>
<th>pH.</th>
<th>X (ml.) Na₂HPO₄</th>
<th>Y (ml.) KH₂PO₄</th>
<th>pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>9.75</td>
<td>5.29</td>
<td>5.00</td>
<td>5.00</td>
<td>6.81</td>
</tr>
<tr>
<td>0.5</td>
<td>9.5</td>
<td>5.59</td>
<td>6.00</td>
<td>4.00</td>
<td>6.98</td>
</tr>
<tr>
<td>1.0</td>
<td>9.0</td>
<td>5.91</td>
<td>7.00</td>
<td>3.00</td>
<td>7.17</td>
</tr>
<tr>
<td>2.0</td>
<td>8.0</td>
<td>6.24</td>
<td>8.00</td>
<td>2.00</td>
<td>7.88</td>
</tr>
<tr>
<td>3.0</td>
<td>7.0</td>
<td>6.47</td>
<td>9.00</td>
<td>1.00</td>
<td>7.73</td>
</tr>
<tr>
<td>4.0</td>
<td>6.0</td>
<td>6.64</td>
<td>9.50</td>
<td>0.50</td>
<td>8.04</td>
</tr>
</tbody>
</table>

6. pH Ranges: 2.2-3.8, 4.0-6.2, 5.8-8.0, 7.8-10.0; 20° C. (Clark and Lubs, 1916)

(A) pH 2.2-3.8. 50 ml. 0.2M-KH phthalate + P ml. 0.2M-HCl, diluted to 200 ml.
(B) pH 4.0-6.2. 50 ml. 0.2M-KH phthalate + Q ml. 0.2M-NaOH, diluted to 200 ml.
(C) pH 5.8-8.0. 50 ml. 0.2M-KH₂PO₄ + R ml. 0.2M-NaOH, diluted to 200 ml.
(D) pH 7.8-10.0. 50 ml. 0.2M-H₂BO₃ and 0.2M-KCl + S ml. 0.2M-NaOH, diluted to 200 ml.

7. pH Range: 6.80-9.60; 25° C. (Michaelis, 1930)

10-Ml. mixtures of X ml. of 0.1M-sodium diethylbarbiturate and Y ml. of 0.1M-HCl.

<table>
<thead>
<tr>
<th>X (ml.) Na salt.</th>
<th>Y (ml.) HCl</th>
<th>pH.</th>
<th>X (ml.) Na salt.</th>
<th>Y (ml.) HCl</th>
<th>pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.22</td>
<td>4.78</td>
<td>6.80</td>
<td>8.23</td>
<td>1.77</td>
<td>8.40</td>
</tr>
<tr>
<td>5.36</td>
<td>4.64</td>
<td>7.00</td>
<td>8.71</td>
<td>1.29</td>
<td>8.60</td>
</tr>
<tr>
<td>5.54</td>
<td>4.46</td>
<td>7.20</td>
<td>9.08</td>
<td>0.92</td>
<td>8.80</td>
</tr>
<tr>
<td>5.81</td>
<td>4.19</td>
<td>7.40</td>
<td>9.36</td>
<td>0.64</td>
<td>9.00</td>
</tr>
<tr>
<td>6.15</td>
<td>3.85</td>
<td>7.60</td>
<td>9.52</td>
<td>0.48</td>
<td>9.20</td>
</tr>
<tr>
<td>6.52</td>
<td>3.38</td>
<td>7.80</td>
<td>9.74</td>
<td>0.26</td>
<td>9.40</td>
</tr>
<tr>
<td>7.16</td>
<td>2.84</td>
<td>8.00</td>
<td>9.85</td>
<td>0.15</td>
<td>9.60</td>
</tr>
</tbody>
</table>

* That is, a solution containing 12.369 g. of H₂BO₃ and 14.911 g. of KCl per litre.
8. pH Range: 8.45-12.77; 24° C. (Sörrenson-Walburn, 1920)

10-ml. mixtures of X ml. of 0.1M-glycine + 0.1M-NaCl* and Y ml. of 0.1M-NaOH.

<table>
<thead>
<tr>
<th>X (ml.) Glycine-NaCl</th>
<th>Y (ml.) NaOH</th>
<th>pH.</th>
<th>X (ml.) Glycine-NaCl</th>
<th>Y (ml.) NaOH</th>
<th>pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>0.5</td>
<td>8.45</td>
<td>5.0</td>
<td>5.0</td>
<td>11.14</td>
</tr>
<tr>
<td>9.0</td>
<td>1.0</td>
<td>8.79</td>
<td>4.9</td>
<td>5.1</td>
<td>11.39</td>
</tr>
<tr>
<td>8.0</td>
<td>2.0</td>
<td>9.22</td>
<td>4.5</td>
<td>5.5</td>
<td>11.62</td>
</tr>
<tr>
<td>7.0</td>
<td>3.0</td>
<td>9.56</td>
<td>4.0</td>
<td>6.0</td>
<td>12.21</td>
</tr>
<tr>
<td>6.0</td>
<td>4.0</td>
<td>9.98</td>
<td>3.0</td>
<td>7.0</td>
<td>12.43</td>
</tr>
<tr>
<td>5.5</td>
<td>4.5</td>
<td>10.32</td>
<td>2.0</td>
<td>8.0</td>
<td>12.66</td>
</tr>
<tr>
<td>5.1</td>
<td>4.0</td>
<td>10.90</td>
<td>1.0</td>
<td>9.0</td>
<td>12.77</td>
</tr>
</tbody>
</table>

* That is, a solution containing 7.505 g. of glycine + 5.85 g. of NaCl per litre.


X ml. of 0.1M-p-toluenesulphonic acid monohydrate (19.012 g. per litre) and Y ml. of 0.1M-sodium p-toluenesulphonate (19.406 g. per litre), diluted to 100.0 ml.

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.9</td>
<td>1.1</td>
<td>1.40</td>
<td>38.8</td>
<td>13.2</td>
<td>1.90</td>
</tr>
<tr>
<td>37.2</td>
<td>12.8</td>
<td>1.50</td>
<td>40.0</td>
<td>10.0</td>
<td>2.00</td>
</tr>
<tr>
<td>27.4</td>
<td>22.4</td>
<td>1.60</td>
<td>42.4</td>
<td>7.6</td>
<td>2.10</td>
</tr>
<tr>
<td>19.0</td>
<td>31.0</td>
<td>1.70</td>
<td>45.6</td>
<td>4.4</td>
<td>2.20</td>
</tr>
<tr>
<td>10.6</td>
<td>33.4</td>
<td>1.80</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X ml. of 0.01M-p-toluenesulphonic acid monohydrate (1.9012 g. per litre) and Y ml. of 0.01M-sodium p-toluenesulphonate (1.9046 g. per litre), diluted to 100.0 ml.

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0</td>
<td>0.0</td>
<td>2.30</td>
<td>12.4</td>
<td>37.6</td>
<td>2.60</td>
</tr>
<tr>
<td>44.2</td>
<td>5.8</td>
<td>2.40</td>
<td>10.0</td>
<td>40.0</td>
<td>3.00</td>
</tr>
<tr>
<td>35.8</td>
<td>14.2</td>
<td>2.60</td>
<td>8.0</td>
<td>42.0</td>
<td>3.10</td>
</tr>
<tr>
<td>27.6</td>
<td>22.4</td>
<td>2.80</td>
<td>0.2</td>
<td>43.8</td>
<td>3.20</td>
</tr>
<tr>
<td>21.2</td>
<td>28.8</td>
<td>2.70</td>
<td>5.0</td>
<td>45.0</td>
<td>3.30</td>
</tr>
<tr>
<td>18.5</td>
<td>31.5</td>
<td>2.80</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X ml. of 0.01M-furoic acid (1.1203 g. per litre) and Y ml. of 0.01M-sodium furoate (1.3403 g. per litre) diluted to 100.0 ml.

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.3</td>
<td>4.8</td>
<td>2.90</td>
<td>14.8</td>
<td>35.2</td>
<td>3.60</td>
</tr>
<tr>
<td>39.6</td>
<td>10.4</td>
<td>3.00</td>
<td>12.3</td>
<td>37.7</td>
<td>3.70</td>
</tr>
<tr>
<td>34.0</td>
<td>16.0</td>
<td>3.10</td>
<td>10.1</td>
<td>39.9</td>
<td>3.80</td>
</tr>
<tr>
<td>28.4</td>
<td>21.0</td>
<td>3.20</td>
<td>8.4</td>
<td>41.6</td>
<td>3.60</td>
</tr>
<tr>
<td>24.8</td>
<td>25.2</td>
<td>3.30</td>
<td>0.7</td>
<td>43.3</td>
<td>4.00</td>
</tr>
<tr>
<td>21.4</td>
<td>28.6</td>
<td>3.40</td>
<td>5.4</td>
<td>44.6</td>
<td>4.10</td>
</tr>
<tr>
<td>18.0</td>
<td>32.0</td>
<td>3.50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Quantitative Inorganic Analysis

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.7</td>
<td>1.3</td>
<td>3.40</td>
<td>22.0</td>
<td>28.0</td>
<td>4.40</td>
</tr>
<tr>
<td>46.6</td>
<td>3.4</td>
<td>3.60</td>
<td>19.4</td>
<td>30.6</td>
<td>4.50</td>
</tr>
<tr>
<td>44.4</td>
<td>5.6</td>
<td>3.60</td>
<td>16.9</td>
<td>33.1</td>
<td>4.80</td>
</tr>
<tr>
<td>42.2</td>
<td>7.8</td>
<td>3.70</td>
<td>14.4</td>
<td>36.6</td>
<td>4.70</td>
</tr>
<tr>
<td>39.9</td>
<td>10.1</td>
<td>3.80</td>
<td>12.1</td>
<td>37.9</td>
<td>4.80</td>
</tr>
<tr>
<td>37.2</td>
<td>12.6</td>
<td>3.90</td>
<td>10.2</td>
<td>39.8</td>
<td>4.90</td>
</tr>
<tr>
<td>34.4</td>
<td>15.6</td>
<td>4.00</td>
<td>8.6</td>
<td>41.4</td>
<td>5.00</td>
</tr>
<tr>
<td>30.8</td>
<td>19.2</td>
<td>4.10</td>
<td>7.2</td>
<td>42.8</td>
<td>5.10</td>
</tr>
<tr>
<td>28.0</td>
<td>22.0</td>
<td>4.20</td>
<td>5.7</td>
<td>44.3</td>
<td>5.20</td>
</tr>
<tr>
<td>25.1</td>
<td>24.9</td>
<td>4.30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.8</td>
<td>1.2</td>
<td>4.80</td>
<td>21.0</td>
<td>29.0</td>
<td>5.60</td>
</tr>
<tr>
<td>46.9</td>
<td>3.1</td>
<td>4.90</td>
<td>17.6</td>
<td>32.4</td>
<td>5.70</td>
</tr>
<tr>
<td>44.4</td>
<td>5.6</td>
<td>5.00</td>
<td>14.7</td>
<td>35.3</td>
<td>5.80</td>
</tr>
<tr>
<td>40.4</td>
<td>9.8</td>
<td>5.10</td>
<td>12.9</td>
<td>38.0</td>
<td>5.90</td>
</tr>
<tr>
<td>36.2</td>
<td>13.8</td>
<td>5.20</td>
<td>9.9</td>
<td>40.1</td>
<td>6.00</td>
</tr>
<tr>
<td>32.6</td>
<td>17.4</td>
<td>5.30</td>
<td>7.8</td>
<td>42.2</td>
<td>6.10</td>
</tr>
<tr>
<td>28.6</td>
<td>21.4</td>
<td>5.40</td>
<td>5.6</td>
<td>44.4</td>
<td>6.20</td>
</tr>
<tr>
<td>24.7</td>
<td>25.3</td>
<td>5.50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 10. pH Range: 2.6-12.0; 18° C.—Universal Buffer Mixture

A mixture of 6.008 g. of A.R. citric acid, 3.893 g. of A.R. potassium dihydrogen phosphate, 1.769 g. of A.R. boric acid, and 5.266 g. of pure diethylbarbituric acid is dissolved in water and made up to 1 litre. The pH values at 18° C. of mixtures of 100 ml. of this solution with various volumes (X) of 0.2N-sodium hydroxide solution (free from carbonate) are tabulated below.

<table>
<thead>
<tr>
<th>pH</th>
<th>X (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>2.0</td>
<td>9.0</td>
<td>72.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>4.3</td>
<td>38.9</td>
<td>9.2</td>
<td>74.0</td>
<td>9.4</td>
</tr>
<tr>
<td>3.0</td>
<td>6.4</td>
<td>41.2</td>
<td>9.6</td>
<td>77.6</td>
<td>9.8</td>
</tr>
<tr>
<td>3.2</td>
<td>8.3</td>
<td>43.5</td>
<td>9.9</td>
<td>87.6</td>
<td>9.7</td>
</tr>
<tr>
<td>3.4</td>
<td>10.1</td>
<td>46.0</td>
<td>10.0</td>
<td>83.9</td>
<td>10.2</td>
</tr>
<tr>
<td>3.6</td>
<td>11.8</td>
<td>48.3</td>
<td>10.4</td>
<td>82.9</td>
<td>10.5</td>
</tr>
<tr>
<td>3.8</td>
<td>13.7</td>
<td>50.0</td>
<td>10.6</td>
<td>83.9</td>
<td>10.8</td>
</tr>
<tr>
<td>4.0</td>
<td>15.6</td>
<td>52.9</td>
<td>11.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>17.6</td>
<td>55.8</td>
<td>11.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>19.9</td>
<td>58.6</td>
<td>11.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>22.4</td>
<td>61.7</td>
<td>11.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>24.8</td>
<td>63.7</td>
<td>11.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>27.1</td>
<td>65.6</td>
<td>12.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>29.5</td>
<td>67.5</td>
<td>12.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>31.8</td>
<td>69.3</td>
<td>12.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.6</td>
<td>34.2</td>
<td>71.0</td>
<td>12.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Johnson and Lindsey, 1939)
Appendix

A. 11. COMPARISON OF METRIC AND OTHER UNITS

Metric system.—The primary unit of length is the metre, which is the distance between two lines, under standard conditions, engraved on a prototype preserved in the Bureau International des Poids et Mesures, Sèvres, France.

The primary unit of weight is the kilogram, which is the mass of a prototype preserved in the same place.

The primary unit of volume is the litre, and is the volume occupied by one kilogram of pure water at 4° C. under a pressure of 760 mm. of mercury (see, however, Section II, 17).

The millilitre (ml.) is the thousandth part of a litre. One millilitre is nearly, but not absolutely, equal to one cubic centimetre (c.c.):

\[ 1000 \text{ ml.} = 1000.028 \text{ c.c.} \]

The redefinition of the litre has recently been considered (see Chemical and Engineering News, 1949, 27, 2996; Annual Reports on the Progress of Chemistry, 1949, 46, 86) as a cubic decimetre. If this new definition be accepted, the millilitre (ml.) is identical with the cubic centimetre (c.c.)

<table>
<thead>
<tr>
<th>UNITS OF LENGTH</th>
<th>1 millimetre (mm.) = 0.03937 inch.</th>
<th>1 inch (in.) = 25.400 millimetres.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 centimetre (cm.)</td>
<td>0.3937 inch.</td>
<td>1 inch = 25.400 centimetres.</td>
</tr>
<tr>
<td>1 metre (m.)</td>
<td>39.370 inches.</td>
<td>1 foot (ft.) = 304.801 millimetres.</td>
</tr>
<tr>
<td>1 metre</td>
<td>3.2808 feet.</td>
<td>1 foot = 30.480 metre.</td>
</tr>
<tr>
<td>1 kilometre (km.)</td>
<td>1093.61 yards.</td>
<td>1 yard (yd.) = 0.91440 metre.</td>
</tr>
<tr>
<td>1 kilometre</td>
<td>0.62137 mile.</td>
<td>1 mile = 1.60934 metres.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>UNITS OF AREA</th>
<th>1 square mm. = 0.001550 sq. in.</th>
<th>1 square in. = 645.16 sq. mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 square cm.</td>
<td>0.1550 sq. in.</td>
<td>1 square in. = 6.4516 sq. cm.</td>
</tr>
<tr>
<td>1 square metre</td>
<td>1550.0 sq. ins.</td>
<td>1 square ft. = 929.03 sq. cm.</td>
</tr>
<tr>
<td>1 square metre</td>
<td>10.7638 sq. ft.</td>
<td>1 square ft. = 0.9290 sq. m.</td>
</tr>
<tr>
<td>1 square metre</td>
<td>1.1960 sq. yds.</td>
<td>1 square yd. = 0.83613 sq. m.</td>
</tr>
<tr>
<td>1 square km.</td>
<td>0.393610 sq. mile.</td>
<td>1 acre = 0.40469 hectare.</td>
</tr>
<tr>
<td>1 hectare</td>
<td>2.4710 acres.</td>
<td>1 square mile = 2.5900 sq. km.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>UNITS OF VOLUME</th>
<th>1 cubic mm. = 0.00006102 cubic in.</th>
<th>1 cubic in. = 16.387 cubic mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cubic cm. (c.c. or ml.)</td>
<td>0.061024 cubic in.</td>
<td>1 cubic in. = 16.387 ml.</td>
</tr>
<tr>
<td>1 cubic m.</td>
<td>61.024 cubic ins.</td>
<td>1 cubic ft. = 0.062317 cubic m.</td>
</tr>
<tr>
<td>1 cubic m.</td>
<td>35.3144 cubic ft.</td>
<td>1 cubic ft. = 28.317 litres.</td>
</tr>
<tr>
<td>1 cubic m.</td>
<td>1.0079 cubic yds.</td>
<td>1 cubic yd. = 0.7645 cubic m.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MEASURES OF LIQUID CAPACITY</th>
<th>Imperial or British Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 gill</td>
<td>= 142.06 ml.</td>
</tr>
<tr>
<td>1 pint</td>
<td>= 4 gills</td>
</tr>
<tr>
<td>1 quart</td>
<td>= 2 pints</td>
</tr>
<tr>
<td>1 gallon</td>
<td>= 4 quarts</td>
</tr>
<tr>
<td></td>
<td>= 4.5460 litres.</td>
</tr>
</tbody>
</table>
Quantitative Inorganic Analysis

Apothecaries' Units (British)

1 minim = 0.059192 ml.
1 fluid scruple = 20 minims = 1.1838 ml.
1 fluid drachm = 3 scruples = 3.5515 ml.
1 fluid ounce = 8 fluid drachms = 28.412 ml.
1 pint = 20 fluid ounces = 568.25 ml.
1 gallon = 8 pints = 4.54596 litres.

1 litre = 1689.41 minims.
= 281.87 fluid drachms.
= 35.196 fluid ounces.

U.S. Units

1 gill = 118.292 ml.  1 litre = 8.4537 gills.
1 pint = 4 gills = 473.167 ml.  = 2.1134 pints.
1 quart = 2 pints = 0.94633 litre.  = 0.26418 gallon.
1 gallon = 4 quarts = 3.78533 litres.

Apothecaries' Units (U.S.)

1 minim = 0.06161 ml.
1 fluid drachm = 60 minims = 3.6061 ml.
1 fluid ounce = 8 fluid drachms = 29.5729 ml.
1 pint = 16 fluid ounces = 473.167 ml.
1 gallon = 8 pints = 3.78533 litres.

UNITS OF MASS

Avoirdupois Weight

1 grain = 64.799 mg.
1 dram = 27.3437 grains = 1.77185 g.
1 ounce = 16 drams = 437.5 grains = 28.34904 g.
1 pound = 16 ounces = 7000 grains = 453.59237 g.
1 stone = 14 pounds = 6350.3 kg.
1 quarter = 28 pounds = 12700.59 kg.
1 hundredweight = 112 pounds = 5080.238 kg.
1 gram = 15.4325 grains.
1 decagram = 10 grams = 564.383 drams.
1 hectogram = 100 grams = 3527.39 ounces.
1 kilogram = 1000 grams = 2204.621 pounds.
1 myriagram = 10 kilograms = 2204621 pounds.
1 quintal = 100 kilograms = 198641 hundredweights.
1 millier = 1 metric ton = 1000 kilograms = 0.9842059 ton.

Troy Weight

1 grain = 64.799 mg.
1 carat = 4 grains = 0.25920 g.
1 pennyweight (dwt.) = 6 carats = 24 grains = 1.29598 g.
1 ounce = 20 pennyweights = 480 grains = 31.1035 g.
1 pound = 12 ounces = 5760 grains = 373.2418 g.

1 gram = 15.4323 grains.
= 3.558 carats.
= 0.643 pennyweights.
= 0.03215 ounce.
Appendix

Apothecaries' Weight

1 grain = 64.799 mg.
1 scruple = 20 grains = 1.29598 g.
1 dram = 3 scruples = 3.88794 g.
1 ounce = 8 drachms = 480 grains = 31.035 g.
1 pound = 12 ounces = 772.2418 g.

1 gram = 15.4323 grains.
= 0.7716 scruples.
= 0.2572 drachms.
= 0.03215 ounce.

A.12. DECIMALS OF AN INCH, I.S.W.G., AND MILLIMETRES

<table>
<thead>
<tr>
<th>Decimals of an Inch</th>
<th>I.S.W.G.</th>
<th>Millimetres</th>
<th>Decimals of an Inch</th>
<th>I.S.W.G.</th>
<th>Millimetres</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.000</td>
<td>10.160</td>
<td>0.040</td>
<td>0.040</td>
<td>1.016</td>
</tr>
<tr>
<td>0.001</td>
<td>0.001</td>
<td>10.080</td>
<td>0.039</td>
<td>0.039</td>
<td>0.914</td>
</tr>
<tr>
<td>0.002</td>
<td>0.002</td>
<td>10.000</td>
<td>0.038</td>
<td>0.038</td>
<td>0.813</td>
</tr>
<tr>
<td>0.003</td>
<td>0.003</td>
<td>9.920</td>
<td>0.037</td>
<td>0.037</td>
<td>0.711</td>
</tr>
<tr>
<td>0.004</td>
<td>0.004</td>
<td>9.840</td>
<td>0.036</td>
<td>0.036</td>
<td>0.610</td>
</tr>
<tr>
<td>0.005</td>
<td>0.005</td>
<td>9.760</td>
<td>0.035</td>
<td>0.035</td>
<td>0.509</td>
</tr>
<tr>
<td>0.006</td>
<td>0.006</td>
<td>9.680</td>
<td>0.034</td>
<td>0.034</td>
<td>0.408</td>
</tr>
<tr>
<td>0.007</td>
<td>0.007</td>
<td>9.600</td>
<td>0.033</td>
<td>0.033</td>
<td>0.307</td>
</tr>
<tr>
<td>0.008</td>
<td>0.008</td>
<td>9.520</td>
<td>0.032</td>
<td>0.032</td>
<td>0.206</td>
</tr>
<tr>
<td>0.009</td>
<td>0.009</td>
<td>9.440</td>
<td>0.031</td>
<td>0.031</td>
<td>0.105</td>
</tr>
<tr>
<td>0.010</td>
<td>0.010</td>
<td>9.360</td>
<td>0.030</td>
<td>0.030</td>
<td>0.004</td>
</tr>
<tr>
<td>0.011</td>
<td>0.011</td>
<td>9.280</td>
<td>0.029</td>
<td>0.029</td>
<td>0.903</td>
</tr>
<tr>
<td>0.012</td>
<td>0.012</td>
<td>9.200</td>
<td>0.028</td>
<td>0.028</td>
<td>0.801</td>
</tr>
<tr>
<td>0.013</td>
<td>0.013</td>
<td>9.120</td>
<td>0.027</td>
<td>0.027</td>
<td>0.700</td>
</tr>
<tr>
<td>0.014</td>
<td>0.014</td>
<td>9.040</td>
<td>0.026</td>
<td>0.026</td>
<td>0.600</td>
</tr>
<tr>
<td>0.015</td>
<td>0.015</td>
<td>8.960</td>
<td>0.025</td>
<td>0.025</td>
<td>0.500</td>
</tr>
<tr>
<td>0.016</td>
<td>0.016</td>
<td>8.880</td>
<td>0.024</td>
<td>0.024</td>
<td>0.400</td>
</tr>
<tr>
<td>0.017</td>
<td>0.017</td>
<td>8.800</td>
<td>0.023</td>
<td>0.023</td>
<td>0.300</td>
</tr>
<tr>
<td>0.018</td>
<td>0.018</td>
<td>8.720</td>
<td>0.022</td>
<td>0.022</td>
<td>0.200</td>
</tr>
<tr>
<td>0.019</td>
<td>0.019</td>
<td>8.640</td>
<td>0.021</td>
<td>0.021</td>
<td>0.100</td>
</tr>
<tr>
<td>0.020</td>
<td>0.020</td>
<td>8.560</td>
<td>0.020</td>
<td>0.020</td>
<td>0.000</td>
</tr>
</tbody>
</table>

A.13. THE GREEK ALPHABET

<table>
<thead>
<tr>
<th>Greek Letter</th>
<th>Greek Name</th>
<th>English Equivalent</th>
<th>Greek Letter</th>
<th>Greek Name</th>
<th>English Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Alpha</td>
<td>a</td>
<td>Ν</td>
<td>Nu</td>
<td>n</td>
</tr>
<tr>
<td>β</td>
<td>Beta</td>
<td>b</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>γ</td>
<td>Gamma</td>
<td>g</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>δ</td>
<td>Delta</td>
<td>d</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>ε</td>
<td>Epsilon</td>
<td>e</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>ζ</td>
<td>Zeta</td>
<td>z</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>η</td>
<td>Eta</td>
<td>η</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>θ</td>
<td>Theta</td>
<td>θ</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>ι</td>
<td>Iota</td>
<td>ι</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>κ</td>
<td>Kappa</td>
<td>k</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>λ</td>
<td>Lambda</td>
<td>l</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>μ</td>
<td>Mu</td>
<td>μ</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
</tr>
<tr>
<td>ν</td>
<td>Nu</td>
<td>ν</td>
<td>Nu</td>
<td>n</td>
<td>n</td>
</tr>
<tr>
<td>ξ</td>
<td>Xi</td>
<td>ξ</td>
<td>Xi</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>ο</td>
<td>Omicron</td>
<td>ο</td>
<td>Omicron</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>π</td>
<td>Pi</td>
<td>π</td>
<td>Pi</td>
<td>p</td>
<td>p</td>
</tr>
<tr>
<td>ρ</td>
<td>Rho</td>
<td>ρ</td>
<td>Rho</td>
<td>p</td>
<td>p</td>
</tr>
<tr>
<td>σ</td>
<td>Sigma</td>
<td>σ</td>
<td>Sigma</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>τ</td>
<td>Tau</td>
<td>τ</td>
<td>Tau</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td>ϒ</td>
<td>Upsilon</td>
<td>ϒ</td>
<td>Upsilon</td>
<td>u</td>
<td>u</td>
</tr>
<tr>
<td>ϕ</td>
<td>Phi</td>
<td>ϕ</td>
<td>Phi</td>
<td>ph</td>
<td>ph</td>
</tr>
<tr>
<td>χ</td>
<td>Chi</td>
<td>χ</td>
<td>Chi</td>
<td>ch</td>
<td>ch</td>
</tr>
<tr>
<td>ψ</td>
<td>Psi</td>
<td>ψ</td>
<td>Psi</td>
<td>ps</td>
<td>ps</td>
</tr>
<tr>
<td>ο</td>
<td>Omega</td>
<td>Ω</td>
<td>Omega</td>
<td>Ω</td>
<td>Ω</td>
</tr>
</tbody>
</table>
A. 14. SUGGESTED SCHEME OF STUDY FOR THE GENERAL CERTIFICATE OF EDUCATION (ADVANCED LEVEL),* ORDINARY NATIONAL CERTIFICATE EXAMINATIONS IN CHEMISTRY, AND EXAMINATIONS OF SIMILAR CHARACTER

The following scheme is suggested as suitable for a course of training in quantitative inorganic analysis for beginners. It covers the requirements of the General Certificate of Education Examination (Advanced Level) of British Universities, the ordinary national certificate in chemistry, and examinations of similar scope. Experiments marked with an asterisk are optional.

**Acidimetry and Alkalimetry**

(i) Preparation of approx. 0·1N-hydrochloric acid (Section III, 4) and standardisation with (a) anhydrous sodium carbonate (method of Note 1 in Section III, 4A) or (b) borax (method of Note 1 in Section III, 4B).

(ii) Preparation of approx. 0·1N-sodium hydroxide solution (Section III, 5; Procedure A) and standardisation with (a) ca. 0·1N-hydrochloric acid (Section III, 6; Procedure A), (b) potassium hydrogen phthalate (Section III, 6; Procedure B), or (c) A.R. succinic acid.

(iii) Determination of Na$_2$CO$_3$ in washing soda with standard hydrochloric acid (Section III, 9).

(iv) Determination of strength of glacial acetic acid with standard sodium hydroxide solution (Section III, 10).

(v) *Determination of H$_2$SO$_4$ in the concentrated acid with standard sodium hydroxide solution (Section III, 11).

(vi) Analysis of commercial caustic soda (mixture of hydroxide and carbonate) (Section III, 14; Procedure B).

(vii) Determination of Na$_2$B$_4$O$_7$ in borax (Section III, 17; titration with standard acid and indicator only).

(viii) Determination of NH$_3$ in ammonium chloride (Section III, 18; indirect method).

**Determinations with Potassium Permanganate Solution**

(i) Preparation of 0·1N-potassium permanganate (Section III, 47).

(ii) Standardisation of the potassium permanganate solution: (a) with arsenious oxide (Section III, 48A; Note 1), (b) with sodium oxalate (Section III, 48B; Note 1), or (c) with anhydrous potassium ferrocyanide (Section III, 48, Procedure D).

(iii) Determination of iron in crystallised ferrous sulphate (Section III, 50).

(iv) Determination of iron in ferric ammonium sulphate (Section III, 52; reduction with stannous chloride as in Section III, 51A).

(v) *Determination of total iron in an iron ore (Section III, 53; reduction with stannous chloride as in Section III, 51A).

(vi) Determination of H$_2$O$_2$ in the commercial solution (Section III, 55).

(vii) Determination of calcium in calcium carbonate (Section III, 54).

(viii) Determination of MnO$_2$ in pyrolusite (Section III, 57; Procedure B).

(ix) *Determination of KNO$_3$ in commercial potassium nitrite (Section III, 58).

**Determinations with Potassium Dichromate Solution**

(i) Preparation of 0·1N-potassium dichromate (Section III, 64).

(ii) Check standardisation of potassium dichromate solution with pure iron (Section III, 65).

* This examination in chemistry now largely supersedes the intermediate science and higher school examinations in Great Britain.
Appendix

(iii) Determination of iron in crystallised ferrous sulphate or ferrous ammonium sulphate (Section III, 66); sodium diphenylamine sulphonate or N-phenylanthranilic acid as indicator.
(iv) Determination of iron in ferric ammonium sulphate (Section III, 67).
(v) *Determination of total iron in an iron ore (Section III, 68).
(vi) *Determination of chromium in chrome alum (Section III, 70).

Iodimetry and Iodometry

(i) Preparation of approx. 0.1N-sodium thiosulphate solution (Section III, 101).
(ii) Standardisation of the thiosulphate solution with: (a) standard potassium iodate solution (Section III, 102A; Note 1), (b) standard potassium dichromate solution (Section III, 102D).
(iii) Preparation of approx. 0.1N-iodine solution (Section III, 103; Method A).
(iv) Standardisation of the iodine solution with: (a) pure arsenious oxide (Section III, 104A), (b) standard sodium thiosulphate solution (Section III, 104B).
(v) Determination of copper in crystallised copper sulphate (Section III, 105).
(vi) Determination of MnO₂ in pyrolusite (Section III, 107).
(vii) Determination of H₂O₂ in the commercial solution (Section III, 110).
(viii) Determination of available chlorine in bleaching powder: (a) iodometric method (Section III, 111; Procedure A), (b) arsenite method (Section III, 111; Procedure B).
(ix) Determination of antimony in tartar emetic (Section III, 113).
(x) *Determination of tin in crystallised stannous chloride (Section III, 118; Procedure A).
(xi) *Determination of purity of crystallised sodium sulphite (Section III, 119).
(xii) *Determination of H₂S in aqueous solution (Section III, 119).

Precipitation Reactions

Use of Standard Solutions of Silver Nitrate and of Ammonium Thiocyanate

(i) Preparation of approx. 0.1N-silver nitrate solution (Section III, 22; Procedure B).
(ii) Standardisation of the silver nitrate solution with standard sodium chloride solution: (a) using potassium chromate as indicator—Mohr’s method (Section III, 23A), (b) using fluorescein as indicator—Fajan’s method (Section III, 23B).
(iii) *Analysis of a mixture of potassium chloride and bromide (Section III, 30).
(iv) Preparation of approx. 0.1N-sodium thiosulphate solution (Section III, 31).
(v) Standardisation of the ammonium thiocyanate solution with standard silver nitrate solution by Volhard’s method (Section III, 31).
(vi) *Determination of silver in a silver alloy (Section III, 32).
(vii) Determination of the HCl content of concentrated hydrochloric acid (Section III, 33).
(viii) *Determination of KCN in commercial potassium cyanide (Section III, 41; Procedure A).

Simple Gravimetric Analysis

(i) *Determination of water of crystallisation in crystallised barium chloride (Section IV, 4).
(ii) *Determination of chlorine in sodium chloride (Section IV, 5).
Quantitative Inorganic Analysis

(iii) *Determination of sulphate in potassium sulphate (Section IV, 6; filter-paper method).

(iv) *Determination of iron in ferrous ammonium sulphate (Section IV, 7).  

A. 15. SUGGESTED SCHEME OF STUDY FOR B.Sc. SPECIAL CHEMISTRY, HONOURS B.Sc. CHEMISTRY, ASSOCIATESHIP OF THE ROYAL INSTITUTE OF CHEMISTRY, AND EXAMINATIONS OF SIMILAR SCOPE

The scheme given below is proposed as a basis for a course in quantitative analysis for advanced courses in chemistry. The experiments marked with an asterisk are of more difficult character; they are suitable for A.R.I.C. students and may be omitted, if desired, by B.Sc. honours students. It is not expected that any one student will be able to carry out all the determinations listed below, but a sufficient number is given to allow a choice at the discretion of the teacher. It need hardly be stated that many teachers will prefer to adopt their own courses, and it is believed that details of most of the necessary determinations will be found in the book.

VOLUMETRIC ANALYSIS

Acidimetry and Alkalimetry

(i) Calibration of weights (Section II, 8).

(ii) Calibration of volumetric apparatus:

(a) volumetric flasks, 250-ml., 500-ml., 1000-ml. (Section II, 20);
(b) pipettes, 10-ml., 25-ml., 50-ml. (Section II, 21);
(c) burette (Section II, 22).

(iii) Preparation of 0·1N-hydrochloric acid (Section III, 3 or III, 4) Standardisation against:

(a) borax (Section III, 4B);
(b) anhydrous sodium carbonate (Section III, 4A).

(iv) Preparation of 0·1N-sodium hydroxide (Section III, 5; Procedure A). Standardisation with:

(a) 0·1N-hydrochloric acid (Section III, 6; Procedure A);
(b) A.R. potassium hydrogen phthalate (Section III, 6; Procedure B).

(v) Determination of strength of glacial acetic acid (Section III, 10).

(vi) Determination of NH₃ in an ammonium salt (Section III, 18; direct method) or of NaNO₃ in Chile saltpetre (Section III, 19).

(vii) Determination of nitrogen by Kjeldahl's method (Section III, 20).

(viii) Determination of nickel with dicyandiamidine sulphate (Section IV, 32D).

Precipitation and Complex-formation Reactions

(i) Preparation and standardisation of 0·1N (or of 0·05N) silver nitrate (Section III, 22 and Section III, 23A and B).

(ii) Determination of chlorine in A.R. barium chloride dihydrate (Section III, 24).

(iii) Determination of bromine in A.R. potassium bromide (Section III, 25; eosin indicator).

(iv) Determination of iodine in A.R. potassium iodide (Section III, 26; di-iododimethylfluorescein indicator).

(v) Determination of chloride and iodide in admixture (Section III, 29A).
Appendix

(vi) Preparation and standardisation of 0·1N-ammonium thiocyanate (Section III, 31).
(vii) Determination of bromine in A.R. potassium bromide (Section III, 34; Volhard's method).
(viii) Determination of chlorate in A.R. potassium chlorate.

Note. Reduce the chlorate with ferrous sulphate solution, Section IV, 58, add an excess (measured volume) of 0·1N-silver nitrate, and coagulate the silver chloride by warming and stirring. Cool, filter, and titrate the filtrate and washings with standard 0·1N-ammonium thiocyanate using ferric alum as indicator, and thus determine the excess of 0·1N-silver nitrate.

Oxidations with Potassium Permanganate

(i) Preparation of 0·1N-potassium permanganate and standardisation with:
(a) arsenious oxide (Section III, 48, Procedure A);
(b) sodium oxalate (Section III, 48, Procedure B);
(c) anhydrous potassium ferrocyanide (Section III, 48, Procedure D).
(ii) Determination of the total iron in an ore (Section III, 53; reduction with:
(a) stannous chloride;
(b) the Jones reductor (Section III, 51).
(iii) Determination of manganese in steel by the bismuthate method (Section III, 60).
(iv) Determination of calcium in A.R. calcium carbonate (Section III, 155; urea hydrolysis method).

Oxidations with Potassium Dichromate

(i) Preparation of 0·1N-potassium dichromate (Section III, 64).
(ii) Determination of ferrous and ferric iron in an iron ore (Section III, 69).
(iii) Determination of chromium in chromite (Section III, 71).

Oxidations with Ceric Sulphate

(i) Preparation of 0·1N-ceric sulphate (Section III, 74, Method A).
(ii) Standardisation with:
(a) arsenious oxide (Section III, 75, Method A);
(b) anhydrous potassium ferrocyanide (Section III, 75, Method D).
(iii) Determination of iron in an ore (Section III, 77; stannous chloride reduction).

IODIMETRY AND Iodomentry

Determinations with Sodium Thiosulphate

(i) Preparation of 0·1N-sodium thiosulphate (Section III, 101) and standardisation with:
(a) potassium iodate (Section III, 102A);
(b) pure copper (Section III, 102D).
(ii) Determination of copper in an ore (Section III, 108).
(iii) Determination of manganese dioxide in pyrolusite (Section III, 107).
(iv) Preparation of 0·1N-iodine (Section III, 103) and standardisation with:
(a) arsenious oxide (Section III, 104A);
(b) 0·1N-sodium thiosulphate (Section III, 104B);
(c) anhydrous sodium thiosulphate (Section III, 104C).
(v) Determination of antimony in tartar emetic (Section III, 113).
(vi) *Determination of antimony and tin in type metal (Section III, 117).
Quantitative Inorganic Analysis

Oxidations with Potassium Iodate

(i) Preparation of 0.1N (0.025M) potassium iodate (Section III, 123).
(ii) Determination of iodine in potassium iodide (Section III, 124).
(iii) Determination of arsenic in commercial arsenious oxide (Section III, 125).
(iv) Determination of copper in copper sulphate pentahydrate (Section III, 126).
(v) Determination of mercury in mercuric chloride (Section III, 127).
(vi) *Determination of tin in hydrated stannous chloride (Section III, 128).
(vii) *Determination of the purity of hydrazine sulphate (Section III, 131).
(viii) Standardisation of a solution of a strong acid (Section III, 99).

Oxidations with Potassium Bromate

(i) Preparation of 0.1N-potassium bromate (Section III, 136).
(ii) Determination of antimony in tartar emetic (Section III, 137; use of internal indicators).
(iii) Determination of aluminium in potash alum via oxinate (Section III, 138).

GRAVIMETRIC ANALYSIS

(i) Determination of chlorido in potassium chloride as AgCl (Section IV, 5).
(ii) Determination of sulphate in potassium sulphate as BaSO_4 (Section IV, 6, (i), filter-paper method, and also precipitation in the presence of agar-agar).
(iii) *Determination of sulphur in iron pyrites (Section IV, 7; Method B).
(iv) Determination of iron in ferrous ammonium sulphate as Fe_3O_4 (Section IV, 8; use of silica crucible and of Main-Smith crucible, Section II, 36).
(v) *Determination of aluminium in potash alum as Al_2O_3 (Section IV, 29C; basic benzoate method, and also as the oxinate, Section IV, 29D).
(vi) Determination of calcium in calcium carbonate as CaCO_3 via CaC_2O_4 (Section IV, 10).
(vii) Determination of magnesium in magnesium sulphate heptahydrate as MgNH_4PO_4·6H_2O and as Mg_2P_2O_7 (Section IV, 11).
(viii) Determination of nickel in nickel ammonium sulphate and in nickel steel as the dimethylglyoxime complex (Section IV, 12).
(ix) Determination of lead in lead nitrate as PbCrO_4 (Section IV, 14B).
(x) *Determination of mercury in mercuric chloride as Hg[2H(CNS)_4] (Section IV, 16B).
(xi) Determination of copper in copper sulphate pentahydrate as Cu_2(CNS)_3·4H_2O (Section IV, 19A).
(xii) *Determination of iron in iron alum with cupferron (Section IV, 31B).
(xiii) *Determination of cobalt with α-nitroso-β-naphthol (Section IV, 32A) or as cobalt anthranilate (Section IV, 32B).
(xiv) Determination of zinc in zinc sulphate heptahydrate as ZnNH_4PO_4 (Section IV, 34A).
(xv) Determination of manganese in potassium permanganate as Mn_2P_2O_7 (Section IV, 35).
(xvi) *Determination of potassium in potassium chloride as K_2Na(OC(ONO_2)_3)·4H_2O (Section IV, 49D, Procedure B).
(xvii) *Determination of silica in a soluble silicate and in an insoluble silicate (Section IV, 70).
(xviii) Determination of carbonate in calcium carbonate or in limestone (Section IV, 76, direct method).
Appendix

Electrolytic Determinations

(i) Determination of copper in copper sulphate pentahydrate (Section IV, 78).
(ii) Determination of lead in lead nitrate (Section IV, 79).
(iii) Determination of nickel in nickel steel (Section IV, 81).
(iv) *Determination of zinc in zinc oxide (Section IV, 84).
(v) *Separation of copper and nickel (Section IV, 86).
(vi) Determination of copper in bronze, using controlled potential of the cathode (Section IV, 89).

Simple Gravimetric Separations

(i) Iron and aluminium (Fe as Fe$_2$O$_3$, Al as Al$_2$O$_3$; Section IV, 90A).
(ii) Nickel and zinc (Ni as the dimethylglyoxime complex, Zn as ZnNH$_2$PO$_4$; Section IV, 90D).
(iii) *Calcium and magnesium (Ca as CaMoO$_4$, Mg as MgNH$_2$PO$_4$,6H$_2$O; Section IV, 90E).
(iv) *Calcium and strontium (Section IV, 90G).
(v) *Sodium and potassium (K as KCIO$_4$, Na by difference; Section IV, 901).

Analysis of Complex Materials

(i) Brass (Sn as SnO$_2$; Cu as Cu$_2$(CNS)$_2$, Pb as PbSO$_4$, Zn as ZnNH$_2$PO$_4$; Section IV, 91).
(ii) Solder (Sn as SnO$_2$, Pb as PbSO$_4$; Section IV, 94).
(iii) Silver coinage alloy (Ag as AgCl, Cu as Cu$_2$(CNS)$_2$, Ni with dimethylglyoxime, Zn as ZnNH$_2$PO$_4$; Section IV, 95).
(iv) *An aluminium alloy (Section IV, 97).
(v) Dolomite (insoluble matter plus silica, combined oxides (Fe$_2$O$_3$ + Al$_2$O$_3$), Ca as CaCO$_3$, Mg as MgNH$_2$PO$_4$,6H$_2$O, CO$_2$ by direct method; Section IV, 98).
(vi) *Felspar (Section IV, 99).
(vii) *Portland cement (Section IV, 100).

COLORIMETRIC ANALYSIS

(i) Determination of ammonia with Nessler's reagent (Section V, 11).
(ii) Determination of iron (Section V, 11; thiocyanate or o-phenanthroline method).
(iii) Determination of manganese in steel (Section V, 14).
(iv) *Determination of chromium in steel (Section V, 17).
(v) *Determination of nickel in steel (Section V, 20).
(vi) Determination of lead in commercial tartaric acid (Section V, 25).
(vii) *Determination of sulphate (Section V, 30).

POTENTIOMETRIC TITRATION METHODS

(i) Titration of 0·1N-acetic acid with 0·1N-sodium hydroxide (Section VI, 7).
(ii) Titration of an iodide solution with 0·1N-potassium permanganate (Section VI, 7).
(iii) Titration of a chloride solution with 0·1N-silver nitrate (Section VI, 7).
(iv) Titration of 0·1N-sodium thiosulphate with 0·1N-iodine (Section VI, 7; dead stop end point).
(v) Standardisation of sodium thiosulphate solution with 0·1N-potassium dichromate (Section VI, 8).
(vi) Determination of copper (Section VI, 10).
(vii) Determination of manganese (Section VI, 12).
(viii) Determination of cobalt (Section VI, 13).
CONDUCTOMETRIC TITRATION METHODS

(i) Titration of 0·01N-hydrochloric acid with 0·1N-sodium hydroxide (Section VII, 4).
(ii) Titration of 0·01N-sulphuric acid with 0·1N-ammonium hydroxide (Section VII, 4).
(iii) Titration of 0·01N-acetic acid with 0·1N-sodium hydroxide (Section VII, 4).
(iv) Titration of 0·01N-acetic acid with 0·1N-ammonium hydroxide (Section VII, 4).
(v) Titration of a mixture of a strong acid and a weaker acid with a strong base (Section VII, 4).
(vi) Titration of 0·01N-silver nitrate with N-potassium chloride (Section VII, 4).

POLAROGRAPHY

(i) Determination of the half-wave potential of the cadmium ion in N-potassium chloride solution (Section VIII, 9).
(ii) Determination of the half-wave potentials of the zinc and manganese ions in N-potassium chloride solution (Section VIII, 10).
(iii) Determination of cadmium in solution (Section VIII, 11).
(iv) Determination of magnesium with 8-hydroxyquinoline (Section VIII, 12).

AMPEROMETRIC TITRATIONS

(i) Determination of lead with standard potassium dichromate solution (Section IX, 3).
(ii) Determination of sulphate with standard lead nitrate solution (Section IX, 4).
(iii) Determination of nickel with dimethylglyoxime (Section IX, 5).

GAS ANALYSIS

(i) *Determination of oxygen in the air (Section X, 9).
(ii) Analysis of coal gas with the Bunte burette (Section X, 6B).
(iii) *Analysis of coal gas with the Orsat apparatus (Section X, 6C).
(iv) Analysis of coal gas with the Ambler apparatus (Section X, 6D).
(v) Determination of a nitrate with the Lunge nitrometer (Section X, 11).
(vi) *Determination of hydrogen peroxide (Section X, 12).
(vii) *Evaluation of pyrolusite (Section X, 13).
(viii) Evaluation of zinc dust (Section X, 15).
(ix) Determination of ammonia in an ammonium salt (Section X, 16).
### Appendix

A. 16. SATURATED SOLUTIONS OF SOME REAGENTS AT 20°C.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Formula</th>
<th>Specific Gravity</th>
<th>Molarity</th>
<th>Quantities Required for 1 Litre of Saturated Solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Grams of Reagent.</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>NH₄Cl</td>
<td>1.075</td>
<td>5.44</td>
<td>291</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>NH₄NO₃</td>
<td>1.312</td>
<td>10.80</td>
<td>863</td>
</tr>
<tr>
<td>Ammonium oxalate</td>
<td>(NH₄)₂C₂O₄·H₂O</td>
<td>1.030</td>
<td>0.295</td>
<td>48</td>
</tr>
<tr>
<td>Ammonium sulphate</td>
<td>(NH₄)₂SO₄</td>
<td>1.243</td>
<td>4.06</td>
<td>535</td>
</tr>
<tr>
<td>Barium chloride</td>
<td>BaCl₂·2H₂O</td>
<td>1.290</td>
<td>1.63</td>
<td>398</td>
</tr>
<tr>
<td>Barium hydroxide</td>
<td>Ba(OH)₂</td>
<td>1.037</td>
<td>0.228</td>
<td>39</td>
</tr>
<tr>
<td>Barium hydroxide</td>
<td>Ba(OH)₂·8H₂O</td>
<td>1.037</td>
<td>0.228</td>
<td>72</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>Ca(OH)₂</td>
<td>1.000</td>
<td>0.222</td>
<td>1.6</td>
</tr>
<tr>
<td>Mercuric chloride</td>
<td>HgCl₂</td>
<td>1.050</td>
<td>0.238</td>
<td>64</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>1.174</td>
<td>4.00</td>
<td>288</td>
</tr>
<tr>
<td>Potassium chromate</td>
<td>K₂CrO₄</td>
<td>1.396</td>
<td>3.00</td>
<td>583</td>
</tr>
<tr>
<td>Potassium dichromate</td>
<td>K₂Cr₂O₇</td>
<td>1.077</td>
<td>0.39</td>
<td>115</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>KOH</td>
<td>1.540</td>
<td>14.50</td>
<td>813</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>1.178</td>
<td>1.97</td>
<td>209</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃·10H₂O</td>
<td>1.178</td>
<td>1.97</td>
<td>563</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>1.197</td>
<td>5.40</td>
<td>316</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>1.539</td>
<td>20.07</td>
<td>803</td>
</tr>
</tbody>
</table>
### FOUR-FIGURE LOGARITHMS

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0000</td>
<td>0043</td>
<td>0086</td>
<td>0128</td>
<td>0170</td>
<td>0212</td>
<td>0253</td>
<td>0294</td>
<td>0334</td>
<td>0374</td>
</tr>
<tr>
<td>11</td>
<td>0044</td>
<td>0085</td>
<td>0128</td>
<td>0170</td>
<td>0212</td>
<td>0253</td>
<td>0294</td>
<td>0334</td>
<td>0374</td>
<td>0414</td>
</tr>
<tr>
<td>12</td>
<td>0086</td>
<td>0128</td>
<td>0170</td>
<td>0212</td>
<td>0253</td>
<td>0294</td>
<td>0334</td>
<td>0374</td>
<td>0414</td>
<td>0455</td>
</tr>
<tr>
<td>13</td>
<td>0128</td>
<td>0170</td>
<td>0212</td>
<td>0253</td>
<td>0294</td>
<td>0334</td>
<td>0374</td>
<td>0414</td>
<td>0455</td>
<td>0496</td>
</tr>
<tr>
<td>14</td>
<td>0170</td>
<td>0212</td>
<td>0253</td>
<td>0294</td>
<td>0334</td>
<td>0374</td>
<td>0414</td>
<td>0455</td>
<td>0496</td>
<td>0536</td>
</tr>
<tr>
<td>15</td>
<td>0212</td>
<td>0253</td>
<td>0294</td>
<td>0334</td>
<td>0374</td>
<td>0414</td>
<td>0455</td>
<td>0496</td>
<td>0536</td>
<td>0577</td>
</tr>
<tr>
<td>16</td>
<td>0253</td>
<td>0294</td>
<td>0334</td>
<td>0374</td>
<td>0414</td>
<td>0455</td>
<td>0496</td>
<td>0536</td>
<td>0577</td>
<td>0618</td>
</tr>
<tr>
<td>17</td>
<td>0294</td>
<td>0334</td>
<td>0374</td>
<td>0414</td>
<td>0455</td>
<td>0496</td>
<td>0536</td>
<td>0577</td>
<td>0618</td>
<td>0659</td>
</tr>
<tr>
<td>18</td>
<td>0334</td>
<td>0374</td>
<td>0414</td>
<td>0455</td>
<td>0496</td>
<td>0536</td>
<td>0577</td>
<td>0618</td>
<td>0659</td>
<td>0700</td>
</tr>
<tr>
<td>19</td>
<td>0374</td>
<td>0414</td>
<td>0455</td>
<td>0496</td>
<td>0536</td>
<td>0577</td>
<td>0618</td>
<td>0659</td>
<td>0700</td>
<td>0741</td>
</tr>
<tr>
<td>20</td>
<td>0414</td>
<td>0455</td>
<td>0496</td>
<td>0536</td>
<td>0577</td>
<td>0618</td>
<td>0659</td>
<td>0700</td>
<td>0741</td>
<td>0782</td>
</tr>
<tr>
<td>21</td>
<td>0455</td>
<td>0496</td>
<td>0536</td>
<td>0577</td>
<td>0618</td>
<td>0659</td>
<td>0700</td>
<td>0741</td>
<td>0782</td>
<td>0823</td>
</tr>
<tr>
<td>22</td>
<td>0496</td>
<td>0536</td>
<td>0577</td>
<td>0618</td>
<td>0659</td>
<td>0700</td>
<td>0741</td>
<td>0782</td>
<td>0823</td>
<td>0864</td>
</tr>
<tr>
<td>23</td>
<td>0536</td>
<td>0577</td>
<td>0618</td>
<td>0659</td>
<td>0700</td>
<td>0741</td>
<td>0782</td>
<td>0823</td>
<td>0864</td>
<td>0905</td>
</tr>
<tr>
<td>24</td>
<td>0577</td>
<td>0618</td>
<td>0659</td>
<td>0700</td>
<td>0741</td>
<td>0782</td>
<td>0823</td>
<td>0864</td>
<td>0905</td>
<td>0946</td>
</tr>
<tr>
<td>25</td>
<td>0618</td>
<td>0659</td>
<td>0700</td>
<td>0741</td>
<td>0782</td>
<td>0823</td>
<td>0864</td>
<td>0905</td>
<td>0946</td>
<td>0987</td>
</tr>
<tr>
<td>26</td>
<td>0659</td>
<td>0700</td>
<td>0741</td>
<td>0782</td>
<td>0823</td>
<td>0864</td>
<td>0905</td>
<td>0946</td>
<td>0987</td>
<td>1028</td>
</tr>
<tr>
<td>27</td>
<td>0700</td>
<td>0741</td>
<td>0782</td>
<td>0823</td>
<td>0864</td>
<td>0905</td>
<td>0946</td>
<td>0987</td>
<td>1028</td>
<td>1069</td>
</tr>
<tr>
<td>28</td>
<td>0741</td>
<td>0782</td>
<td>0823</td>
<td>0864</td>
<td>0905</td>
<td>0946</td>
<td>0987</td>
<td>1028</td>
<td>1069</td>
<td>1110</td>
</tr>
<tr>
<td>29</td>
<td>0782</td>
<td>0823</td>
<td>0864</td>
<td>0905</td>
<td>0946</td>
<td>0987</td>
<td>1028</td>
<td>1069</td>
<td>1110</td>
<td>1151</td>
</tr>
</tbody>
</table>

**MEAN DIFFERENCES**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.45</td>
<td>0.89</td>
<td>1.33</td>
<td>1.77</td>
<td>2.21</td>
<td>2.65</td>
<td>3.09</td>
<td>3.53</td>
</tr>
<tr>
<td>11</td>
<td>0.46</td>
<td>0.90</td>
<td>1.34</td>
<td>1.78</td>
<td>2.22</td>
<td>2.66</td>
<td>3.10</td>
<td>3.54</td>
</tr>
<tr>
<td>12</td>
<td>0.47</td>
<td>0.90</td>
<td>1.34</td>
<td>1.78</td>
<td>2.22</td>
<td>2.66</td>
<td>3.10</td>
<td>3.54</td>
</tr>
<tr>
<td>13</td>
<td>0.48</td>
<td>0.90</td>
<td>1.34</td>
<td>1.78</td>
<td>2.22</td>
<td>2.66</td>
<td>3.10</td>
<td>3.54</td>
</tr>
<tr>
<td>14</td>
<td>0.49</td>
<td>0.90</td>
<td>1.34</td>
<td>1.78</td>
<td>2.22</td>
<td>2.66</td>
<td>3.10</td>
<td>3.54</td>
</tr>
<tr>
<td>15</td>
<td>0.50</td>
<td>0.91</td>
<td>1.35</td>
<td>1.80</td>
<td>2.24</td>
<td>2.68</td>
<td>3.12</td>
<td>3.56</td>
</tr>
<tr>
<td>16</td>
<td>0.51</td>
<td>0.91</td>
<td>1.35</td>
<td>1.80</td>
<td>2.24</td>
<td>2.68</td>
<td>3.12</td>
<td>3.56</td>
</tr>
<tr>
<td>17</td>
<td>0.52</td>
<td>0.91</td>
<td>1.35</td>
<td>1.80</td>
<td>2.24</td>
<td>2.68</td>
<td>3.12</td>
<td>3.56</td>
</tr>
<tr>
<td>18</td>
<td>0.53</td>
<td>0.91</td>
<td>1.35</td>
<td>1.80</td>
<td>2.24</td>
<td>2.68</td>
<td>3.12</td>
<td>3.56</td>
</tr>
<tr>
<td>19</td>
<td>0.54</td>
<td>0.92</td>
<td>1.36</td>
<td>1.81</td>
<td>2.25</td>
<td>2.70</td>
<td>3.14</td>
<td>3.60</td>
</tr>
<tr>
<td>20</td>
<td>0.55</td>
<td>0.92</td>
<td>1.36</td>
<td>1.81</td>
<td>2.25</td>
<td>2.70</td>
<td>3.14</td>
<td>3.60</td>
</tr>
<tr>
<td>21</td>
<td>0.56</td>
<td>0.92</td>
<td>1.36</td>
<td>1.81</td>
<td>2.25</td>
<td>2.70</td>
<td>3.14</td>
<td>3.60</td>
</tr>
<tr>
<td>22</td>
<td>0.57</td>
<td>0.92</td>
<td>1.36</td>
<td>1.81</td>
<td>2.25</td>
<td>2.70</td>
<td>3.14</td>
<td>3.60</td>
</tr>
<tr>
<td>23</td>
<td>0.58</td>
<td>0.93</td>
<td>1.38</td>
<td>1.83</td>
<td>2.27</td>
<td>2.71</td>
<td>3.15</td>
<td>3.61</td>
</tr>
<tr>
<td>24</td>
<td>0.59</td>
<td>0.93</td>
<td>1.38</td>
<td>1.83</td>
<td>2.27</td>
<td>2.71</td>
<td>3.15</td>
<td>3.61</td>
</tr>
<tr>
<td>25</td>
<td>0.60</td>
<td>0.93</td>
<td>1.38</td>
<td>1.83</td>
<td>2.27</td>
<td>2.71</td>
<td>3.15</td>
<td>3.61</td>
</tr>
<tr>
<td>26</td>
<td>0.61</td>
<td>0.94</td>
<td>1.39</td>
<td>1.84</td>
<td>2.28</td>
<td>2.72</td>
<td>3.16</td>
<td>3.62</td>
</tr>
<tr>
<td>27</td>
<td>0.62</td>
<td>0.94</td>
<td>1.39</td>
<td>1.84</td>
<td>2.28</td>
<td>2.72</td>
<td>3.16</td>
<td>3.62</td>
</tr>
<tr>
<td>28</td>
<td>0.63</td>
<td>0.94</td>
<td>1.39</td>
<td>1.84</td>
<td>2.28</td>
<td>2.72</td>
<td>3.16</td>
<td>3.62</td>
</tr>
<tr>
<td>29</td>
<td>0.64</td>
<td>0.95</td>
<td>1.40</td>
<td>1.85</td>
<td>2.29</td>
<td>2.73</td>
<td>3.17</td>
<td>3.63</td>
</tr>
</tbody>
</table>

**Notes:**
- The table contains logarithmic values and mean differences for a range of numbers.
- The entries in the table are rounded to four figures.
- The mean differences are calculated to further refine the logarithmic values.
- This table is a part of a larger set of logarithmic tables used for calculations involving multiplication and division.
FOUR~FIGURE

I

0

55 7404
56 7482
57 7559
58 7634
59 7709

1
7412
74:90
7566
7642
7716

60 7782 7789
61 7853 7860
62 7924 7931
63 7993 8000
64 8062 8089

I2 I3 I4

II

LOGARITHMS

I8 I9

885

5

6 1 7

7419 7427 7435
7497 7505 7513
71574 7682 7689
7649 7667 7664
7723 7731 7738

74·j,3
7520
7697
7672
7745

7451 7459
75~8 7536
7604 7612
7679 7686
7752 7760

7466
754:1
7619
7694
7767

7474 1
7551 1
7627 1
7701 1
7774 1

7796
7868
7938
8007
8075

7803
7875
7945
8014
8082

7810
7882
7952
8021
8089

7818
7889
7959
8028
8096

7825
7896
7966
8036
8102

7832
7903
7973
8041
8109

7839
7910
7980
8048
8116

7846
7917
7987
8055
8122

11

~~I ~~i:i~I;19
2 2 3
2 2 3
2 2 3
1 2 3
1 2 3

1 1 2
1 1 2
1 1 2
1 1 2
1 1 2

4 5 5 6
4 5 5 6
4 6 5 6
4 4 li 6
4 4 (j 6

3 4 4 6
3 4 4 6
3 3 4 6
3 3 4 5

8136
8202
8267
B331
8395

8142
8209
8274
83B8
8401

8149
8215
8280
8344
8407

8156
8222
8287
8351
8414

8162
8228
8293
8357
8420

8169
8235
8299
8363
8426

8176
8241
8306
8370
8432

8182
8248
8312
8376
8439

8189 1 1 2 3 3 '.I:
8254 1 1 2 3 3 4
8319 1 1 2 3 3 4
8382 1 1 2 3 3 4
8445 1 1 2 2 3 4

6
5
5
4
4

8451
8513
8573
8633
74 8692

8457
8519
8579
8639
8698

8463
8525
8585
8645
8704

8470
8631
8691
8651
8710

84,76
8537
8597
8657
8716

8482
8543
8603
8663
8722

8488
8649
8609
8669
8727

8494
8655
8615
8675
8733

8500
8561
8621
8681
8739

8606
8567
8627
8686
8745

1 1 2 2 3
1 1 2 2 3
1 1 2 2 3
1 1 2 2 3
1 1 2 2 3

4
4
4
4

75 8751
76 8808
"i"i 8865
78 8921
79 8976

8756
8814
8871
8927
8982

8762
8820
8876
8932
8987

8768
8825
8882
8938
8993

8774
8831
8887
8943
8998

8779
8837
8893
8949
9004

8785
8842
8809
8954
9009

8791
8848
8904
8960
9015

8797
8854
8910
8965
9020

8802
8859
8915
8971
9020

1 1 2 2
1 1 2 2

80 9031
81 008S
82 9138
83 9101
84 9M3

9036
9090
9148
9196
9248

9042
9096
9149
9201
9253

9047
{1101
9154
9206
9268

9053
9106
9159
9212
9263

9058
9U2
9165
9217
9269

9063
9117
0170
9222
92740

9069
9122
9170
9227
9279

9074
9128
9180
9232

70
71
72
73

9079
9133
9186
9238
9284 9289

6 6
6 6
6 6

5 6
3 3 4 5 6 6

8129
8195
8261
8325
8388

65
66
67
68
69

7
7
7
7
7

4
4
4
4

4 4

IJ 6

6 6

Ii 6
j) 6
l5 6
Ii 6
6 5

6 5

Ii 5
(i

5

a

3 4 5 5
3 4 5 5
1 1 2 2 3 3 4 4 5
1 1 2 2 :3 3 ,t 4 6
1 1 2 2 a 3 4 4 5
1 1 2
I 1 2
1 I 2
1 I 2
1 1 2

a

2 3 3
2 3 3
2 3 II
2 3 3

4 4 li
4 4 6
446
4 4 5
2 3 3 4 4 15

85 9294 9299 9304 9309 9315 9320 9826 9330 9335 9340 1 1 2 2 3 3 445
86 9345 9350 0350 9360 9365 9370 9375 9380 9385 9390 1 1 2 2 3 3 4 4 li

87 9395 9400 9405 9410 9416 9420 9425 9430 9435 9440 0 1 1 2 2 3 344
88 94'15 9450 9455 9460 9466 9469 9474 9479 9484 9489 0 1 1 2 2 3 3 4 4
89 9494 9499 9604 9609 9513 9518 9523 9528 95a3 9538 0 1 1 2 2 3 344
90
91
92
93
94

9542
9590
9638
9685
9731

9547
9095
9643
9689
9736

9552
9800
9647
96114
9741

9557
9605
9652
9699
9745

9562
9609
9657
9703
9750

9566
9614
9661
9708
9754

9571
9619
9666
9713
9759

9576
9624
9671
9717
9763

9581
9628
9675
9722
9768

9586 0 1 1
9633 0 1 1
9680 0 1 1
9727 0 1 1
9773 0 1 1

95 9777 9782 11786 9791 9795 1)800 9805 9809 9814 9818 0 1

2
2
2
2
2

2
2
2
2
2

344
344
344
344
3 344
a
3
3
3

1 2 2 3 344

96 9823 9827 9832 9836 9841 9845 9850 9854 9859 9863 0 1 1 2 2 3 344

97 9868 9872 9877 9881 9886 9890 9894 9899 9903 91108 0 1 1 2 2 3 344
98 9912 9917 9921 9926 9930 9934 9939 9943 9948 9962 0 1 1 2 2 3 344
99 9956 9961 9965 9969 9974 9978 9983 99S7 9991 9996 0 1 1 2 2 3 334

0

:L

2

3

4

5

6

'i

I

8 I 9

1 2 314 5 6 "/ 8 9


The five-figure logarithm tables (but in a modified set-out) are taken from E. Hope, *The Chemists' Year Book*, 1939, and are reproduced by kind permission of the publishers, Messrs. Sherratt and Hughes, Timperley, Cheshire, England. Permission to reproduce five-figure logarithm tables was also kindly granted by Messrs. G. Bell and Sons Ltd., Portugal Street, London, W.C.2, England, from their *Synopsis of Applicable Mathematics* by L. Silberstein, and also by Dr. A. Lange from his *Handbook of Chemistry*, 2nd Edition, 1937 (Handbook Publishers Inc., Sandusky, Ohio, U.S.A.).
<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0000</td>
<td>043</td>
<td>067</td>
<td>130</td>
<td>173</td>
<td>217</td>
<td>260</td>
<td>303</td>
<td>346</td>
<td>389</td>
</tr>
<tr>
<td>101</td>
<td>432</td>
<td>475</td>
<td>518</td>
<td>561</td>
<td>604</td>
<td>647</td>
<td>699</td>
<td>732</td>
<td>772</td>
<td>807</td>
</tr>
<tr>
<td>102</td>
<td>660</td>
<td>693</td>
<td>746</td>
<td>786</td>
<td>830</td>
<td>872</td>
<td>915</td>
<td>957</td>
<td>1000</td>
<td>1043</td>
</tr>
<tr>
<td>103</td>
<td>224</td>
<td>260</td>
<td>295</td>
<td>330</td>
<td>365</td>
<td>400</td>
<td>436</td>
<td>472</td>
<td>508</td>
<td>544</td>
</tr>
<tr>
<td>104</td>
<td>703</td>
<td>745</td>
<td>787</td>
<td>828</td>
<td>870</td>
<td>912</td>
<td>953</td>
<td>995</td>
<td>008</td>
<td>041</td>
</tr>
<tr>
<td>105</td>
<td>02</td>
<td>110</td>
<td>100</td>
<td>202</td>
<td>243</td>
<td>284</td>
<td>325</td>
<td>366</td>
<td>407</td>
<td>449</td>
</tr>
<tr>
<td>106</td>
<td>631</td>
<td>672</td>
<td>713</td>
<td>754</td>
<td>795</td>
<td>836</td>
<td>877</td>
<td>918</td>
<td>959</td>
<td>1000</td>
</tr>
<tr>
<td>107</td>
<td>336</td>
<td>379</td>
<td>420</td>
<td>461</td>
<td>502</td>
<td>543</td>
<td>584</td>
<td>625</td>
<td>666</td>
<td>707</td>
</tr>
<tr>
<td>108</td>
<td>054</td>
<td>093</td>
<td>132</td>
<td>171</td>
<td>210</td>
<td>249</td>
<td>288</td>
<td>327</td>
<td>366</td>
<td>405</td>
</tr>
<tr>
<td>109</td>
<td>743</td>
<td>782</td>
<td>822</td>
<td>862</td>
<td>902</td>
<td>941</td>
<td>981</td>
<td>020</td>
<td>060</td>
<td>100</td>
</tr>
<tr>
<td>110</td>
<td>04</td>
<td>139</td>
<td>179</td>
<td>218</td>
<td>259</td>
<td>299</td>
<td>339</td>
<td>379</td>
<td>419</td>
<td>459</td>
</tr>
<tr>
<td>111</td>
<td>232</td>
<td>273</td>
<td>314</td>
<td>355</td>
<td>396</td>
<td>437</td>
<td>478</td>
<td>519</td>
<td>559</td>
<td>600</td>
</tr>
<tr>
<td>112</td>
<td>522</td>
<td>563</td>
<td>604</td>
<td>645</td>
<td>686</td>
<td>727</td>
<td>768</td>
<td>809</td>
<td>850</td>
<td>891</td>
</tr>
<tr>
<td>113</td>
<td>054</td>
<td>093</td>
<td>132</td>
<td>171</td>
<td>210</td>
<td>249</td>
<td>288</td>
<td>327</td>
<td>366</td>
<td>405</td>
</tr>
<tr>
<td>114</td>
<td>490</td>
<td>531</td>
<td>572</td>
<td>613</td>
<td>654</td>
<td>695</td>
<td>736</td>
<td>777</td>
<td>818</td>
<td>859</td>
</tr>
<tr>
<td>115</td>
<td>06</td>
<td>070</td>
<td>108</td>
<td>146</td>
<td>185</td>
<td>223</td>
<td>262</td>
<td>300</td>
<td>339</td>
<td>378</td>
</tr>
<tr>
<td>116</td>
<td>440</td>
<td>481</td>
<td>522</td>
<td>563</td>
<td>604</td>
<td>645</td>
<td>686</td>
<td>727</td>
<td>768</td>
<td>809</td>
</tr>
<tr>
<td>117</td>
<td>519</td>
<td>560</td>
<td>601</td>
<td>642</td>
<td>683</td>
<td>724</td>
<td>765</td>
<td>806</td>
<td>847</td>
<td>888</td>
</tr>
<tr>
<td>118</td>
<td>078</td>
<td>118</td>
<td>158</td>
<td>198</td>
<td>238</td>
<td>278</td>
<td>318</td>
<td>358</td>
<td>398</td>
<td>438</td>
</tr>
<tr>
<td>119</td>
<td>306</td>
<td>346</td>
<td>386</td>
<td>426</td>
<td>466</td>
<td>506</td>
<td>546</td>
<td>586</td>
<td>626</td>
<td>666</td>
</tr>
<tr>
<td>120</td>
<td>940</td>
<td>980</td>
<td>102</td>
<td>106</td>
<td>110</td>
<td>114</td>
<td>118</td>
<td>122</td>
<td>126</td>
<td>130</td>
</tr>
<tr>
<td>121</td>
<td>818</td>
<td>858</td>
<td>898</td>
<td>938</td>
<td>978</td>
<td>1017</td>
<td>1057</td>
<td>1097</td>
<td>1137</td>
<td>1177</td>
</tr>
<tr>
<td>122</td>
<td>600</td>
<td>640</td>
<td>679</td>
<td>719</td>
<td>759</td>
<td>799</td>
<td>839</td>
<td>879</td>
<td>919</td>
<td>959</td>
</tr>
<tr>
<td>123</td>
<td>106</td>
<td>106</td>
<td>106</td>
<td>106</td>
<td>106</td>
<td>106</td>
<td>106</td>
<td>106</td>
<td>106</td>
<td>106</td>
</tr>
<tr>
<td>124</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>125</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>126</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>127</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>128</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>129</td>
<td>000</td>
<td>000</td>
<td>000</td>
<td>000</td>
<td>000</td>
<td>000</td>
<td>000</td>
<td>000</td>
<td>000</td>
<td>000</td>
</tr>
</tbody>
</table>

**FIVE-Figure LOGARITHMS: 100–150**
FIVE-FIGURE LOGARITHMS: 200—250

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>Proportional Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>30</td>
<td>103</td>
<td>125</td>
<td>146</td>
<td>168</td>
<td>190</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>201</td>
<td>320</td>
<td>341</td>
<td>363</td>
<td>384</td>
<td>406</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>202</td>
<td>255</td>
<td>287</td>
<td>318</td>
<td>349</td>
<td>381</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>203</td>
<td>750</td>
<td>771</td>
<td>793</td>
<td>814</td>
<td>836</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>204</td>
<td>663</td>
<td>694</td>
<td>666</td>
<td>678</td>
<td>690</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>205</td>
<td>31</td>
<td>175</td>
<td>197</td>
<td>218</td>
<td>239</td>
<td>260</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>206</td>
<td>238</td>
<td>260</td>
<td>282</td>
<td>304</td>
<td>326</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>207</td>
<td>597</td>
<td>618</td>
<td>639</td>
<td>660</td>
<td>681</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>208</td>
<td>806</td>
<td>827</td>
<td>849</td>
<td>870</td>
<td>890</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>209</td>
<td>32</td>
<td>015</td>
<td>035</td>
<td>056</td>
<td>077</td>
<td>098</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>222</td>
<td>243</td>
<td>265</td>
<td>286</td>
<td>308</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>211</td>
<td>228</td>
<td>250</td>
<td>272</td>
<td>294</td>
<td>316</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>212</td>
<td>315</td>
<td>337</td>
<td>359</td>
<td>381</td>
<td>403</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>213</td>
<td>424</td>
<td>446</td>
<td>468</td>
<td>490</td>
<td>512</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>214</td>
<td>521</td>
<td>543</td>
<td>565</td>
<td>587</td>
<td>609</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>215</td>
<td>624</td>
<td>646</td>
<td>668</td>
<td>690</td>
<td>712</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>216</td>
<td>724</td>
<td>746</td>
<td>768</td>
<td>790</td>
<td>812</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>217</td>
<td>241</td>
<td>263</td>
<td>285</td>
<td>307</td>
<td>329</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>218</td>
<td>342</td>
<td>364</td>
<td>386</td>
<td>408</td>
<td>430</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>219</td>
<td>444</td>
<td>466</td>
<td>488</td>
<td>510</td>
<td>532</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>546</td>
<td>568</td>
<td>590</td>
<td>612</td>
<td>634</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>221</td>
<td>649</td>
<td>671</td>
<td>693</td>
<td>715</td>
<td>737</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>222</td>
<td>750</td>
<td>772</td>
<td>794</td>
<td>816</td>
<td>838</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>223</td>
<td>225</td>
<td>247</td>
<td>269</td>
<td>291</td>
<td>313</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>224</td>
<td>328</td>
<td>350</td>
<td>372</td>
<td>394</td>
<td>416</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>431</td>
<td>453</td>
<td>475</td>
<td>497</td>
<td>519</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>226</td>
<td>534</td>
<td>556</td>
<td>578</td>
<td>600</td>
<td>622</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>227</td>
<td>637</td>
<td>659</td>
<td>681</td>
<td>703</td>
<td>725</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>228</td>
<td>229</td>
<td>251</td>
<td>273</td>
<td>295</td>
<td>317</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>229</td>
<td>330</td>
<td>352</td>
<td>374</td>
<td>396</td>
<td>418</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>434</td>
<td>456</td>
<td>478</td>
<td>499</td>
<td>521</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>231</td>
<td>537</td>
<td>559</td>
<td>581</td>
<td>603</td>
<td>625</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>232</td>
<td>640</td>
<td>662</td>
<td>684</td>
<td>706</td>
<td>728</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>233</td>
<td>743</td>
<td>765</td>
<td>787</td>
<td>809</td>
<td>831</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>234</td>
<td>235</td>
<td>257</td>
<td>279</td>
<td>301</td>
<td>323</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>235</td>
<td>340</td>
<td>362</td>
<td>384</td>
<td>406</td>
<td>428</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>236</td>
<td>445</td>
<td>467</td>
<td>489</td>
<td>511</td>
<td>533</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>237</td>
<td>548</td>
<td>570</td>
<td>592</td>
<td>614</td>
<td>636</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>238</td>
<td>651</td>
<td>673</td>
<td>695</td>
<td>717</td>
<td>739</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>239</td>
<td>240</td>
<td>262</td>
<td>284</td>
<td>306</td>
<td>328</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>343</td>
<td>365</td>
<td>387</td>
<td>409</td>
<td>431</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>241</td>
<td>446</td>
<td>468</td>
<td>490</td>
<td>512</td>
<td>534</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>242</td>
<td>549</td>
<td>571</td>
<td>593</td>
<td>615</td>
<td>637</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>243</td>
<td>652</td>
<td>674</td>
<td>696</td>
<td>718</td>
<td>740</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>244</td>
<td>245</td>
<td>267</td>
<td>289</td>
<td>311</td>
<td>333</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>246</td>
<td>348</td>
<td>370</td>
<td>392</td>
<td>414</td>
<td>436</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>247</td>
<td>449</td>
<td>471</td>
<td>493</td>
<td>515</td>
<td>537</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>248</td>
<td>550</td>
<td>572</td>
<td>594</td>
<td>616</td>
<td>638</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>249</td>
<td>653</td>
<td>675</td>
<td>697</td>
<td>719</td>
<td>741</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>251</td>
<td>273</td>
<td>295</td>
<td>317</td>
<td>339</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

-30 103-40 950
Quantitative Inorganic Analysis

6. pH Ranges: 2.2-3.8, 4.0-6.2, 5.8-8.0, 7.8-10.0; 20° C. (Clark and Lubs, 1916)

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂HPO₄.</td>
<td>KH₂PO₄.</td>
<td></td>
<td>Na₂HPO₄.</td>
<td>KH₂PO₄.</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>9.75</td>
<td>5.29</td>
<td>5.29</td>
<td>5.29</td>
<td>6.81</td>
</tr>
<tr>
<td>0.5</td>
<td>9.5</td>
<td>5.69</td>
<td>6.0</td>
<td>4.0</td>
<td>6.98</td>
</tr>
<tr>
<td>1.0</td>
<td>9.0</td>
<td>5.91</td>
<td>7.0</td>
<td>3.0</td>
<td>7.17</td>
</tr>
<tr>
<td>2.0</td>
<td>8.0</td>
<td>6.24</td>
<td>8.0</td>
<td>2.0</td>
<td>7.88</td>
</tr>
<tr>
<td>3.0</td>
<td>7.0</td>
<td>6.47</td>
<td>9.0</td>
<td>1.9</td>
<td>7.73</td>
</tr>
<tr>
<td>4.0</td>
<td>6.0</td>
<td>6.64</td>
<td>9.5</td>
<td>0.5</td>
<td>8.04</td>
</tr>
</tbody>
</table>

7. pH Range: 6.80-9.60; 25° C. (Michaelis, 1930)

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na salt.</td>
<td>HCl.</td>
<td></td>
<td>Na salt.</td>
<td>HCl.</td>
<td></td>
</tr>
<tr>
<td>5.22</td>
<td>4.78</td>
<td>8.80</td>
<td>8.23</td>
<td>1.77</td>
<td>8.40</td>
</tr>
<tr>
<td>5.35</td>
<td>4.64</td>
<td>7.00</td>
<td>8.71</td>
<td>1.29</td>
<td>8.60</td>
</tr>
<tr>
<td>5.54</td>
<td>4.46</td>
<td>7.20</td>
<td>9.08</td>
<td>0.92</td>
<td>8.80</td>
</tr>
<tr>
<td>5.81</td>
<td>4.19</td>
<td>7.40</td>
<td>9.36</td>
<td>0.04</td>
<td>9.00</td>
</tr>
<tr>
<td>6.15</td>
<td>3.85</td>
<td>7.60</td>
<td>9.52</td>
<td>0.43</td>
<td>9.20</td>
</tr>
<tr>
<td>6.62</td>
<td>3.38</td>
<td>7.80</td>
<td>9.74</td>
<td>0.26</td>
<td>9.40</td>
</tr>
<tr>
<td>7.16</td>
<td>2.84</td>
<td>8.00</td>
<td>9.85</td>
<td>0.15</td>
<td>9.60</td>
</tr>
</tbody>
</table>
Appendix

8. \( \text{pH} \) Range: 8.45–12.77; 24° C. (Sorensen-Walbaum, 1920)

<table>
<thead>
<tr>
<th>X (ml.) Glycine-NaCl</th>
<th>Y (ml.) NaOH</th>
<th>pH</th>
<th>X (ml.) Glycine-NaCl</th>
<th>Y (ml.) NaOH</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>0.5</td>
<td>8.45</td>
<td>5.0</td>
<td>0.0</td>
<td>11.14</td>
</tr>
<tr>
<td>9.0</td>
<td>1.0</td>
<td>8.79</td>
<td>5.0</td>
<td>1.0</td>
<td>11.39</td>
</tr>
<tr>
<td>9.0</td>
<td>2.0</td>
<td>9.22</td>
<td>5.0</td>
<td>2.0</td>
<td>11.92</td>
</tr>
<tr>
<td>7.0</td>
<td>3.0</td>
<td>9.56</td>
<td>4.0</td>
<td>3.0</td>
<td>12.21</td>
</tr>
<tr>
<td>6.0</td>
<td>4.0</td>
<td>9.98</td>
<td>3.0</td>
<td>4.0</td>
<td>12.48</td>
</tr>
<tr>
<td>5.5</td>
<td>4.5</td>
<td>10.32</td>
<td>2.5</td>
<td>5.0</td>
<td>12.66</td>
</tr>
<tr>
<td>5.1</td>
<td>4.0</td>
<td>10.90</td>
<td>2.0</td>
<td>6.0</td>
<td>12.77</td>
</tr>
</tbody>
</table>

* That is, a solution containing 7.605 g. of glycine + 5.85 g. of NaCl per litre.


<p>| X ml. of 0.1M-p-toluensulfonic acid monohydrate (19.012 g. per litre) and Y ml. of 0.1M-sodium p-toluensulfonate (19.406 g. per litre), diluted to 100.0 ml. |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.9</td>
<td>1.1</td>
<td>1.40</td>
<td>36.8</td>
<td>1.3</td>
<td>1.90</td>
</tr>
<tr>
<td>37.2</td>
<td>12.8</td>
<td>1.60</td>
<td>40.0</td>
<td>10.0</td>
<td>2.00</td>
</tr>
<tr>
<td>27.4</td>
<td>22.0</td>
<td>1.90</td>
<td>42.4</td>
<td>7.6</td>
<td>2.10</td>
</tr>
<tr>
<td>19.0</td>
<td>31.0</td>
<td>1.70</td>
<td>46.6</td>
<td>4.4</td>
<td>2.20</td>
</tr>
<tr>
<td>16.6</td>
<td>33.4</td>
<td>1.80</td>
<td>48.9</td>
<td>12.4</td>
<td>2.30</td>
</tr>
</tbody>
</table>

<p>| X ml. of 0.01M-p-toluensulfonic acid monohydrate (1.0012 g. per litre) and Y ml. of 0.01M-sodium p-toluensulfonate (1.9046 g. per litre), diluted to 100.0 ml. |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0</td>
<td>0.0</td>
<td>2.30</td>
<td>12.4</td>
<td>27.6</td>
<td>2.90</td>
</tr>
<tr>
<td>44.2</td>
<td>5.8</td>
<td>2.40</td>
<td>10.0</td>
<td>40.0</td>
<td>3.00</td>
</tr>
<tr>
<td>35.8</td>
<td>14.2</td>
<td>2.50</td>
<td>8.0</td>
<td>42.0</td>
<td>3.10</td>
</tr>
<tr>
<td>27.6</td>
<td>22.4</td>
<td>2.60</td>
<td>6.2</td>
<td>43.8</td>
<td>3.20</td>
</tr>
<tr>
<td>21.2</td>
<td>23.8</td>
<td>2.70</td>
<td>5.0</td>
<td>45.0</td>
<td>3.30</td>
</tr>
<tr>
<td>18.5</td>
<td>31.5</td>
<td>2.80</td>
<td>45.2</td>
<td>3.40</td>
<td>3.40</td>
</tr>
</tbody>
</table>

<p>| X ml. of 0.01M-furoic acid (1.1203 g. per litre) and Y ml. of 0.01M-sodium furate (1.3403 g. per litre), diluted to 100.0 ml. |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.2</td>
<td>4.8</td>
<td>2.00</td>
<td>14.8</td>
<td>55.2</td>
<td>3.60</td>
</tr>
<tr>
<td>39.6</td>
<td>10.4</td>
<td>3.00</td>
<td>12.3</td>
<td>37.7</td>
<td>3.70</td>
</tr>
<tr>
<td>34.0</td>
<td>16.0</td>
<td>3.10</td>
<td>10.1</td>
<td>39.9</td>
<td>3.80</td>
</tr>
<tr>
<td>28.4</td>
<td>21.6</td>
<td>3.20</td>
<td>8.4</td>
<td>41.6</td>
<td>3.90</td>
</tr>
<tr>
<td>24.8</td>
<td>25.2</td>
<td>3.30</td>
<td>6.7</td>
<td>43.3</td>
<td>4.00</td>
</tr>
<tr>
<td>21.4</td>
<td>28.6</td>
<td>3.40</td>
<td>5.4</td>
<td>44.6</td>
<td>4.10</td>
</tr>
<tr>
<td>18.0</td>
<td>32.0</td>
<td>3.50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Quantitative Inorganic Analysis

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>48-7</td>
<td>1-3</td>
<td>3-40</td>
<td>22-0</td>
<td>28-0</td>
<td>4-40</td>
</tr>
<tr>
<td>46-6</td>
<td>3-4</td>
<td>3-50</td>
<td>19-4</td>
<td>30-6</td>
<td>4-60</td>
</tr>
<tr>
<td>44-4</td>
<td>5-6</td>
<td>3-60</td>
<td>16-9</td>
<td>33-1</td>
<td>4-60</td>
</tr>
<tr>
<td>42-2</td>
<td>7-8</td>
<td>3-70</td>
<td>14-4</td>
<td>35-6</td>
<td>4-70</td>
</tr>
<tr>
<td>39-9</td>
<td>10-1</td>
<td>3-80</td>
<td>12-1</td>
<td>37-9</td>
<td>4-80</td>
</tr>
<tr>
<td>37-2</td>
<td>12-6</td>
<td>3-90</td>
<td>10-2</td>
<td>39-8</td>
<td>4-90</td>
</tr>
<tr>
<td>34-4</td>
<td>15-8</td>
<td>4-00</td>
<td>8-6</td>
<td>41-4</td>
<td>5-00</td>
</tr>
<tr>
<td>30-8</td>
<td>19-2</td>
<td>4-10</td>
<td>7-2</td>
<td>42-8</td>
<td>5-10</td>
</tr>
<tr>
<td>28-0</td>
<td>22-0</td>
<td>4-20</td>
<td>5-7</td>
<td>44-3</td>
<td>5-20</td>
</tr>
<tr>
<td>25-1</td>
<td>24-9</td>
<td>4-30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>Y (ml.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>48-8</td>
<td>1-2</td>
<td>4-80</td>
<td>21-0</td>
<td>29-0</td>
<td>5-60</td>
</tr>
<tr>
<td>46-6</td>
<td>3-1</td>
<td>4-90</td>
<td>17-6</td>
<td>32-4</td>
<td>5-70</td>
</tr>
<tr>
<td>44-4</td>
<td>5-6</td>
<td>5-00</td>
<td>14-7</td>
<td>35-3</td>
<td>5-80</td>
</tr>
<tr>
<td>40-4</td>
<td>9-6</td>
<td>5-10</td>
<td>12-0</td>
<td>38-0</td>
<td>5-90</td>
</tr>
<tr>
<td>36-2</td>
<td>13-8</td>
<td>5-20</td>
<td>9-9</td>
<td>40-1</td>
<td>6-00</td>
</tr>
<tr>
<td>32-6</td>
<td>17-4</td>
<td>5-30</td>
<td>7-8</td>
<td>42-2</td>
<td>6-10</td>
</tr>
<tr>
<td>28-6</td>
<td>21-4</td>
<td>5-40</td>
<td>5-6</td>
<td>44-4</td>
<td>6-20</td>
</tr>
<tr>
<td>24-7</td>
<td>25-3</td>
<td>5-50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

10. pH Range: 2-6-12-0; 15° C.—Universal Buffer Mixture
   (Johnson and Lindsey, 1930)

A mixture of 6-008 g. of A.R. citric acid, 3-803 g. of A.R. potassium dihydrogen phosphate, 1-789 g. of A.R. boric acid, and 5-266 g. of pure diethylbarbituric acid is dissolved in water and made up to 1 litre. The pH values at 15° C. of mixtures of 100 ml. of this solution with various volumes (X) of 0-2N-sodium hydroxide solution (free from carbonate) are tabulated below.

<table>
<thead>
<tr>
<th>pH</th>
<th>X (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
<th>pH</th>
<th>X (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-6</td>
<td>2-0</td>
<td>5-8</td>
<td>36-5</td>
<td>9-0</td>
<td>72-7</td>
</tr>
<tr>
<td>2-8</td>
<td>4-3</td>
<td>6-0</td>
<td>38-9</td>
<td>9-2</td>
<td>74-0</td>
</tr>
<tr>
<td>3-0</td>
<td>6-4</td>
<td>6-2</td>
<td>41-2</td>
<td>9-4</td>
<td>75-9</td>
</tr>
<tr>
<td>3-2</td>
<td>8-3</td>
<td>6-4</td>
<td>43-5</td>
<td>9-6</td>
<td>77-6</td>
</tr>
<tr>
<td>3-4</td>
<td>10-1</td>
<td>6-6</td>
<td>46-0</td>
<td>9-8</td>
<td>79-3</td>
</tr>
<tr>
<td>3-6</td>
<td>11-8</td>
<td>6-8</td>
<td>48-3</td>
<td>10-0</td>
<td>80-8</td>
</tr>
<tr>
<td>3-8</td>
<td>13-7</td>
<td>7-0</td>
<td>50-6</td>
<td>10-2</td>
<td>82-0</td>
</tr>
<tr>
<td>4-0</td>
<td>16-5</td>
<td>7-2</td>
<td>52-9</td>
<td>10-4</td>
<td>82-9</td>
</tr>
<tr>
<td>4-2</td>
<td>17-6</td>
<td>7-4</td>
<td>55-8</td>
<td>10-6</td>
<td>83-9</td>
</tr>
<tr>
<td>4-4</td>
<td>19-9</td>
<td>7-6</td>
<td>58-6</td>
<td>10-8</td>
<td>84-9</td>
</tr>
<tr>
<td>4-6</td>
<td>22-4</td>
<td>7-8</td>
<td>61-7</td>
<td>11-0</td>
<td>86-0</td>
</tr>
<tr>
<td>4-8</td>
<td>24-8</td>
<td>8-0</td>
<td>63-7</td>
<td>11-2</td>
<td>87-7</td>
</tr>
<tr>
<td>5-0</td>
<td>27-1</td>
<td>8-2</td>
<td>65-6</td>
<td>11-4</td>
<td>89-7</td>
</tr>
<tr>
<td>5-2</td>
<td>29-5</td>
<td>8-4</td>
<td>67-5</td>
<td>11-6</td>
<td>92-0</td>
</tr>
<tr>
<td>5-4</td>
<td>31-8</td>
<td>8-6</td>
<td>69-3</td>
<td>11-8</td>
<td>95-0</td>
</tr>
<tr>
<td>5-6</td>
<td>34-2</td>
<td>8-8</td>
<td>71-0</td>
<td>12-0</td>
<td>99-8</td>
</tr>
</tbody>
</table>
Appendix

A, 11. COMPARISON OF METRIC AND OTHER UNITS

Metric system.—The primary unit of length is the metre, which is the distance between two lines, under standard conditions, engraved on a prototype preserved in the Bureau International des Poids et Mesures, Sèvres, France.

The primary unit of weight is the kilogram, which is the mass of a prototype preserved in the same place.

The primary unit of volume is the litre, and is the volume occupied by one kilogram of pure water at 4°C, under a pressure of 760 mm. of mercury (see, however, Section II, 17).

The millilitre (ml.) is the thousandth part of a litre. One millilitre is nearly, but not absolutely, equal to one cubic centimetre (c.c.):

\[ 1000 \text{ ml.} = 1000.028 \text{ c.c.} \]

The redefinition of the litre has recently been considered (see Chemical and Engineering News, 1949, 27, 2996; Annual Reports on the Progress of Chemistry, 1949, 46, 86) as a cubic decimetre. If this new definition be accepted, the millilitre (ml.) is identical with the cubic centimetre (c.c.).

### UNITS OF LENGTH

<table>
<thead>
<tr>
<th>Metric Unit</th>
<th>Equivalent in Imperial Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 millimetre (mm.)</td>
<td>0.03937 inch</td>
</tr>
<tr>
<td>1 centimetre (cm.)</td>
<td>0.3937 inch</td>
</tr>
<tr>
<td>1 metre (m.)</td>
<td>39.370 inches</td>
</tr>
<tr>
<td>1 kilometre (km.)</td>
<td>0.91440 mile</td>
</tr>
</tbody>
</table>

### UNITS OF AREA

<table>
<thead>
<tr>
<th>Metric Unit</th>
<th>Equivalent in Imperial Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 square mm.</td>
<td>0.001550 sq. in.</td>
</tr>
<tr>
<td>1 square cm.</td>
<td>0.1550 sq. in.</td>
</tr>
<tr>
<td>1 square metre</td>
<td>1.1960 sq. yds.</td>
</tr>
<tr>
<td>1 square km.</td>
<td>36.104 sq. mile</td>
</tr>
<tr>
<td>1 hectare</td>
<td>2.4710 acres</td>
</tr>
</tbody>
</table>

### UNITS OF VOLUME

<table>
<thead>
<tr>
<th>Metric Unit</th>
<th>Equivalent in Imperial Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cubic cm. (c.c. or ml)</td>
<td>0.06102 cubic in.</td>
</tr>
<tr>
<td>1 cubic in.</td>
<td>16.387 cubic mm.</td>
</tr>
<tr>
<td>1 cubic ft.</td>
<td>28.317 cubic in.</td>
</tr>
<tr>
<td>1 cubic yd.</td>
<td>0.7645 cubic ft.</td>
</tr>
</tbody>
</table>

### MEASURES OF LIQUID CAPACITY

**Imperial or British Units**

<table>
<thead>
<tr>
<th>Imperial Unit</th>
<th>Metric Equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 gill</td>
<td>142.06 ml.</td>
</tr>
<tr>
<td>1 pint</td>
<td>568.25 ml.</td>
</tr>
<tr>
<td>1 quart</td>
<td>1.13649 litres</td>
</tr>
<tr>
<td>1 gallon</td>
<td>4.546096 litres</td>
</tr>
<tr>
<td>1 litre</td>
<td>7.598 pints</td>
</tr>
<tr>
<td>1 gallon</td>
<td>0.88000 quart</td>
</tr>
<tr>
<td>1 gallon</td>
<td>0.22000 gallon</td>
</tr>
</tbody>
</table>
FIVE-FIGURE LOGARITHMS: 450-600

894

0

PnOPOETIONAL PARTS

1

2

3

4

I I
5

6

"/

350
447
543
639
734

8

9

1 2 8 4[ 5

450
451
452
453
454

65 321
418
514
610
706

331
428
523
619
715

341
437
533
629
725

360
456
552
648
744

369
466
562
657
753

379
475
571
667
763

388
485
581
676
772

495
591
686
782

504
600
696
792

1 2 3 4
1 2 3 4,
1 2 3 4
1 2 3 4
1 2 3 4:

455
456
457
458
459

801
896
992
66 087
181

811
906
001
096
191

820 830 839

849

916
011
106
200

925
020
115
210

935
030
124
219

944
039
134
229

858
954
049
144
238

868
963
058
153
247

877
973
068
162
257

887
982
077
172
266

3 4
.1 2 3 4
1 2 3 4
1 2 a 4
1 2 3 4

460
461
462
463
464

276
370
464
558
652

285
380
474
567
661

295
389
483
577
671

305
398
492
586
680

314
408
502
596
689

323
417
511
605
699

332
427
521
614
708

342
436
530
624
717

351
445
539
633
727

301
455
549
642
736

1 2 3 4
1 2 3 4
1 2 3 4
1 2 3 4
1 2 :3 4

I)
(I
(I

465
466
467
468
469

745
839
932
67 025
117

755 764
8~8 857
941 950
034 043
127 136

773
867
960
052
145

783
876
969
062
154

792
885
978
071
164

801 Sll
894 904,
987 996
080 089
173 182

913
006
090
191

820 820

922
015
108
200

1 2 3 4
1 2 :1 41 2 3 4

I)
I)

1 2 3 4

3 4

Ii
5

470
471
472
473
474

210
302
304
486
578

219
311
403
495
587

22B 237 247

321
413
504
596

330
422
514
605

330
431
523
614

256
348
440
532
624

265
357
449
641
633

274
367
450
550
642

284
376
468
560
651

203
385
477
560
1360

I 2 3 4
1 2 3 4
I 2 :1 4
1 2 3 4
1 2 3 4

I)
I)
()

475
476
477
478
479

669
761
852
943
68 034

678
770
861
952
043

688
779
870
961
052

697
788
879
070
Q61

706
797
888
970
070

715
897
988
079

724
815
1106
997
088

733
825
915
006
097

742
834
925
015
106

752
B43
034
024
115

1 2 3
1 2 3
1 2 3
1 2 3
1 2 3

481
482
483
484

480

124
215
305
395
485

133
224
314
404
494

142
233
323
413
502

151
242
332
422
511

100
251
341
431
520

169
260
350
440
529

178
269
359
449
538

187
.278
368
458
547

196
287
377
467
556

205
296
3B6
476
565

485
486
487
488
489

574
664
753
842
931

583
673
762
851
940

592
681
771
860
949

601
690
780
869
958

610
699
789
878
966

610
708
797
886
975

628
717
806
895
984

637
726
815
004
993

646
735
824
913
002

655
744
833
922
011

490
491
492
493
494

69 020
108
197
285
373

028
117
205
293
381

037
126
214
302
390

046
135
223
311
399

01)5
144
232
320
408

064
152
241
320
417

073·082090099
161 170 179 188
249 258 267 276
338 346 31)5 364
425 434 443 452

495
496
497
498
499

461
548
636
723
8LO

469
557
644
732
819

478
566
653
740
827

487
574
662
749
836

496
583
671
758
845·

504
592
679
767
854

513
601
688
775
862

500

897 906 914 923 932

940

949 958 966 975

I

0

1

2

3

B06

4 1 5

I

6

522
609
697
784
871

7

3D8 408

531
618
705
703
880

8

539
627
714
801
8SS

9

'65 821-'69 975

1 2

1

2

4

/)

5
5
5
5

5

1I
II

5
5

5

Ii

5

5
Ii
5
I'i

4

5

1 .2 3
1 .2 3
1 2 3
1 2 3

4
4
4
4
4

Ii
II

1 2 3
1 2 3
1 2 3
1 2 3
1 2 3

4
4
4

2

3

4

.j,

5

4
4
4
4
4
4
4
4

1
1
1
1

2
.2
.2
2
1 2

a 4
3 ,t
a 4
:1 4

4
4
4

1 2
1 .2
1 2

3 3
3 3
3 3

4
4
4

:1

4

1 2 3 3
1 2 3 3
1

2 3 3

4
4

8 0

8 9
8 Il
8 {}
8 9

6 7 8 {)
7 S 9
7 8 9

6

/)

Ii

7 8 9

6 7
6 7
6 7
6 7
6 7

5

4
4
4

1

[6

7 8 9
6 7 8 0

6 7 8 8
6 7 8 8
6 7 8 8
6 7 8 8
6 7 7 8
6
6
6
6
6

7 7 8

7
6
6
6

7 8
7 8
7 8

7 8

6 7
6 7
6 7
5 tl 7
(I
6 7
13

0

(I

8

8
8
8
8

5 Ii 7 8
5 6 7 8
5 6 7 8
II d 7 8
I) 6 7 8

6
6
I'i 6
I'i 6
II 6
II

5

7 S
7 8
7 8
7 8
7 8

I)

8

II

8
8

()
7
6 7
5 6 7
Ii 6 7

8

5 6 7 8
5 6 7
II (I 7
II 6 7
Il (l 7
5 6 7

8
8
8

8
8

4
4:

5 6 7 8
()
6 7 8
5 6 '7 8
5 6 7 8
6 6 7 8

1:1,

II

6 '7 8

1 2 3 41 5 16 7 8 9


<table>
<thead>
<tr>
<th>PROPORTIONAL PARTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>0123456789</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>FIVE-Figure Logarithms: 600-650</td>
</tr>
<tr>
<td>--------------------------------</td>
</tr>
<tr>
<td>0 1 2 3 4 5 6 7 8 9</td>
</tr>
<tr>
<td>-----------------------------</td>
</tr>
<tr>
<td>600 77.816 822 830 837 844</td>
</tr>
<tr>
<td>601 887 936 903 909 916</td>
</tr>
<tr>
<td>602 900 957 974 981 988</td>
</tr>
<tr>
<td>603 792 090 046 053 061</td>
</tr>
<tr>
<td>604 104 111 118 125 132</td>
</tr>
<tr>
<td>605 176 183 190 197 204</td>
</tr>
<tr>
<td>606 247 254 262 269 276</td>
</tr>
<tr>
<td>607 310 318 326 334 341</td>
</tr>
<tr>
<td>608 360 368 405 412 419</td>
</tr>
<tr>
<td>609 463 459 476 483 490</td>
</tr>
<tr>
<td>610 533 540 547 554 561</td>
</tr>
<tr>
<td>611 604 611 618 626 633</td>
</tr>
<tr>
<td>612 675 682 689 696 704</td>
</tr>
<tr>
<td>613 746 753 760 767 774</td>
</tr>
<tr>
<td>614 817 524 811 888 885</td>
</tr>
<tr>
<td>615 888 595 902 909 916</td>
</tr>
<tr>
<td>616 966 963 970 977 984</td>
</tr>
<tr>
<td>617 79 029 036 043 050</td>
</tr>
<tr>
<td>618 158 108 115 122 129</td>
</tr>
<tr>
<td>619 165 168 180 190 197</td>
</tr>
<tr>
<td>620 230 246 262 269 276</td>
</tr>
<tr>
<td>621 309 316 323 330 337</td>
</tr>
<tr>
<td>622 379 386 393 400 407</td>
</tr>
<tr>
<td>623 449 456 463 470 477</td>
</tr>
<tr>
<td>624 513 520 527 534 541</td>
</tr>
<tr>
<td>625 583 590 602 609 616</td>
</tr>
<tr>
<td>626 677 684 691 698 705</td>
</tr>
<tr>
<td>627 770 777 784 791 798</td>
</tr>
<tr>
<td>628 879 886 893 900 907</td>
</tr>
<tr>
<td>629 935 841 848 855 862</td>
</tr>
<tr>
<td>630 995 941 948 955 962</td>
</tr>
<tr>
<td>631 80 003 010 017 024</td>
</tr>
<tr>
<td>632 072 079 086 092 099</td>
</tr>
<tr>
<td>633 140 147 154 161 168</td>
</tr>
<tr>
<td>634 199 206 213 220 227</td>
</tr>
<tr>
<td>635 277 284 291 298 305</td>
</tr>
<tr>
<td>636 348 355 362 369 376</td>
</tr>
<tr>
<td>637 414 421 428 435 442</td>
</tr>
<tr>
<td>638 488 495 502 509 516</td>
</tr>
<tr>
<td>639 550 557 564 571 578</td>
</tr>
<tr>
<td>640 618 625 632 639 646</td>
</tr>
<tr>
<td>641 688 695 702 709 716</td>
</tr>
<tr>
<td>642 734 741 748 755 762</td>
</tr>
<tr>
<td>643 821 828 835 842 849</td>
</tr>
<tr>
<td>644 889 906 909 916 923</td>
</tr>
</tbody>
</table>

-77 816—81 851
<table>
<thead>
<tr>
<th>Proportional Parts</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>81 201 208 206 211 318 295</td>
<td>325 231 289 235 251</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>651</td>
<td>355 365 371 378 356</td>
<td>391 398 405 411 418</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>652</td>
<td>425 431 438 445 461</td>
<td>458 465 471 479 456</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>653</td>
<td>491 498 505 611 518</td>
<td>625 531 538 546 551</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>654</td>
<td>555 564 571 578 684</td>
<td>591 598 604 611 618</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>655</td>
<td>634 631 637 644 651</td>
<td>657 654 651 657 654</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>656</td>
<td>695 700 704 710 717</td>
<td>723 730 737 743 750</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>657</td>
<td>757 763 770 776 783</td>
<td>790 796 803 809 816</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>658</td>
<td>823 829 836 842 849</td>
<td>856 862 869 876 883</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>659</td>
<td>889 895 902 908 915</td>
<td>921 928 935 941 948</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>660</td>
<td>954 961 968 974 981</td>
<td>987 994 990 997 1004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>661</td>
<td>820 827 834 840 847</td>
<td>854 860 867 874 881</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>662</td>
<td>896 893 900 907 914</td>
<td>921 928 935 942 949</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>663</td>
<td>161 168 174 171 177</td>
<td>184 191 197 204 210</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>664</td>
<td>217 223 230 236 243</td>
<td>250 256 263 269 276</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>665</td>
<td>292 289 295 302 308</td>
<td>315 321 328 334 341</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>666</td>
<td>347 354 360 367 374</td>
<td>380 387 394 400 406</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>667</td>
<td>418 419 420 423 429</td>
<td>445 452 458 465 471</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>668</td>
<td>478 484 491 497 504</td>
<td>510 517 523 530 536</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>669</td>
<td>543 549 556 562 569</td>
<td>575 582 589 595 601</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>670</td>
<td>607 614 620 627 633</td>
<td>640 646 653 659 666</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>671</td>
<td>672 679 685 692 698</td>
<td>705 711 718 724 730</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>672</td>
<td>737 743 750 756 763</td>
<td>780 777 782 789 796</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>673</td>
<td>808 805 811 818 825</td>
<td>832 840 847 853 860</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>674</td>
<td>865 872 879 886 893</td>
<td>898 905 912 919 926</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>675</td>
<td>930 937 943 950 957</td>
<td>963 969 976 983 990</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>676</td>
<td>996 993 999 996 993</td>
<td>1002 1009 1016 1023 1030</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>677</td>
<td>83 090 096 092 089</td>
<td>104 107 110 113 116</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>678</td>
<td>125 129 133 142 149</td>
<td>155 161 167 173 180</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>679</td>
<td>187 193 200 206 213</td>
<td>219 225 232 238 244</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>680</td>
<td>251 257 264 270 276</td>
<td>283 289 296 302 308</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>681</td>
<td>318 323 327 334 340</td>
<td>347 353 359 366 372</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>682</td>
<td>378 386 391 398 404</td>
<td>410 417 423 429 436</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>683</td>
<td>442 448 455 461 468</td>
<td>474 480 487 494 501</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>684</td>
<td>506 512 518 525 531</td>
<td>537 544 550 556 563</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>685</td>
<td>569 575 582 588 594</td>
<td>601 607 613 620 626</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>686</td>
<td>629 635 641 648 655</td>
<td>664 670 677 683 689</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>687</td>
<td>690 695 702 708 715</td>
<td>723 730 736 743 749</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>688</td>
<td>759 765 771 778 784</td>
<td>790 797 803 809 816</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>689</td>
<td>822 828 835 841 847</td>
<td>853 860 867 874 881</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>690</td>
<td>884 890 896 903 909</td>
<td>916 923 929 936 942</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>691</td>
<td>948 954 960 967 973</td>
<td>980 986 992 998 1004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>692</td>
<td>841 847 853 859 865</td>
<td>872 879 885 892 900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>693</td>
<td>907 913 919 925 931</td>
<td>938 945 951 958 965</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>694</td>
<td>130 136 142 148 154</td>
<td>161 167 173 179 186</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>695</td>
<td>198 205 211 217 223</td>
<td>230 236 242 248 255</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>696</td>
<td>261 267 273 279 286</td>
<td>292 298 304 311 317</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>697</td>
<td>323 329 335 342 349</td>
<td>356 362 369 376 383</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>698</td>
<td>386 392 398 404 410</td>
<td>417 423 429 436 443</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>699</td>
<td>448 454 460 466 473</td>
<td>479 485 491 497 504</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>510 516 522 528 535</td>
<td>541 547 553 559 566</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### FIVE-FIGURE LOGARITHMS: 700—750

<table>
<thead>
<tr>
<th>700</th>
<th>701</th>
<th>702</th>
<th>703</th>
<th>704</th>
<th>705</th>
<th>706</th>
<th>707</th>
<th>708</th>
<th>709</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>841</td>
<td>842</td>
<td>843</td>
<td>844</td>
<td>845</td>
<td>846</td>
<td>847</td>
<td>848</td>
<td>849</td>
</tr>
<tr>
<td>715</td>
<td>716</td>
<td>717</td>
<td>718</td>
<td>719</td>
<td>720</td>
<td>721</td>
<td>722</td>
<td>723</td>
<td>724</td>
</tr>
<tr>
<td>735</td>
<td>736</td>
<td>737</td>
<td>738</td>
<td>739</td>
<td>740</td>
<td>741</td>
<td>742</td>
<td>743</td>
<td>744</td>
</tr>
<tr>
<td>755</td>
<td>756</td>
<td>757</td>
<td>758</td>
<td>759</td>
<td>760</td>
<td>761</td>
<td>762</td>
<td>763</td>
<td>764</td>
</tr>
<tr>
<td>775</td>
<td>776</td>
<td>777</td>
<td>778</td>
<td>779</td>
<td>780</td>
<td>781</td>
<td>782</td>
<td>783</td>
<td>784</td>
</tr>
<tr>
<td>795</td>
<td>796</td>
<td>797</td>
<td>798</td>
<td>799</td>
<td>800</td>
<td>801</td>
<td>802</td>
<td>803</td>
<td>804</td>
</tr>
</tbody>
</table>

**Proportional Parts**

<table>
<thead>
<tr>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

---

**84 510—87 558**
<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>87</td>
<td>506</td>
<td>612</td>
<td>518</td>
<td>523</td>
<td>529</td>
<td>535</td>
<td>541</td>
<td>547</td>
<td>553</td>
</tr>
<tr>
<td>751</td>
<td>604</td>
<td>570</td>
<td>576</td>
<td>581</td>
<td>587</td>
<td>593</td>
<td>599</td>
<td>605</td>
<td>610</td>
<td>616</td>
</tr>
<tr>
<td>752</td>
<td>622</td>
<td>628</td>
<td>633</td>
<td>639</td>
<td>645</td>
<td>651</td>
<td>657</td>
<td>663</td>
<td>669</td>
<td>675</td>
</tr>
<tr>
<td>753</td>
<td>680</td>
<td>686</td>
<td>692</td>
<td>697</td>
<td>703</td>
<td>708</td>
<td>714</td>
<td>720</td>
<td>726</td>
<td>732</td>
</tr>
<tr>
<td>754</td>
<td>737</td>
<td>743</td>
<td>749</td>
<td>755</td>
<td>761</td>
<td>767</td>
<td>773</td>
<td>779</td>
<td>785</td>
<td>791</td>
</tr>
<tr>
<td>755</td>
<td>790</td>
<td>796</td>
<td>802</td>
<td>808</td>
<td>814</td>
<td>820</td>
<td>826</td>
<td>832</td>
<td>838</td>
<td>844</td>
</tr>
<tr>
<td>756</td>
<td>852</td>
<td>858</td>
<td>864</td>
<td>870</td>
<td>876</td>
<td>882</td>
<td>888</td>
<td>894</td>
<td>900</td>
<td>906</td>
</tr>
<tr>
<td>757</td>
<td>912</td>
<td>918</td>
<td>924</td>
<td>930</td>
<td>936</td>
<td>942</td>
<td>948</td>
<td>954</td>
<td>960</td>
<td>966</td>
</tr>
<tr>
<td>758</td>
<td>972</td>
<td>978</td>
<td>984</td>
<td>990</td>
<td>996</td>
<td>1002</td>
<td>1008</td>
<td>1014</td>
<td>1020</td>
<td>1026</td>
</tr>
<tr>
<td>759</td>
<td>824</td>
<td>830</td>
<td>836</td>
<td>842</td>
<td>848</td>
<td>854</td>
<td>860</td>
<td>866</td>
<td>872</td>
<td>878</td>
</tr>
<tr>
<td>760</td>
<td>883</td>
<td>889</td>
<td>895</td>
<td>901</td>
<td>907</td>
<td>913</td>
<td>919</td>
<td>925</td>
<td>931</td>
<td>937</td>
</tr>
<tr>
<td>761</td>
<td>938</td>
<td>944</td>
<td>950</td>
<td>956</td>
<td>962</td>
<td>968</td>
<td>974</td>
<td>980</td>
<td>986</td>
<td>992</td>
</tr>
<tr>
<td>762</td>
<td>998</td>
<td>1004</td>
<td>1010</td>
<td>1016</td>
<td>1022</td>
<td>1028</td>
<td>1034</td>
<td>1040</td>
<td>1046</td>
<td>1052</td>
</tr>
<tr>
<td>763</td>
<td>225</td>
<td>231</td>
<td>237</td>
<td>243</td>
<td>249</td>
<td>255</td>
<td>261</td>
<td>267</td>
<td>273</td>
<td>279</td>
</tr>
<tr>
<td>764</td>
<td>285</td>
<td>291</td>
<td>297</td>
<td>303</td>
<td>309</td>
<td>315</td>
<td>321</td>
<td>327</td>
<td>333</td>
<td>339</td>
</tr>
<tr>
<td>765</td>
<td>345</td>
<td>351</td>
<td>357</td>
<td>363</td>
<td>369</td>
<td>375</td>
<td>381</td>
<td>387</td>
<td>393</td>
<td>399</td>
</tr>
</tbody>
</table>

**Proportional Parts**

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>-------</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td><strong>850</strong></td>
<td>92</td>
<td>942</td>
<td>947</td>
<td>952</td>
<td>957</td>
<td>962</td>
<td>967</td>
<td>972</td>
</tr>
<tr>
<td><strong>851</strong></td>
<td>93</td>
<td>993</td>
<td>998</td>
<td>998</td>
<td>998</td>
<td>998</td>
<td>998</td>
<td>998</td>
</tr>
<tr>
<td><strong>852</strong></td>
<td>93</td>
<td>049</td>
<td>049</td>
<td>054</td>
<td>059</td>
<td>064</td>
<td>069</td>
<td>074</td>
</tr>
<tr>
<td><strong>853</strong></td>
<td>055</td>
<td>100</td>
<td>105</td>
<td>110</td>
<td>115</td>
<td>120</td>
<td>125</td>
<td>130</td>
</tr>
<tr>
<td><strong>854</strong></td>
<td>146</td>
<td>151</td>
<td>156</td>
<td>161</td>
<td>166</td>
<td>171</td>
<td>176</td>
<td>181</td>
</tr>
<tr>
<td><strong>855</strong></td>
<td>197</td>
<td>202</td>
<td>207</td>
<td>212</td>
<td>217</td>
<td>222</td>
<td>227</td>
<td>232</td>
</tr>
<tr>
<td><strong>856</strong></td>
<td>247</td>
<td>252</td>
<td>257</td>
<td>262</td>
<td>267</td>
<td>272</td>
<td>277</td>
<td>282</td>
</tr>
<tr>
<td><strong>857</strong></td>
<td>251</td>
<td>256</td>
<td>261</td>
<td>266</td>
<td>271</td>
<td>276</td>
<td>281</td>
<td>286</td>
</tr>
<tr>
<td><strong>858</strong></td>
<td>239</td>
<td>244</td>
<td>249</td>
<td>254</td>
<td>259</td>
<td>264</td>
<td>269</td>
<td>274</td>
</tr>
<tr>
<td><strong>859</strong></td>
<td>269</td>
<td>274</td>
<td>279</td>
<td>284</td>
<td>289</td>
<td>294</td>
<td>299</td>
<td>304</td>
</tr>
<tr>
<td><strong>860</strong></td>
<td>350</td>
<td>355</td>
<td>360</td>
<td>365</td>
<td>370</td>
<td>375</td>
<td>380</td>
<td>385</td>
</tr>
<tr>
<td><strong>861</strong></td>
<td>300</td>
<td>305</td>
<td>310</td>
<td>315</td>
<td>320</td>
<td>325</td>
<td>330</td>
<td>335</td>
</tr>
<tr>
<td><strong>862</strong></td>
<td>350</td>
<td>355</td>
<td>360</td>
<td>365</td>
<td>370</td>
<td>375</td>
<td>380</td>
<td>385</td>
</tr>
<tr>
<td><strong>863</strong></td>
<td>390</td>
<td>395</td>
<td>400</td>
<td>405</td>
<td>410</td>
<td>415</td>
<td>420</td>
<td>425</td>
</tr>
<tr>
<td><strong>864</strong></td>
<td>702</td>
<td>707</td>
<td>712</td>
<td>717</td>
<td>722</td>
<td>727</td>
<td>732</td>
<td>737</td>
</tr>
<tr>
<td><strong>865</strong></td>
<td>752</td>
<td>757</td>
<td>762</td>
<td>767</td>
<td>772</td>
<td>777</td>
<td>782</td>
<td>787</td>
</tr>
<tr>
<td><strong>866</strong></td>
<td>802</td>
<td>807</td>
<td>812</td>
<td>817</td>
<td>822</td>
<td>827</td>
<td>832</td>
<td>837</td>
</tr>
<tr>
<td><strong>867</strong></td>
<td>852</td>
<td>857</td>
<td>862</td>
<td>867</td>
<td>872</td>
<td>877</td>
<td>882</td>
<td>887</td>
</tr>
<tr>
<td><strong>868</strong></td>
<td>902</td>
<td>907</td>
<td>912</td>
<td>917</td>
<td>922</td>
<td>927</td>
<td>932</td>
<td>937</td>
</tr>
<tr>
<td><strong>869</strong></td>
<td>952</td>
<td>957</td>
<td>962</td>
<td>967</td>
<td>972</td>
<td>977</td>
<td>982</td>
<td>987</td>
</tr>
<tr>
<td><strong>870</strong></td>
<td>201</td>
<td>206</td>
<td>211</td>
<td>216</td>
<td>221</td>
<td>226</td>
<td>231</td>
<td>236</td>
</tr>
<tr>
<td><strong>871</strong></td>
<td>220</td>
<td>225</td>
<td>230</td>
<td>235</td>
<td>240</td>
<td>245</td>
<td>250</td>
<td>255</td>
</tr>
<tr>
<td><strong>872</strong></td>
<td>240</td>
<td>245</td>
<td>250</td>
<td>255</td>
<td>260</td>
<td>265</td>
<td>270</td>
<td>275</td>
</tr>
<tr>
<td><strong>873</strong></td>
<td>260</td>
<td>265</td>
<td>270</td>
<td>275</td>
<td>280</td>
<td>285</td>
<td>290</td>
<td>295</td>
</tr>
<tr>
<td><strong>874</strong></td>
<td>280</td>
<td>285</td>
<td>290</td>
<td>295</td>
<td>300</td>
<td>305</td>
<td>310</td>
<td>315</td>
</tr>
<tr>
<td><strong>875</strong></td>
<td>300</td>
<td>305</td>
<td>310</td>
<td>315</td>
<td>320</td>
<td>325</td>
<td>330</td>
<td>335</td>
</tr>
<tr>
<td><strong>876</strong></td>
<td>320</td>
<td>325</td>
<td>330</td>
<td>335</td>
<td>340</td>
<td>345</td>
<td>350</td>
<td>355</td>
</tr>
<tr>
<td><strong>877</strong></td>
<td>340</td>
<td>345</td>
<td>350</td>
<td>355</td>
<td>360</td>
<td>365</td>
<td>370</td>
<td>375</td>
</tr>
<tr>
<td><strong>878</strong></td>
<td>360</td>
<td>365</td>
<td>370</td>
<td>375</td>
<td>380</td>
<td>385</td>
<td>390</td>
<td>395</td>
</tr>
<tr>
<td><strong>879</strong></td>
<td>400</td>
<td>405</td>
<td>410</td>
<td>415</td>
<td>420</td>
<td>425</td>
<td>430</td>
<td>435</td>
</tr>
</tbody>
</table>

-92 942—95 408
## Five-Figure Logarithms: 900—950

Below is a table of five-figure logarithms from 900 to 950.

<table>
<thead>
<tr>
<th>Proportional Parts</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>900</strong></td>
<td>95</td>
<td>424</td>
<td>429</td>
<td>434</td>
<td>439</td>
<td>444</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>901</strong></td>
<td>427</td>
<td>432</td>
<td>437</td>
<td>442</td>
<td>447</td>
<td>452</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>902</strong></td>
<td>425</td>
<td>430</td>
<td>435</td>
<td>440</td>
<td>445</td>
<td>450</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>903</strong></td>
<td>509</td>
<td>574</td>
<td>578</td>
<td>583</td>
<td>588</td>
<td>593</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>904</strong></td>
<td>517</td>
<td>622</td>
<td>626</td>
<td>631</td>
<td>636</td>
<td>641</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>905</strong></td>
<td>607</td>
<td>674</td>
<td>679</td>
<td>684</td>
<td>689</td>
<td>694</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>906</strong></td>
<td>713</td>
<td>718</td>
<td>723</td>
<td>727</td>
<td>732</td>
<td>737</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>907</strong></td>
<td>761</td>
<td>766</td>
<td>771</td>
<td>775</td>
<td>780</td>
<td>785</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>908</strong></td>
<td>809</td>
<td>813</td>
<td>818</td>
<td>823</td>
<td>828</td>
<td>832</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>909</strong></td>
<td>850</td>
<td>856</td>
<td>861</td>
<td>866</td>
<td>871</td>
<td>876</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>910</strong></td>
<td>904</td>
<td>909</td>
<td>914</td>
<td>919</td>
<td>924</td>
<td>929</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>911</strong></td>
<td>923</td>
<td>928</td>
<td>933</td>
<td>938</td>
<td>943</td>
<td>948</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>912</strong></td>
<td>960</td>
<td>965</td>
<td>970</td>
<td>975</td>
<td>980</td>
<td>985</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>913</strong></td>
<td>993</td>
<td>998</td>
<td>1003</td>
<td>1008</td>
<td>1013</td>
<td>1018</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>914</strong></td>
<td>104</td>
<td>109</td>
<td>114</td>
<td>119</td>
<td>124</td>
<td>129</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>915</strong></td>
<td>142</td>
<td>147</td>
<td>152</td>
<td>157</td>
<td>162</td>
<td>167</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>916</strong></td>
<td>190</td>
<td>195</td>
<td>200</td>
<td>205</td>
<td>210</td>
<td>215</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>917</strong></td>
<td>237</td>
<td>242</td>
<td>247</td>
<td>252</td>
<td>257</td>
<td>262</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>918</strong></td>
<td>284</td>
<td>289</td>
<td>294</td>
<td>299</td>
<td>304</td>
<td>309</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>919</strong></td>
<td>322</td>
<td>327</td>
<td>332</td>
<td>337</td>
<td>342</td>
<td>347</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>920</strong></td>
<td>359</td>
<td>364</td>
<td>369</td>
<td>374</td>
<td>379</td>
<td>384</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>921</strong></td>
<td>420</td>
<td>425</td>
<td>430</td>
<td>435</td>
<td>440</td>
<td>445</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>922</strong></td>
<td>473</td>
<td>478</td>
<td>483</td>
<td>488</td>
<td>493</td>
<td>498</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>923</strong></td>
<td>520</td>
<td>525</td>
<td>530</td>
<td>535</td>
<td>540</td>
<td>545</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>924</strong></td>
<td>587</td>
<td>592</td>
<td>597</td>
<td>602</td>
<td>607</td>
<td>612</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>925</strong></td>
<td>619</td>
<td>624</td>
<td>629</td>
<td>634</td>
<td>639</td>
<td>644</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>926</strong></td>
<td>681</td>
<td>686</td>
<td>691</td>
<td>696</td>
<td>701</td>
<td>706</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>927</strong></td>
<td>755</td>
<td>760</td>
<td>765</td>
<td>770</td>
<td>775</td>
<td>780</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>928</strong></td>
<td>802</td>
<td>807</td>
<td>812</td>
<td>817</td>
<td>822</td>
<td>827</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>929</strong></td>
<td>848</td>
<td>853</td>
<td>858</td>
<td>863</td>
<td>868</td>
<td>873</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>930</strong></td>
<td>895</td>
<td>900</td>
<td>905</td>
<td>910</td>
<td>915</td>
<td>920</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>931</strong></td>
<td>942</td>
<td>947</td>
<td>952</td>
<td>957</td>
<td>962</td>
<td>967</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>932</strong></td>
<td>985</td>
<td>990</td>
<td>995</td>
<td>1000</td>
<td>1005</td>
<td>1010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>933</strong></td>
<td>004</td>
<td>009</td>
<td>014</td>
<td>019</td>
<td>024</td>
<td>029</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>934</strong></td>
<td>092</td>
<td>097</td>
<td>102</td>
<td>107</td>
<td>112</td>
<td>117</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>935</strong></td>
<td>140</td>
<td>145</td>
<td>150</td>
<td>155</td>
<td>160</td>
<td>165</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>936</strong></td>
<td>187</td>
<td>192</td>
<td>197</td>
<td>202</td>
<td>207</td>
<td>212</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>937</strong></td>
<td>239</td>
<td>244</td>
<td>249</td>
<td>254</td>
<td>259</td>
<td>264</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>938</strong></td>
<td>291</td>
<td>296</td>
<td>301</td>
<td>306</td>
<td>311</td>
<td>316</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>939</strong></td>
<td>344</td>
<td>349</td>
<td>354</td>
<td>359</td>
<td>364</td>
<td>369</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>940</strong></td>
<td>392</td>
<td>397</td>
<td>402</td>
<td>407</td>
<td>412</td>
<td>417</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>941</strong></td>
<td>439</td>
<td>444</td>
<td>449</td>
<td>454</td>
<td>459</td>
<td>464</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>942</strong></td>
<td>497</td>
<td>502</td>
<td>507</td>
<td>512</td>
<td>517</td>
<td>522</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>943</strong></td>
<td>550</td>
<td>555</td>
<td>560</td>
<td>565</td>
<td>570</td>
<td>575</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>944</strong></td>
<td>599</td>
<td>604</td>
<td>609</td>
<td>614</td>
<td>619</td>
<td>624</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>945</strong></td>
<td>652</td>
<td>657</td>
<td>662</td>
<td>667</td>
<td>672</td>
<td>677</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>946</strong></td>
<td>695</td>
<td>700</td>
<td>705</td>
<td>710</td>
<td>715</td>
<td>720</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>947</strong></td>
<td>743</td>
<td>748</td>
<td>753</td>
<td>758</td>
<td>763</td>
<td>768</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>948</strong></td>
<td>791</td>
<td>796</td>
<td>801</td>
<td>806</td>
<td>811</td>
<td>816</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>949</strong></td>
<td>844</td>
<td>849</td>
<td>854</td>
<td>859</td>
<td>864</td>
<td>869</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>950</strong></td>
<td>892</td>
<td>897</td>
<td>902</td>
<td>907</td>
<td>912</td>
<td>917</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: The table continues with logarithms from 920 to 950.
<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>950</td>
<td>97</td>
<td>77</td>
<td>77</td>
<td>77</td>
<td>78</td>
<td>78</td>
<td>79</td>
<td>79</td>
<td>79</td>
<td>79</td>
</tr>
<tr>
<td>951</td>
<td>91</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>86</td>
<td>87</td>
<td>87</td>
<td>88</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>952</td>
<td>94</td>
<td>91</td>
<td>91</td>
<td>92</td>
<td>92</td>
<td>92</td>
<td>93</td>
<td>93</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>953</td>
<td>95</td>
<td>95</td>
<td>95</td>
<td>96</td>
<td>96</td>
<td>97</td>
<td>97</td>
<td>97</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>954</td>
<td>98</td>
<td>00</td>
<td>00</td>
<td>01</td>
<td>01</td>
<td>01</td>
<td>01</td>
<td>01</td>
<td>01</td>
<td>01</td>
</tr>
<tr>
<td>955</td>
<td>99</td>
<td>01</td>
<td>01</td>
<td>02</td>
<td>02</td>
<td>02</td>
<td>02</td>
<td>02</td>
<td>02</td>
<td>02</td>
</tr>
<tr>
<td>956</td>
<td>02</td>
<td>03</td>
<td>03</td>
<td>04</td>
<td>04</td>
<td>04</td>
<td>04</td>
<td>04</td>
<td>04</td>
<td>04</td>
</tr>
<tr>
<td>957</td>
<td>01</td>
<td>06</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>958</td>
<td>13</td>
<td>14</td>
<td>14</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>959</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>960</td>
<td>22</td>
<td>29</td>
<td>29</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>961</td>
<td>37</td>
<td>27</td>
<td>27</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>962</td>
<td>37</td>
<td>32</td>
<td>32</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>963</td>
<td>36</td>
<td>30</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>964</td>
<td>41</td>
<td>42</td>
<td>41</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>965</td>
<td>41</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>966</td>
<td>41</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>967</td>
<td>41</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>968</td>
<td>41</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>969</td>
<td>41</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
</tr>
</tbody>
</table>

---

FIVE-Figure Logarithms: 950—1000

Proportional Parts

-97 772—99 996
The following abbreviations are used:—

D. = determination
v = volumetric
g = gravimetric
o = colorimetric
e = electrolytic
gv = gas-volumetric
p = potentiometric
m = micro

Absorbents for carbon dioxide, 506: for water, 508.
Absorption apparatus for the determination of carbon dioxide, 506, 507: coefficient, 59V.

Ammonia, D. of: in an ammonium salt (v), 244: with Nessler's reagent (e), 643.
Ammonium, D. of: as chloroplatinate (g), 491: by nitrometer (gv), 812.
Ammoniacal cuprous chloride reagent, 803.
Ammoniacal nickel cyanide reagent, 801.
Ammonium hexanitro-cerate, 301: purification of, 301, 302.
Ammonium molybdate reagent, 381, 390.
Ammonium sulphato-cerate, 301.

Analysis: elementary, samples and solutions for, 854: schemes for study of, 876, 878.

Anhydride, 506.

Anthraquinone, 444.

Antimony, D. of: as oxidised pyro-gallate (g), 439: as tetroxide (g), 435, 436: as trisulphide (g), 435, 438: by chloramine-T (v), 576: by iodine (v), 350, 351, 353: by potassium bromate (v), 369, 371: by potassium iodate (v), 362: by potassium iodide-pyridine method (c), 662, 663: by potassium permanganate (v), 363: in antimonates (v), 351: in type metal (v), 353.

Antimony electrode, 683: applications of, 683.

Bunte, 790: fused silica, 179; glass, 178; heating, 185; Hempel, 784: iron, 179; micro, for quantitative filtration, 823; miscellaneous, for micro-analysis: nickel, 179; Orsat-Lunge, 792; platinum, 179, 220; porcelain, 179; Shepherd, 794: silver, 179; U.S. Bureau of Mines, 800.

Arndt’s alloy, 248.

Aquametry, 698.

Aqueous vapour, pressure of, 782.

Arsenic, D. of: as ammonium uranyl arsenate (g), 433, 435; as magnesium pyrosilicate (g), 433, 434; as silver arsenate (v), 262; as trisulphide (g), 433, 434; by Gutzeit’s method (c), 656, 657-9; by inorganic method (c), 656, 657-9: by molybdenum blue method (c), 656, 657-61; by potassium bromate (v), 369, 370; by potassium iodate (v), 362; by Sanger-Black-Gutzeit method (c), 656, 659-61: in arsenates, by sodium thiosulphate (v), 351.

Arsenious oxide, purification of, 341: standard solution of, 341, 342.

Arsenate and arsenate in admixture, D. of (g), 434.

Ascarite, 506.

Arsenic, 123.

Ashless tablets, 210.

Atomic weights, table of, 841.

Availa.ble chlorine, 349, 350, 711.

Azolitmin, 55.

Back e.m.f., 130.

Bakelite apparatus, 180.


Balancing method, 604, 608.

Barium, D. of: (v), 267; as chromate (g), 471: as sulphate (g), 476, 480.

Barium hydroxide, standard solution of, 239.

Barium peroxide, analysis of, with potassium iodate (v), 364.

Barr- layer cells, 612.


Basic acetate method, 117.

Beaker cover, Fisher “speedy-vap”, 190.

Beakers, 178: covers for, 190: micro, 820.

Benedetti-Pichler drier, 819.

Benzonic acid, 237.
Index

Cadmium, D. of: as CdNH₂PO₄·H₂O or as pyrophosphate (g), 428, 430; as anthranilate (g), 428, 430; as metal (g), 522; as molybdate (g), 427, 428; as β-naphthaquinoline complex (g), 427, 428; as oxinate (g), 374; as pyridine thiocyanate (g), 428, 429; as quinaldinate (g), 428, 430; by oxine (v), 373.


Calcium, D. of: as carbonate (g), 411, 414; as molybdate (g), 478, 487; as oxide (urea hydrolysis method) (v), 392; as oxalate monohydrate (g), 411; (m), 437; as oxide (g), 411, 414; as tungstate (g), 478; by potassium permanganate (v), 282: in felspar, 590: in limestone or dolomite, 584, 587.


Carbon, oxidation of, 566.

Carbon dioxide in air, D. of (v), 242.

Calomel electrodes, 676-8, 696, 755.

Carbonates, carbonate oxycarbonate, D. in mixtures of (v), 242.

Carbosorb, 506.

Carbon in steel, D. of, 566.

Carbon tetrachloride, 331, 360.

Carbonic acid, D. of: as carbonate (g), 500; as oxinate (g), 428, 430; by oxine (v), 374; by phenylthiodyantol acid (g), 461, 462; by potassium ferrocyanide solution (p), 374; by pyridine-ammonium thiosalicylate standard method, 401, 403, 463; (v), 280: in steel, 576.

Colloid state, 104.

Colorimeters, 598: Duboscq type, 608: filter, 598: filters for, 614-16: hydroscopic, 600, 604: photo-electric, 598, 616-26: one-cell type, 616-20 (" Eel," 616; Hilger Biochem absorptiometer, 618; Bausch and Lomb monochromatic," 619; Unica G.P. photo-electric, 603); two-cell type, 620-5 (Hilger-Spekker absorptiometer, 620); Fisher spectrophotometer, 623; Coleman, model 8, 525: plunger type, 608.

Colorimetric analysis, 598; criteria for satisfactory, 641: general discussion of, 651: some general remarks upon, 641: visual, 598: theory of, 596.

Colorimetric titration, 607.

Colour change interval, 47.

Colour measurement, classification of methods of, 603.

Colour standards, permanent, 603, 606.


Common ion, quantitative effects of, 14.


Completeness of deposition, 132, 629.

Complex formation reactions, 38: general discussion of, 250: theory of, 71.


Concentration cells, 80.

Conductivity bridge, 723: Mullard, 723, 724, 725.

Conductivity cells, 721-2, 725: platinising electrodes of, 721; D. of cell constants of, 722, 723.

Conductivity water, preparation of, 178.

Conductometric titrations, 36, 718: apparatus and measurements, 720-5; applications of, 725-30; some experimental details for, 730-2.

Congo red, 55.

Control determination, 146.

Controlled cathode potential electrolysis, 150, 527.

Controlled potential at the cathode, applications of, 725-30: D. of copper in bronze, 519: D. of copper in copper base and tin base alloys, 527.

Controlled potential electro-analysis, 530: apparatus for automatic control of cathode potential, 530; D.C. output unit for, 532; high tension power pack for, 537; operation of apparatus, 536; potentiometer for, 536; valve voltage meter for, 534; various unit for, 532: general considerations, 536, 527; manual apparatus for, 137, 533.

Controlled potential in electrolytic separation of metals, theory of, 150, 528.

Copper, D. of: as benzoin oxime (g), 430, 432: as cuprous thiocyanate (g), 430, 431: as metal (e), 519: as pyridine thiocyanate (g), 430, 432: as quinaldinate (g), 431, 432: as salicylidoximate (g), 430, 432: by diethizone (e), 666, 667: by ethylendio-

Coulomb, 129.

Counter e.m.f., 130.

Counter ions, 105.

Cresol red, 55.


Crushing and grinding, 189.

Cubic centimetre, 191, 873.

Cupernon, 119.

Cuprn, 121.

Cuprous oxide, 803.

Cuprous sulphate-β-naphtol reagent, 803.

Current density, effect upon the character of the deposit, 135.

Cyanide, D. of: as silver cyanide (g), 434: by silver nitrate (v), 203.

Damping of balances, 170.

Dead-stop technique, 692, 704, 710.

Decantation, washing by, 216.

Decomposition potential, 129.

Decomposition voltage, 130: table of, 130.

Dehydrite, 506.

Depolariser, 517.

Deposit, character of, 135.

Deposition potentials, 134.

Depositions with controlled potential at the cathode, 527.

Desiccators, 180: desiccants for, 181; micro, 816-20; uses of, 181: vacuum, 181.

Dessicators, 606.

Deyarda’s alloy, 248.

Diethylsufolorescin, 76, 225.

Differential titration, 689, 690.

Diffusion current, 735, 739.

Digestion, 110.

Diiodomethylorescin, 254.

Dilution method, 603.

Dimethylglyoxime, 118, 417, 418: sodium salt, 118.

Diphenylation, 91, 203.

Diphenylbenzidine, 91, 293.

Diphénylacarbazole, 78, 264, 651.

Diphenylthiocarbazone, 644.

Direct weighing, 155.

Displacement titrations, 60, 728: borax with a strong acid, 67: potassium cyanide with a strong acid, 66; sodium carbonate with a strong acid, 67.

Dissociation constants, 5: calculations involving, 9, 10, 11: primary and secondary, 8: table of (acids and bases), 7: true or thermodynamic, 6.

Distribution coefficient, 140, 141: method, 140.

Dithio, 683.

Dithizone, 684, 685.

Dolomite, analysis of, 892.

Dolomite, analysis of, 552.

Drying of precipitates, 217.

Drying time, 190.

Drierite, 606.

Dropping mercury electrode (cathode), 734, 735, 736: advantages of, 736: assembly, 750-5.


Drying of precipitates, 217.

Dubosq-type colorimeter, 608: use of, 610.

Duplication method, 603, 607.

Electropode, 707.

Electric oven, 186.

Electrical units, 128.

Electrolysis due to wiping, 101, 816.

Electro-analytical theory of, 128, 528.

Electrochemical equivalent, 129: series, 80.

Electrode potentials, 78: change of, during titration of an oxidant and a reductant, 57: table of standard, 80.
Index


Electrode reactions, 131.

Electrode vessel, 515.

Electrolysis: controlled potential, 138, 527; internal, 138; rapid, 135, 519: slow, 135, 519: unit, 509; commercial forms of, 509, 510.

Electrolytic determination, 509.

Electrolytic dissociation, 1.

Electrolytes, weak, 3.

Electrolytic separation of metals, 134, 526: with controlled cathode potential, 136, 527, 529.

Elementary analysis. samples and solutions for, 854; schemes of, 876.

E.m.f., of voltaic cells, 81: polarisation, 130.

Emission spectrography, 96.

Emulsoids, 105, 106.


Emulsion, 76, 253.

Equilibrium constants, 4: of oxidation-reduction reactions, 83.

Equivalence point, 35, 47.

Equilibrat system, advantages of, 43.


Erioglaucine, 30, 304.

Eriochrome Black T, 387.

Eriochrome Pink T, 387.

Eriochrome Black T, 387.

Eriochrome Black T, 387.

Errors: absolute, 142: classification of, 143: curve, 144: determine or constant, 143: indeterminate or accidental, 144: in quantitative analysis, 142: in weighing, 161: minimisation of, 146: probable, 144: relative, 142: titration, 35.

p-Ethyloxyhrysozide, 360, 370.

Ethyl ether, extractions with 140: peroxide in, 517.

Ethylene diamine, 125: use in separation of copper and mercury, 126.

Explosion and combustion, methods of analysis, 804.

External indicators, 93, 292, 379.

Extinction, 793.

Extinction coefficient, 600, 601: molecular, 600, 601: specific, 600, 601.

Extraction of: of solid mixtures by solvents, 139: of solutions by solvents, 140.

Faraday, 129: laws of, 128.

Felspar, analysis of, 638.

Ferric alum indicator, 257.

Ferric iron, D. of: by mercurous perchlorate (v), 388: by potassium dichromate, after reduction (v), 293: by sodium thiosulphate (v), 306: by tannic acid (v), 310: by vanadium sulphate (v), 334 (see also under Iron).


Ferrimyanides, D. of: by sodium thiosulphate (v), 306.

Ferriac, 303 (see o-Phenanthroline ferrous sulphate).

Ferrous ammonium sulphate (Mohr's salt): purification of, 271.

Ferrous iron, D. of: by ceric sulphate (v), 307, 308: (m), 309: by manganic sulphate (v), 313: by potassium dichromate (v), 295: by potassium iodate (v), 366: by potassium permanganate (v), 276 (see also under Iron).

Ferrous and ferrie iron in an ore, D. of: 296.

Filter beakers, 206: use of, 207.


Filter papers, 207: use of, 208.


Filter tubes, 282: use of, 283.

Filters, 284, see Light Filters.


Flame photometry, 214: spectrophotometer, 216.


Flocculation values, 107.

Fluorescein, 76, 252.

Fluorides, D. of: as calcium fluoride (g), 494, 495: as lead chlorofluoride (v), 261: as triphenyl tin fluoride (g), 494: as triphenyl tin fluoride (g), 494, 495: by thorium nitrate (v), 393.

Fluorimeter, 635.

Fluorimetry, 635, 636: apparatus for, 636.

Fluorides, D. of: (g), 505: by thorium nitrate (v), 393.

Fluorine, 100.

Formates, D. of: as calcium fluoride (g), 484, 485: as lead chlorofluoride (g), 484: (v), 281: as triphenyl tin fluoride (g), 494, 495: by thorium nitrate (v), 393.

Fluoride, 100.

Fomates, D. of: by potassium permanganate (v), 289.

Fractional combustion: of gases, 770: pipette, 793.


Furfuryl, 118.

Furfuryl alcohol, 277.

Fusions: with potassium pyrosulphate, 557: with sodium carbonate, 558.
Index


Gas measuring vessels, calibration of, 783.

Gas volumes : automatic correction to N.T.P., 782: correction for temperature and pressure, 781.

Gas volumeter, Lung's, 782.

Gas volumetric analysis, 808.

Gauss's method of double weighing, 160.

Gels, 106.

Greases for glass stopcocks, 200.

German silver, 562.

Germantin in steel, D. of : as dioxide (g), 580.

Glass electrode, 684: determinations of, 685, 686.

Glassware, 178: cleaning of, 193.

Glass volumes: automatic correction to temperature and pressure, 781.

Graduated cylinders, 203.

Graduation, 16.

Gravimetric analysis, 397: calculations of, 398; forms in which elements and radicals are commonly precipitated, 101: micro-, 814: systematic, general discussion of, 419: technique of, 206; theory of, 100.

Gravimetric separations, simple : aluminium and chromium, 650; calcium and barium, 652; calcium and magnesium, 561, 585, 587; calcium and strontium, 592; calcium, strontium and barium, 553; iron and aluminium, 545, 546, 589; iron and chromium, 549, 550; manganese and zinc, 561; nickel and zinc, 551; sodium and potassium, 554, 569.

Gravimetric distinctions, 209.

Greece alphabet, 375.

Ground solution, 734.

Gun metal, analysis of, 581.

Half-wave potentials, 730, 741: of the sodium ion in N-potassium chloride, D. of, 702: of the zinc and manganese ions in N-potassium chloride, D. of, 784.

Halides, D. in admixture : by adsorption indicators (v), 256: by indirect method (v), 205.


Heating apparatus, 185.

Heinrich cylinders, 608.


Hempel-Winkler gas burette, 784.

Hemazethylenetetramine, 456.

Hot plates, 186.

Hydrazine, D. of : by potassium iodate (v), 306.

Hydrazine hydrate, 455, 456.


Hydrochloric acid, D. of : by thorium nitrate (v), 393.


Hydrogen ion concentration, 23: in buffer solutions, 30, 803; in hydrolysed salts, 27-30, 60-8 (see also under pH).

Hydrogen ion exponent, 233 (see also under pH).

Hydrogen ion concentration, 23: in buffer solutions, 30, 803; in hydrolysed salts, 27-30, 60-8 (see also under pH).


Hydrolyses constant, 27; and degree of hydrolysis, 27-30.

Hydroxides, precipitations at controlled pH, 115.

Hydroxyamine, D. of : by potassium bromate (v), 375.

Hydroxyhydrouryloxyarsionic acid, 123, 124.

Hydroxyquinoline, 126, 467: preparation of, 126.

Hydroxyquinoline, 119: determination of metals by, 571: precipitations with, 120.

Hypochlorites, 255: by direct method (v), 256.

Hypochlorites, D. of : by potassium iodate (v), 350: as silver chloride (g), 406.

Hypophosphites, D. of : as MgNH4PO4.6H2O or as magnesium pyrophosphato (g), 501: as mercuric chloride as mercurous chloride (g), 501.

Hypoosulphites, D. of : by thiocyanate solution (v), 260.

Ignition of crucibles, 212, 213: of precipitates, 217.
Iron and titanium in admixture, D. of, 321. 
Isopropyl ether, extraction with, 140. 
I.S.W.G., inches and millimetres, 875. 

Jones reductor, 222, 227: applications and limitations of, 278, 279: preparation of, 278. 
Journals of analytical chemistry, 850. 

Kilogram, international prototype, 153, 873. 
Kjeldahl-Gunning process, 249. 
Kjeldahl’s method for nitrogen, 458. 

Lambert’s law, 590. 
Lawrence Smith method, 591. 
Lead amalgam, preparation of, 321: use of, 321. 
Lead, D. of: as chromate (g), 420, 421: as dioxide (e), 520: as iodate (g), 420, 422: (v), 422: as molybdate (g), 420, 421: as salicylaldoximate (g), 420, 422: as sulphide (c), 664, 665: as sulphide (g), 420: by dithizone (c), 664, 665: by sodium thiosulphate (v), 347: in brass, 547, 557: in nickel silver, 562: in steel, 579: in tartaric acid (c), 665. 
Lead dioxide, analysis of (v), 546, 564. 
Lilichig’s method for cyanide, (v), 263. 
Light filters, 598, 614: choice of, 615, 616. 
Limestone or dolomite, analysis of, 582. 
Limiting cathode potential, 529 (see also Controlled potential electro-analysis). 
Limiting current, with dropping mercury cathode, 739, 740: factors affecting, 737. 
Liquid capacity, measures of: apothecaries (British), 874: apothecaries (U.S.A.), 874: Imperial or British, 273: U.S., 874. 
Literature of analytical chemistry, 846. 
Lithium, D. of: as sulphate (g), 460: in admixture with sodium and potassium, 490. 
Litmus, 54. 
Litre, 191, 373. 
Logarithms : five-figure, 886: four-figure, 884. 
Lovibond comparator, 839, 840. 
Lubricants for glass stopcocks, 200. 
Lunge gas volumeter, 782: nitrometer, 808. 

Macerated filter-paper, 210, 410. 
Magnesia mixture, 435. 
Magnesium, D. of: as MgNH4PO4·6H2O (g), 414, 418; (m), 856: as 2-salicylaldoximate (g), 381: as oxinate (g), 373, 481: as pyrophosphate (g), 414, 416: by oxine (v), 373: by titan yellow (e), 668, 669: in an aluminium alloy, 581: in felspar, 590: in limestone or dolomite, 596, 667: in Portland cement, 594.

Index 911

Ilkov's equation, 798. 
Incineration of filter paper, apart from the precipitate, 219: in the presence of the precipitate, 219. 
Indicator electrodes, 688: dropping mercury, 734-6: rotating micro, 736. 
Internal electrolysis, 138. 
International prototype kilogram, 153. 
Iodates, D. of: as silver iodide (g), 497. 
Iodides, D. of: as palladium iodide (g), 493: as silver iodide (g), 493: by potassium iodate (v), 301: by silver nitrate (v), 264: by Volhard’s method, 265. 
Iodometric method for standardising acids, 330. 
Iodometry and iodimetry, 328: detection of end point in, 330: general discussion of, 329. 
Iodine, purification by sublimation, 185. 
Iodine monochloride solution, preparation of, 303. 
Ion-electron method, 39. 
Ionic equations, for calculation of equivalents, 47. 
Ionic strength, 6. 
Ionisation constants of acids, 5: table of, 7. 
Nickel silver, analysis of, 562.
Nickel ware, 179.
Nitrates, D. of: as nitron nitrate (g), 505: by gas volumeter (gv), 809: by nitrometer (gv), 808: in Chili salt-petre (v), 248.
Nitrates, D. of: by ceric sulphate (v), 308: by chloramine-T (v), 377: by a-naphthylamine and sulphanylic acid (g), 644: by N-(1-naphthyl)-ethylene diamine and sulphanilic acid (g), 645: by potassium permanganate (v), 238.
Nitrogen, D. by Kjeldahl’s method (v), 248.
Nitron, 123.
A-MNitroso-N-phenanthol, 122.
Nitroso-R-salt, 655.
Nitrous acid: removal of, 518 (see also under Nitrites).
Normal solutions, 36, 37: preparation of, 45.
Normality, 43.
Note-book, 397.
N-Phenylanthranilic acid, 293, 303.
Ohm, 128: law of, 128.
Opacity, 600.
Organic precipitants, 117.
Orsat apparatus, 792.
Orsat-Lunge apparatus, 792: use of, 792-5.
Ortho-phenanthroline ferrous sulphate (see o-Phenanthroline ferrous sulphate).
Overvoltage, 132.
Osmic acid solution, 303.
Oxalates, D. of: as calcium carbonate (g), 502; as calcium oxide (g), 502; as calcium oxalate monohydrate (g), 507; as calcium oxalate (m), 507: by ceric sulphate (v), 307: by manganic sulphate (v), 286.
Oxidants, 89: equivalent weights of, 41: table of, 42.
Oxidation, 38: number method, 41.
Oxidation-reduction cells, 81.
Oxidation-reduction curve, 87.
Oxidation-reduction indicators, 90: table of, 92.
Oxidation-reduction titrations: change of potential during, 87: indicators for detection of end points in, 90-3: potentiometric methods for determining end points in, 93, 691, 709.
Oxidising agents, 41: table of, 42.
Oxine, 119: determination of metals by (v), 371: precipitations with, 120.
Palladium, D. of: as metal via palladous cyanide (g), 444: by dimethylglyoxime (g), 444, 445: by 2-cyclo-hexanedione dioxime (g), 444, 445.
para-Hydroxyphenylarsonic acid, 123, 479.
Parallax, errors due to, 200.
Parallel determinations, 146.
Partition coefficient, 140, 141.
Peptisation, 106, 107.
Perchlorates, D. of: as potassium perchlorate (g), 496, 497: as silver chlorate (g), 496.
Periodates, D. of: as silver iodate (g), 497.
Peroxides, D. of: by nitrometer or gas volumeter (gv), 810: by potassium iodate (v), 236.
Peroxides, D. of: by potassium permanganate (v), 236.
Peroxides, D. of: by potassium permanganate (v), 236.
o-Phenanthroline, 646, 647.
o-Phenanthroline ferrons sulphate, 90, 272, 293, 303.
Phenolphthalein, 54.
Phenol red, 55.
Phenosafranine, 76.
N-M-Phenylanthranilic acid, 293, 303.
Phenylthiohydantoic acid, 122.
Phosphates, D. of: as MgNH4PO4·6H2O or as magnesium pyrophosphate (g), 498; via ammonium phosphomolybdate (g), 496, 500; as molybdyl oxinate via ammonium phosphomolybdate (g), 380, 381: as ammonium phosphomolybdate (g), 380-1.
Phosphates, D. of: as MgNH4PO4·6H2O or as magnesium pyrophosphate (g), 501: by mercuric chloride as mercurous chloride (g), 601.
Phosphoric acid, action on indicators, 65, 66: D. in commercial acid (v), 246: neutralisation of, 54.
Phosphorus, D. of: (v) 380 (see Phosphates): in phosphor bronze, 562: in steel, 569.
Photo-cells, 611.
Photo-electric colorimeters, 611: commercial forms of, 616-25: one-cell types, 616-20: two-cell types, 620-5.
Photo-electric filter photometer method, 604, 611.
Photo-emissive cells, 611.
Platinum apparatus, 179: care and use of, 220: cleaning and preservation of, 221.
Potassium iodate solution: for standardisation of acids, 330; indicators for, 360; oxidising properties of, 358, 369; preparation of 0.02M., 361.


Potassium iodide-starch paper, preparation of, 349.

Potassium permanganate solution: application in alkaline solution, 329; discussion of substances for standardisation, 270; oxidising properties of, 288; permanence of, 275; preparation of 0.1N., 271; reduction of, 468; standardisation of, by arsenious oxide, 272; by ferrous ammonium sulphate, 275; by metallic iron, 274; by oxalic acid, 276; by potassium ferrocyanide (anhydrous), 274; by potassium tetroxalate, 275; by sodium oxalate, 278.

Potassium tetroxalate, 238.

Potassium thiocyanate solution: preparation of 0.1N., 250; standardisation of, 257.

Potassium titanyl oxalate, 650.

Potential mediators, 92.

Potentials: decomposition, 129, 130: electrode, 78; oxidation, 82, 83; standard or normal, 79, 80; standard oxidation, 82.

Potentiometer, 678; Tinsley general-utility, 678.

Potentiometric titrations, 36, 93, 673; differential method, 690; theory of, 93–4, 673–5.

Potentiometric titrations, experimental details for classical method, 688–91; neutralisation reactions, 690, 708; oxidation-reduction reactions, 691, 709; precipitation reactions, 601, 709.

Potentiometric titrations, simplified electrode systems and methods, 602–8: bimetallic system, 603; dead stop technique, 692; commercial apparatus, 889, 894–4.

Precipitants, organic, 117.

Precipitate: drying and ignition of, 217; effect of acids upon the solubility of, 20; effect of solvent upon the solubility of, 21; formation, 108; ignition of, 217–24; incineration of filter-paper apart from the, 219; incineration of the filter-paper in presence of, 217; purity of, 109; washing of, 111, 208, 215.

Precipitation, 112, 206; and supersaturation, 108; completeness of, 14; conditions of, 110; discussion of, 206; factors determining a successful analysis by, 100; fractional, 17, 112; of hydroxides, 113; of sulphides, 113; practical points concerning, 206.

Precipitation methods, 100.

Precipitation reactions, 36, 37, 697, 709, 729; theory of, 69.

Precision, 143.

Pregl drying block, 810, 821, 828; micro-desiccator, 815.
Index

Pressure bottle, 347.
Preventive solution, 269.
Primary standards, requirements of, 46.
Probable error, 144.
Probability curve, 144.
n-Propylarsonic acid, 123.
Protective colloid, 107.
Purification of substances, 184.
Pyridine, 124.
Pyrogallol, 125: in gas analysis, 802.
Pyrolusite (see Manganese dioxide).
Quartz (Vitreosil) filtering-crucibles, 213.
Quinaldinic acid, 124: recovery of, 125.
Quinhydrone electrode, 681: advantages of, 682: disadvantages of, 681, 682.
Radiator, 187.
Red lead, analysis of (v), 285, 346.
Redox processes, 39.
Reducing agents, 38, 39: equivalent weights of, 43: table of, 42.
Relative mean deviation, 142.
Residual current, 727, 730.
Residual process, 226.
Rest point, 155.
Rhoamine G6, 76.
Rhodizonic acid, sodium salt, 287.
Rider, 151.
Rose crucible, 465.
Salicylaldoxime, 121.
Salt bridge, 675, 722.
Salt effect, 17.
Salts, 3.
Samples, crushing and grinding of, 189: solution of, 189: weighing of, 189 (see also Analysed samples).
Saturated solutions of some reagents, 883.
Schemes of study, 876, 878.
Screened indicators, 66.
Screens, perforated, for crucibles, 222.
Selenium, D. of: as element (g), 442, 443: by potassium permanganate (v), 290: by sodium thiosulphate (v), 291.
Selenium and tellurium in admixture, D. of: (g), 441, 442, 443: (v), 291.
Shepherd apparatus, 794.
Significant figures, 147.
Silica apparatus, 179.
Silver apparatus, 179.
Silver coinage alloy, analysis of, 566.
Silver, D. of: as chloride (g), 422, 423: as metal (c), 524: by 0·1N ammonium thiocyanate (v), 251: in alloys (v), 257: in silver coinage alloys, 565.
Silver nitrate solution: preparation of, 251: standardisation of, with sodium chloride and potassium chromate indicator, 251: with sodium chloride and adsorption indicator, 251.
Silver reductor, 224: preparation of silver for, 224: use of, 225, 296, 309.
Silver-silver chloride electrode, 678.
Simple gravimetric analysis, 398: micro-, 835.
Snipe feather, 827.
Soap solution, preparation of standard, 383.
Soda lime, 506.
Sodium anthraquinone-β-sulphonate, 802.
Sodium thiosulphate, 334.
Sodium cobaltinitrite reagent, 478, 488.
Sodium, D. of: as magnesium uranyl acetate (g), 482, 483: as zinc uranyl acetate (g), 482, 483: as magnesium or zinc uranyl acetate (v), 387: as sulphate (g), 482: in felspar, 690.
Sodium diethylidithiocarbamate, 666.
Sodium diphenylamine sulphonate, 293, 294.
Sodium hyposulphite, 503: with sodium anthraquinone-β-sulphonate, 602.
Sodium peroxide, analysis of (v), 284.
Sodium thiosulphate, 284.
Sodium thiosulphate, anhydrous, as a primary standard, 354: preparation of, 354.

Sodium, D. of: 508.

Sol, 106.

Solder, analysis of, 563, 564.

Solubilities of inorganic substances, at various temperatures, table of, 506.

Solubility product, 47.

Storage of solutions, 204.

Supporting electrolyte, 734, 737, 738.

Suspensoids, 105, 106.

Systematic gravimetric analysis, 419.

Tannin, 123.

Tare, 181: for micro-analysis, 610.

Tartrazine, 257.

Tellurium, D. of: as dioxide (g), 442, 443: as element (g), 442, 443: by ceric sulphate (v), 310: by potassium dichromate (v), 310: by potassium permanganate (v), 310: in mixtures with selenium (g), 441: (v), 201.

Temperature, standard, 192: correction for 1-litre volumetric flasks, 192.

Test papers, 182.

Thallium, D. of: as thallous chromate (g), 477, 478: as thallous cobaltinitrite (g), 477, 478: by potassium iodate (v), 365.

Thermometric valve titrimeters, commercial, 694-8: use of, 710, 711.

Thiocyanate and chloride in admixture, D. of: (v), 365.

Thiocyanate, D. of: as barium sulphate (g), 498: by iodine (v), 354.

Thioglycollic acid, 646.


Sodium, D. of: 508.

Sulphate, D. of: 403: with agar-agar as coagulant, 404: with picric acid as coagulant, 408: by benzidine sulphate method (c), 666, 670.

Sulphates, D. of: 310.

Sulphate ion concentration, calculation of, in a saturated aqueous solution, 8, 10.

Sulphides, D. of: as barium sulphate (g), 498: by iodine (v), 355.

Sulphides, precipitation of, 113.

Sulphides, D. of: as barium sulphate (g), 498: by iodine (v), 354.

Sulphonaphthaleins, 65.


Sulphurous acid and sulphites, D. of: as silver thiocyanate (g), 493: as cuprous thiocyanate (g), 261: by potassium dichromate (v), 441: with picric acid as coagulant, 403: with agar-agar as coagulant, 404: with picric acid as coagulant, 408: by benzidine sulphate method (c), 666, 670.

Sulphates, D. of: 310.

Sulphide ion concentration, calculation of, in a saturated aqueous solution, 8, 10.

Sulphides, D. of: as barium sulphate (g), 498: by iodine (v), 355.

Sulphides, precipitation of, 113.

Sulphides, D. of: as barium sulphate (g), 498: by iodine (v), 354.

Sulphonaphthaleins, 65.
Titanium, D. of: as titania (g) via cupferron complex, 474; via para-
hydroxyphenylacrylonitrile acid complex, 474, 475; via selenious acid complex, 474, 475; via tannin and antipyrine complexes, 474; by cadmium re-
ductor and ceric sulphate (v), 228; by hydrogen peroxide (c), 449; by Jones reductor and potassium per-
manganate (v), 318; by liquid zinc amalgam and ferris ammonium sul-
phate (v), 320; by oxine (v), 374; in felspar, 590; in steel, 576.
Titan yellow, 668.

Titanous chloride solution, preparation of, 314; sulphate solution, preparation of, 315; standa-
drisation of, by ferrous ammonium sulphate (v), 316; by iron (v), 315.
Titanous salts, reducing properties of, 314.

Titration, 311; curves, 58, 59, 61, 63, 65, 67, 70, 88; error, 35; of box.
ax with a strong acid, 67; of potassium cyanide with 0. strong acid, 66; of sodium carbonate with a strong acid, 67.

Titration apparatus, commercial, 689, 694-8.

Titration methods, operation, 769; colori-
metric, 607; conductometric, 718; displacement, 66, 728; poten-
tiometric, 93, 673; precipitation, 66, 70, 77.

Transmission, 600, 601.

Troposolin O, 55.

Tungsten, D. of: as barium tungstate (g), 491, 492; as trioxide (g) via benzidine complex, 491; via tannin and anti-
pyryne complexes, 491, 492; as tussgl oxyinate (g), 491, 492; by lead amalgam and potassium per-
manganate (v), 321; in steel, 574.

Turbidimeter, 6315.

Turbidity method, 76; and end point, 77.

Tyndall effect, 105.

Type metal, D. of antimony and tin in (v), 353.

Units of area, 875; of length, 873; of mass, 874; of volume, 191, 873.

Universal indicators, 56.

Uranium, D. of: as uranoac acid (g), 470; via cupferron complex (g), 470, 471; by Jones reductor and potassium per-
manganate or ceric sulphate (v), 318; by oxine (g), 470, 471; (v), 470.

Urea, D. of: by nitrometer (gy), 612.

Vanadium, D. of: as mercurous vanadate (g), 469; as phosphotungstovanadic acid (c), 650, 651; as silver vanadate (g), 469, 470; by hydrogen peroxide (c), 650, 651; by Jones reductor and potassium per-
manganate (v), 319; by potassium iodate (v), 367; by sulphur dioxide and potassium per-

manganate (v), 319; in steel, 572, 581.

Vanadious (vanadium, II) salts, reductions with, 322.

Vanadious sulphate (VO\textsubscript{3}) : preparation of, 323; standardisation of, 324.

Vapour pressure of water, table of, at various temperatures, 782.

Vapour pressure of water, table of, at various temperatures, 782.

Vinegar, D. of acetio acid content of (v), 241.

Vitreosil filtering crucibles, 213.

Volhard procedure, 256, 258, 259; theory of, 73.

Volt, 129.

Voltaic cells, 81.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.

Volts, 129.
zirconium, D. of: as dioxide (g) via basic selenite, 476, 477; via para-hydroxyphenylarsenate (g), 476; via mandelate, 476, 477; via n-propylarsenate, 476; as normal selenito (g), 476; (v), 300; as pyrophosphate (g), 476, 477; in steel, 577.

zinc dust, evaluation of (gv), 512.

zinc spirals, amalgamated: preparation of, 225; use of, 225.