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A System of Chemical Analysis

(QUALITATIVE AND SEMI-QUANTITATIVE)

for the

Common Elements

by

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CALIFORNIA INSTITUTE OF TECHNOLOGY

NEW YORK

PRENTICE-HALL, INC.

PRENTICE-HALL CHEMISTRY SERIES

WENDELL M. LATIMER, PH.D., *Editor*

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70 FIFTH AVENUE, NEW YORK

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First Printing...January 1939
Second Printing...October 1940
Third Printing...January 1946
Fourth Printing...March 1949
Fifth Printing...August 1950

PRINTED IN THE UNITED STATES OF AMERICA

TO

ARTHUR AMOS NOYES

Preface

The system of analysis presented in this book is the result of an experimental investigation by the author and numerous associates which has been in progress for a period of over ten years, and which has had for its purpose the development of an analytical system which would provide not only reliable and sensitive qualitative information in regard to the constituents present in the material being analyzed, but also, without an undue expenditure of time or labor, sufficient quantitative information to eliminate in many cases the need for further quantitative determinations.

The practical value of the conventional system of qualitative analysis has been materially reduced by the advances which have been made in the technique of spectrographic methods, by the developments in the field of microchemistry, and by the increase in the number and use of specific organic reagents for the purely qualitative detection of the elements; especially is this true of those qualitative systems which provide relatively little quantitative information. And, although there has also been a corresponding activity in the development and study of highly precise methods for the quantitative determination of single constituents, practical experience has indicated that there is very frequently a demand for both qualitative and quantitative information regarding a given material or substance, but that the purpose for which the quantitative information is needed requires only approximate values and does not seem to justify the time and labor involved in carrying out the usual series of highly precise quantitative determinations.

This system of analysis is designed to meet this demand and consists, first, of a system of qualitative analysis, largely conventional in its methods, in which the separations of both groups and single elements have been studied and, where necessary, modified or changed until each constituent is detected and isolated without undue loss, but in which an effort has been made not to increase very materially the time required for the analysis over that necessary for properly carrying out a conventional qualitative system. In certain cases, where the procedures have of necessity been time-consuming or laborious in order that more quantitative separations might be obtained, simpler and more rapid, but less exact, optional procedures have been provided which can be used at the judgment

of the analyst. Distribution and distillation methods have been used for certain of the separations, not only because they have proved effective, but also because it seems that the traditional adherence to precipitation methods has prevented methods based upon other principles from being developed to their fullest extent. Sulfide separations are used frequently because in a surprising number of cases they were found to be much superior to alternative methods; the objectionable features of hydrogen sulfide as a laboratory reagent did not seem adequate justification for the use of less-effective analytical procedures.

A system for the separation of the various constituents having been developed, methods for the estimation of the amount of each of the constituents thus separated are provided. These methods, largely volumetric, have been selected primarily on the basis of rapidity and simplicity of technique in order that the estimation shall require a minimum of time. However, many of these methods are conventional quantitative determinations for the particular constituents and can be used for more accurate analyses if desired.

Considerable experimental data are presented in order to show both the effectiveness and the limitations of the various separations and estimations which have been studied; such data also serve to give the student a better perspective of analytical methods, to develop a more critical attitude on his part, and to stimulate his interest in carrying out similar studies. It is realized that the practical value of such a system as is described above is materially decreased by being restricted to the so-called "common elements"; however, adequate experimental data have not been collected at the present time to enable even the more important of the "rarer elements" to be included.

The material in this book has been used for several years in mimeographed form as the text for the course in analytical chemistry given in the sophomore year at the California Institute of Technology. In addition, as various portions of the system have been developed, they have been extensively tested by selected groups of students in this course. From the instructional point of view, the author has found that the correlation of a more exact system of qualitative analysis with the quantitative course presents certain advantages. The qualitative analysis which can be given in the freshman course in general chemistry is seldom adequate to provide the student with either a sufficient mastery of the technique of the subject to give him confidence in his experimental ability, or with

that valuable foundation of systematized inorganic chemistry which is so uniquely given by an intensive study of a qualitative system. This lack of a background of inorganic chemistry is likely to be emphasized at the present time because the trend, however desirable it may be, toward an extensive presentation of physio-chemical principles in the quantitative course necessarily limits the range of factual chemistry with which the student is made familiar. On the other hand, courses in qualitative analysis in the upper years are likely to be regarded as a continuation of the freshman subject and may fail to sustain the interest of the abler students.

In the system presented here, training in the precise measurements of volumetric and gravimetric analysis is provided in the preliminary preparation and standardization of the solutions required for the volumetric determinations. In addition, many of the single determinations which are commonly included in courses in quantitative analysis can be carried out by slight modifications of the systematic procedures; these modifications will be obvious or are suggested in notes to the procedures. Even when such single determinations are being carried out, it has been found of value for the student to have constantly before him the qualitative separations of that constituent and thus to acquire more familiarity with the treatment of complex substances and with the steps necessary for the elimination of interfering constituents.

Many of the standardization procedures and certain of the procedures for the estimation of a constituent have been discussed in considerable historical and experimental detail. This has been done in order that the student may appreciate that such methods are often the result of constant study over considerable periods of time, and that he may obtain a better appreciation of the numerous factors which may have to be considered in the experimental study of a method. In general, it has been found that the intensive study of a few well-chosen methods is of more value than a more diffused review of a wider field. An outline of a suggested course for one year is given in the Appendix.

It is believed that the advances which have been made in the content and presentation of the first-year college course in general chemistry is justification for the assumption that the student has acquired some familiarity with the laws of definite proportions and combining weights and even with the simple principles of the mass-action law. The author feels that the teachers of general-chemistry courses have a just cause for resentment in the assumption implicit

in many of the texts on analytical chemistry that so little of this material has been absorbed from the course in general chemistry. However, the author is not in sympathy with the concept that the courses in analytical chemistry, especially those in qualitative analysis, should serve primarily as an excuse for an exposition of the entire field of modern chemical theory. The physical principles underlying the procedures have been presented in this book only as and where they have been needed to explain the experimental observations and facts at hand. It is believed that there is an advantage in this close correlation between experiment and theory, even though the presentation of the theoretical material cannot be made as systematically as when it is collected in a separate section of the book.

Although a large amount of experimental work has been expended in the development and testing of this system of analysis, the author is aware that imperfections and limitations from both the technical and instructional points of view still exist. Because of this, any suggestions for improvement or notice of errors of procedure or text will be received with genuine appreciation.

ERNEST H. SWIFT

Acknowledgments

The author wishes, first, to acknowledge his great indebtedness to Arthur A. Noyes, late Professor of Chemistry at the California Institute of Technology, to whom this book is dedicated. He not only gave freely of advice and assistance during a large part of the experimental development but also was a constant source of inspiration and encouragement. With his consent and coöperation, many of the methods used by Professor Noyes in his *Qualitative Chemical Analysis* were made the basis for the study of the more quantitative separations required in this system of analysis and frequently have been adopted with little modification. In addition, the author was so fortunate as to have been among those associated with Professor Noyes and with Professor W. C. Bray in the experimental development of their *System of Qualitative Analysis for the Rare Elements;* any merit which this book may possess can reflect in only a small measure the value of that association and experience.

It would have been impossible to have carried out the experimental work involved in the development of this system of analysis without the aid which has been given by a large number of assistants and students. An attempt has been made to acknowledge this assistance specifically in the discussion of the various procedures and methods. The author is also grateful to those of his classes who have used this material in preliminary mimeographed form for their spirit of coöperation and for many valuable suggestions. In addition, certain sections of this book have been so influenced by the advice, experience, or experimental work of certain associates that it is desired to mention these more general contributions here. These sections and those contributing to them are as follows: Preparation of the sample and solution, Mr. J. B. Hatcher; precipitation and separation of the Copper and Tin Groups, Mr. R. C. Aussieker; analysis of the Tin Group, Dr. Chester Wilson and Dr. R. C. Barton; analysis of the Ammonium Sulfide Group, Dr. R. C. Barton; analysis of the Alkaline Earth and Alkali Groups, Dr. Carter Gregory; and the analysis for the acidic constituents, Mr. Theodore Vermeulen, Mr. R. W. Dodson, Mr. D. K. Beavon, and Mr. R. N. Wimpress.

Dr. Charles D. Coryell, Dr. Clifford S. Garner, Mr. R. W. Dodson, and Mr. J. B. Hatcher have each read a large portion or all of the manuscript and have made many valuable contributions.

The index has been prepared by Mr. J. B. Hatcher, who has also rendered very valuable assistance in preparing the manuscript for the printer and in reading the proof.

The author wishes to express his appreciation to Professor T. H. Morgan for his kindness in having made available laboratory space in the Kerckhoff Marine Biological Laboratory of the California Institute of Technology at Corona del Mar, California. Much of the experimental work has been carried on there in the summer periods under exceptionally favorable surroundings; the friendly coöperation of Professor G. E. MacGinitie and the members of that laboratory has contributed to the pleasant associations of those periods.

ERNEST H. SWIFT

Contents

Part I

THE PREPARATION OF STANDARD SOLUTIONS

PROCEDURE		PAGE
	THE ANALYTICAL BALANCE	3
	Principles and Construction of the Analytical Balance	3
	The Use of the Analytical Balance	8
	The Determination of the Point of Rest	8
I.	Method of Long Swings	10
II.	Method of Short Swings	12
III.	The Determination of the Sensitivity of a Balance	13
	Methods of Weighing	14
	The Correction for Buoyancy	16
IV.	The Calibration of a Set of Weights	16
	General Rules for the Use of the Balance	21
	VOLUMETRIC METHODS OF ANALYSIS	22
	General Discussion	22
	Precipitation Methods of Volumetric Analysis	26
V.	The Preparation of a Standard Silver Nitrate Solution	26
VI.	The Preparation and Standardization of a Thiocyanate Solution	32
	The Applications of Precipitation Methods	46
	Oxidation and Reduction Methods of Volumetric Analysis	47
	Discussion	47
	Permanganate Methods of Volumetric Analysis	53
VII.	The Preparation of a Permanganate Solution	59
VIII.	The Standardization of Permanganate Solutions	60
IX.	The Preparation and Standardization of Ferrous Sulfate Solutions	66
	The Applications of Permanganate Methods	67
	Iodometric Methods of Volumetric Analysis	68
	Discussion	68

PROCEDURE		PAGE
X.	The Preparation of Iodine Solutions	69
XI.	The Preparation of Starch Solutions	70
XII.	The Standardization of Iodine Solutions	71
XIII.	The Preparation of Thiosulfate Solutions	77
XIV.	The Standardization of Thiosulfate Solutions	80
	The Applications of Iodometric Methods	84
	The Use of Standard Solutions of Other Oxidizing Agents in Volumetric Analysis	84
	The Use of Oxidation-Reduction (Potential) Indicators in Volumetric Analysis	85
	Neutralization (and Displacement) Methods of Volumetric Analysis	89
	General Discussion	89
	The Preparation of Standard Solutions of Acids and Bases	97
XV.	The Preparation of Carbonate-Free Solutions of Sodium Hydroxide	99
XVI.	The Standardization of Sodium Hydroxide Solutions	100
XVII.	The Preparation and Standardization of Hydrochloric Acid Solutions	103
	The Applications of Neutralization and Displacement Methods	109
	GRAVIMETRIC METHODS OF ANALYSIS	110
	General Principles of Gravimetric Methods	110
	I. Factors Affecting the Solubility of the Precipitate	110
	II. (1) Factors Affecting the Physical Characteristics of the Precipitate	116
	(2) Factors Affecting the Composition and Purity of the Precipitate	119
	III. Factors Affecting the Composition and Stability of the Weighed Precipitate	128
	The Operations of Gravimetric Analysis	132
	The Filtering of Precipitates	132
	The Washing of Precipitates	137
XVIII.	The Gravimetric Standardization of a Hydrochloric Acid Solution	139

Part II

THE SYSTEM OF ANALYSIS FOR THE BASIC CONSTITUENTS

PROCEDURE		PAGE
	The Preparation of the Sample, Preliminary Observations, and Preparation of the Solution for the Analysis	153
1.	Preparation of the Sample	153
2.	Treatment of Solutions or Suspensions	157
3.	Preliminary Observations and Tests	158
4.	The Elimination of Organic Material	166
	Preparation of the Solution for the Analysis	169
	General Discussion of the Solution of Solid Substances	169
5.	Treatment of the Sample with Nitric Acid	171
6.	Treatment of the Sample with (1) Hydrochloric and (2) Hydrochloric and Nitric Acids	178
7.	(1) Treatment of the Sample with Perchloric Acid; (2) Detection and Estimation of Silica by the Use of Hydrofluoric Acid	182
8.	Fusion of the Sample with Sodium Carbonate	189
	Separation of the Basic Constituents into Groups	193
	General Discussion of the Group Separations	193
	Precipitation of the Hydrogen Sulfide Group and Separation of the Copper and Tin Groups	197
11.	Precipitation of the Hydrogen Sulfide Group	197
12.	Separation of the Copper Group from the Tin Group	211
13.	Precipitation of the Tin Group	216
	The Analysis of the Copper Group	221
21.	Solution of the Copper Group Sulfides in Nitric Acid	221
22.	Detection and Precipitation of Silver	223
23.	Estimation of Silver	226
24.	Precipitation of Lead	229
25.	Estimation of Lead	232
26.	Precipitation of Bismuth and Detection of Copper	236
27.	Estimation of Bismuth	238
28.	Precipitation and Estimation of Copper	242
29.	Detection of Cadmium	247
30.	Estimation of Cadmium	249

PROCEDURE PAGE

ANALYSIS OF THE TIN GROUP ... 251

General Discussion of Methods for the Analysis of the Tin Group ... 251
41A. Optional Method for the Analysis of the Tin Group ... 254
41. Solution of the Tin Group Sulfides ... 256
42. Separation and Detection of Arsenic ... 258
43. Estimation of Arsenic ... 263
44. Precipitation of Mercury ... 264
45. Estimation of Mercury ... 267
46. Precipitation of Antimony ... 269
47. Estimation of Antimony ... 270
48. Detection and Precipitation of Tin ... 274
49. Estimation of Tin ... 275

PRECIPITATION OF THE AMMONIUM SULFIDE GROUP; SEPARATION OF IRON; REMOVAL OF PHOSPHATE; AND SEPARATION OF THE ALUMINUM AND ZINC GROUPS ... 281

51. Precipitation of the Ammonium Sulfide Group ... 281
52. Detection and Separation of Iron ... 291
53. Iodometric Estimation of Iron ... 298
53A. Optional Method for the Estimation of Iron by Titration with Permanganate ... 300
54. Removal of Phosphate ... 305
55. Separation of the Zinc and Aluminum Groups ... 309

THE ANALYSIS OF THE ZINC GROUP ... 321

61. The Precipitation and Separation of Zinc as Sulfide ... 321
62. Estimation of Zinc ... 331
63. Precipitation of Nickel and Cobalt (and Iron), and the Separation of Iron from Nickel and Cobalt ... 332
64. Separation of Nickel and Cobalt ... 336
64A. Optional Method of Detecting Nickel and Cobalt ... 340
65. Estimation of Nickel ... 342
66. Estimation of Cobalt ... 344

THE ANALYSIS OF THE ALUMINUM GROUP ... 347

71. Destruction of Oxalate, Precipitation of Manganese, and Detection of Chromium ... 347
72 Estimation of Manganese ... 351
73. Precipitation of Aluminum ... 354
74. Estimation of Aluminum ... 356
75. Estimation of Chromium ... 358

PROCEDURE PAGE

THE ANALYSIS OF THE ALKALINE EARTH GROUP 361

81. Precipitation of the Alkaline Earth Group 361
The Separation of the Alkaline Earth Group Elements. 366
82. Precipitation of Barium 368
83. Estimation of Barium 370
84. Precipitation of Strontium 372
85. Estimation of Strontium 373
86. Precipitation of Calcium 375
87. Estimation of Calcium 378
88. Precipitation of Magnesium 380
89. Estimation of Magnesium 381

THE ANALYSIS OF THE ALKALI GROUP 385

91. The Detection of the Alkali Group and Estimation of the Total Amount of Sodium and Potassium Present 385
92. Precipitation of Potassium 389
93. Estimation of Potassium 393
94. Precipitation of Sodium 394
95. Estimation of Sodium 395
96. Detection and Estimation of Ammonia 401

PART III

THE SYSTEM OF ANALYSIS FOR THE ACIDIC CONSTITUENTS

THE ANALYSIS OF THE ACIDIC CONSTITUENTS 409

General Discussion 409
111. Preparation of a Solution for the Analysis of the Acidic Constituents 413
Preliminary Tests for Certain Groups of the Acidic Constituents 415
112. Detection of Oxidizing Anions 415
113. Detection of Reducing Anions 417
114. Detection of Constituents of the Cyanide, Halide, and Oxy-Halogen Groups 418
115. Detection of Sulfate, Sulfite, Oxalate, Fluoride, or Chromate 420

THE ANALYSIS FOR SULFIDE, CYANIDE, AND SULFITE 422

121. Volatilization and Detection of Sulfide and Cyanide .. 422
122. Separation and Estimation of Sulfide 426
123. Detection and Estimation of Cyanide 427
124. Separation and Estimation of Sulfite 429

PROCEDURE PAGE

THE ANALYSIS FOR FERROCYANIDE AND FERRICYANIDE . . 433

131. Precipitation of Ferrocyanide and Ferricyanide 433
132. Separation and Detection of Ferrocyanide and Ferricyanide 435
133. Estimation of Ferrocyanide 438
134. Estimation of Ferricyanide 440

THE ANALYSIS OF THE HALIDE GROUP 443

141. Precipitation of the Halide Group 443
142. Metathesis of the Silver Halide Group Precipitate by Sulfide 446
143. Detection and Separation of Iodide and Detection of Thiocyanate 448
144. Estimation of Iodide 452
145. Elimination of Thiocyanate (and Iodide) 452
146. Detection and Separation of Bromide 455
147. Estimation of Bromide 457
148. Detection and Estimation of Chloride 457

THE ANALYSIS OF THE OXY-HALOGEN GROUP 459

151. Precipitation of the Oxy-Halogen Group 459
152. Separation and Estimation of Hypochlorite 461
153. Detection and Estimation of Perchlorate 464
154. Detection of Periodate 466

THE ANALYSIS OF THE PHOSPHATE GROUP 469

161. Precipitation of the Phosphate Group 469
162. Separation of Phosphate and Arsenate from Arsenite and Oxalate 471
163. Detection and Estimation of Arsenate 473
164. Detection of Phosphate 474
165. Detection of Arsenite 475
166. Precipitation of Oxalate 476

THE DETECTION AND ESTIMATION OF SULFATE AND OF FLUORIDE 478

171. Precipitation of Sulfate 478
172. Precipitation of Fluoride 480

THE ANALYSIS OF THE SODIUM CARBONATE SOLUTION FOR NITRATE, NITRITE, BORATE, AND ACETATE 483

181. Detection and Estimation of Nitrate and Nitrite 483
182. Detection and Estimation of Nitrite 486
183. Detection of Borate 488
184. Detection of Acetate 490

PROCEDURE PAGE

THE ANALYSIS OF THE RESIDUE FROM THE SODIUM CARBONATE TREATMENT ... 493

General Discussion ... 493

191. Detection of Sulfide and Cyanide in the Sodium Carbonate Residue ... 493

192. Detection of the Halides in the Sodium Carbonate Residue ... 495

193. Detection of Borate in the Sodium Carbonate Residue. 497

THE ANALYSIS OF THE ORIGINAL MATERIAL FOR CARBONATE ... 499

201. Detection and Estimation of Carbonate ... 499

APPENDIX

A SUGGESTED COURSE OF INSTRUCTION ... 505

QUESTIONS AND PROBLEMS ... 509

The Analytical Balance ... 509
Accuracy, Precision, Errors, and Significant Figures ... 512
Volumetric Methods of Analysis ... 515
Gravimetric Methods ... 530
Sulfide Precipitations and Separations ... 533
Hydroxide Precipitations and Separations ... 535
Miscellaneous Problems ... 536

TABLES ... 539

I. The Solubility-Product Values of Certain Slightly Soluble Salts ... 539
II. Molal and Formal Reduction Potentials ... 540
III. The Approximate Precipitation *p*H and Solubility Products of the Oxides and Hydroxides of Certain Elements ... 544
IV. Ionization Constants of Acids and Bases ... 545
V. Dissociation Constants of Certain Complex Ions. 546
VI. International Atomic Weights ... 547

REAGENTS AND CHEMICALS ... 548

Solutions ... 548
Solids ... 552
Test Solutions ... 552

EQUIPMENT ... 559

INDEX ... 563

Tabular Outlines

OUTLINE		PAGE
I.	Preparation of the Sample, Preliminary Observations, and Preparation of the Solution	152
II.	Separation of the Basic Constituents into Groups	194
III.	Precipitation of the Hydrogen Sulfide Group and Separation of the Copper and Tin Groups	196
IV.	The Analysis of the Copper Group	220
V.	The Analysis of the Tin Group	252
V-A.	Optional Method for the Analysis of the Tin Group	254
VI.	Precipitation of the Ammonium Sulfide Group; Separation of Iron; Removal of Phosphate; and Separation of the Aluminum and Zinc Groups	280
VII.	The Analysis of the Zinc Group	320
VIII.	The Analysis of the Aluminum Group	346
IX.	The Analysis of the Alkaline Earth Group	360
X.	The Analysis of the Alkali Group	386
XI.	Separation of the Acidic Constituents into Groups	410
XII.	Preliminary Tests for Certain Groups of the Acidic Constituents	415
XIII.	The Analysis for Sulfide, Cyanide, and Sulfite	421
XIV.	The Analysis for Ferrocyanide and Ferricyanide	432
XV.	The Analysis of the Halide Group	442
XVI.	The Analysis of the Phosphate Group	468
XVII.	The Analysis of the Sodium Carbonate Solution for Nitrate, Nitrite, Borate, and Acetate	484
XVIII.	The Analysis of the Residue from the Sodium Carbonate Treatment	492

Part I

THE PREPARATION OF STANDARD SOLUTIONS

The Analytical Balance

PRINCIPLES AND CONSTRUCTION OF THE ANALYTICAL BALANCE

Discussion. The analytical balance is an instrument for comparing masses, and "weighing" is essentially the operation of making a comparison of the mass of an unknown object with the known mass of certain "weights."[1]

The balance consists in principle of a horizontal lever, known as the beam, supported at its center on an agate knife edge (the central knife edge) and carrying at each end agate knife edges (the terminal knife edges) which support the pans on which the objects and weights are placed. As the pans which carry the object and weights are flexibly supported on the terminal knife edges, it follows that applying a load to the pan is the same as concentrating this load at the terminal knife edge. Therefore, when an object O is placed on a pan, a rotational moment, OL, is produced (where L is the distance from the point of support, or central knife edge, to the terminal knife edge supporting the applied load). When the object is balanced by applying weights to the opposite pan, an equal and opposing moment, WL_2, will have been produced, and

$$OL_1 = WL_2. \tag{1}$$

---

[1] To be exact, distinction should be made between the *mass* and the *weight* of a body. The mass M of an object is the quantity of matter of which it is composed, whereas the weight W is the force resulting from the attraction of gravity between this mass and that of the earth; the relation between them is expressed by the equation

$$W = Mg, \tag{1}$$

where g is the gravitational constant.

As g may vary at different locations on the earth's surface, it is seen that W can vary, and that it is the mass which it is desired to determine. In using the balance, the weight of an object, W_1, is usually compared with the weight, W_2, of certain standard masses or "weights." However, at a given location

$$W_1 = M_1 g, \tag{2}$$

and

$$W_2 = M_2 g. \tag{3}$$

It therefore follows that the weight is always directly proportional to the mass and that when $W_1 = W_2$, then $M_1 = M_2$ and a comparison of masses is made. It has become so customary to designate the process of making this comparison as "weighing" and to speak of the mass as the weight that hereafter the term *weight* will be used to designate mass.

If L_1 and L_2 are made equal, it follows that $O = W$. In order to protect the knife edges from damage when the instrument is not in use, means are provided for raising the beam and pans from the knife edges; this arresting mechanism is controlled by means of the milled head labeled "beam-arrest control" shown in Fig. 1. Means are also provided for arresting the motion of the pans, and this mechanism is

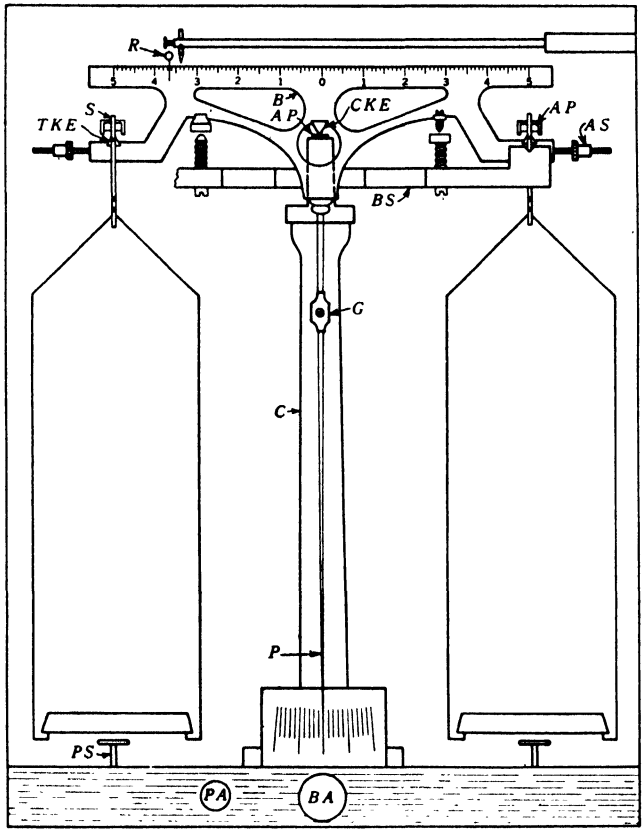

Fig. 1. The Essentials of the Analytical Balance. *BA*—beam-arrest control; *C*—column or post; *B*—beam; *P*—pointer; *G*—movable weight for adjusting sensitivity; *R*—rider; *TKE*—terminal knife edge, *CKE*—central knife edge; *S*—stirrup; *AP*—agate plate; *BS*—beam support; *PS*—pan support; *AS*—adjusting screw.

controlled by the button labeled "pan-arrest control." In some balances these controls are combined.

It is obvious that the essential parts of the balance are the beam and knife edges, and the design and construction of these largely determine the qualities of the balance. The principal requirements of a good beam are rigidity and strength with minimum weight, and these

conflicting qualifications have led to much research both as to the design and the material used in its construction. Various designs can be noted by reference to the catalogues of balance manufacturers. The materials most commonly used at present are aluminum alloys and brass or phosphor-bronze alloys.

The material used for the knife edges is a special grade of agate, used because of its hardness, durability, and resistance to corrosion. The central and terminal knife edges bear against agate plates set in the "post" and in the pan "stirrups," respectively.

The relative positions of the knife edges are of fundamental importance in determining the performance of the balance. First, and obviously, the central knife edge or point of support should be above the center of gravity of the beam system in order for it to be in stable equilibrium; also, as will be shown later, the distance between these two points is an important factor in determining the "sensitivity," that is, the response of the balance to a given difference in the load on the pans. The sensitivity is conventionally measured in terms of the deflection of the pointer produced by an excess in weight of 1 milligram on either pan. Referring to Fig. 2, it is seen that the sensitivity, S, can be expressed in more general terms as

$$S = \frac{\Delta r}{w}, \qquad (2)$$

where Δr is the change in the point of rest upon adding an excess of weight, w, to either pan. Second, the knife edges should be parallel to each other and perpendicular to the plane of rotation of the beam in order to avoid excessive frictional effects and possible variation in arm length as the beam oscillates. Third, the knife edges should be in the same horizontal plane in order that the sensitivity of the balance remain constant with varying loads. That this is true can be seen from the following analysis of the factors determining the sensitivity of the balance.

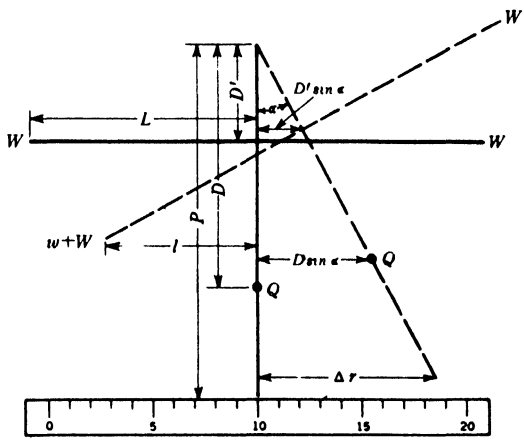

Fig. 2. Principles of the Balance.

In Fig. 2 are shown the fundamentals of a balance system. Let Q represent the weight of the beam and unloaded pan system with the

center of gravity in the position shown; W is the weight applied to each pan and w is the excess of weight applied to one pan; α is the angle of deflection made by the rotating beam; L is the arm length; D is the distance from the point of support to the center of gravity of the beam system, while D' is the distance from the point of support to the center of gravity of the applied weights. This latter center of gravity is obviously on a line joining the two terminal knife edges, since, owing to the fact that the pans are flexibly suspended from the terminal knife edges, the pan load can be considered as centered at the suspending knife edge. It is apparent that as w is applied, a moment equal to w times its horizontal distance from the point of support will be set up which will cause displacement of the beam system until the moment due to the weight Q times its horizontal distance from the point of support plus that due to $2W$ times its horizontal distance from the point of support becomes equal to the displacing moment. Referring to Fig. 2, the displacing moment due to w is seen to be

$$wl, \tag{3}$$

and the restoring moments will be

$$QD \sin \alpha \tag{4}$$

and

$$2WD' \sin \alpha. \tag{5}$$

At equilibrium the displacing moments must equal the restoring moments, and therefore

$$wl = QD \sin \alpha + 2WD' \sin \alpha. \tag{6}$$

For very small angles, which can be justifiably assumed in this case, as the actual deflections of a balance are relatively small, l approaches L and the value of sin α approaches that of tan α. Therefore Equation 5 can be rewritten as follows:

$$wL = \tan \alpha(QD + 2WD'). \tag{7}$$

As previously shown, the sensitivity, S, of the balance can be expressed in terms of the applied excess weight and the deflection, Δr, of the pointer as follows:

$$S = \frac{\Delta r}{w},$$

and from Fig. 2 it is seen that

$$\tan \alpha = \frac{\Delta r}{P}, \tag{8}$$

where P is the length of the pointer, and therefore it follows that

$$\tan \alpha = \frac{Sw}{P}. \tag{9}$$

Substituting this expression for tan α in Equation 7, the following general formula for the sensitivity of the balance is obtained:

$$S = \frac{LP}{(QD + 2WD')}. \tag{10}$$

An inspection of this equation shows that if the terminal knife edges are in the same plane with the central knife edge, then D' becomes zero, and the equation is simplified to the form

$$S = \frac{LP}{DQ}. \tag{11}$$

This shows that the sensitivity is directly proportional to the arm length, inversely proportional to the distance from the point of support to the center of gravity and to the weight of the beam system, but *independent* of the applied load. If the terminal knife edges are below the central knife edge, then, as shown in Equation 10, the sensitivity becomes *less* as the load ($2W$) is increased. If the terminal knife edges are *above* the central knife edge or point of support, Equation 10 has the form

$$S = \frac{LP}{(QD - 2WD')}, \tag{12}$$

and it is seen that as $2W$ is increased, the sensitivity increases, until $2WD'$ becomes equal to QD, when it becomes infinite and the balance becomes unstable.

From these considerations it would appear that if the balance is constructed with the terminal knife edges in a plane with the central knife edge, the sensitivity would remain constant; however, owing to bending of the beam with the applied load and to frictional forces, the sensitivity would be likely to decrease. Because of this, in manufacturing practice the terminal edges are often placed slightly above the central one, and occasionally balances will be found in which the sensitivity may actually increase with applied load. A means of changing the sensitivity is provided by the adjustable weight on the pointer, which by being shifted changes the value of D. Increasing the sensitivity of balances by increasing the arm length, L, is limited practically by the mechanical difficulty in building a

rigid beam of great length and light weight, and by the fact that the period of oscillation of the balance increases as the arm length is increased; this last increases the time required for making a weighing.

THE USE OF THE ANALYTICAL BALANCE

P. I. The Determination of the Point of Rest

Discussion. The first operation in the use of the balance is the determination of the "*point of rest*," that is, the reading of the pointer when the beam assembly is released and has assumed its equilibrium position.[2] The obvious method of doing this would be to set the beam in motion, allow it to come to rest, and then carefully observe the position of the pointer on its scale. Such a static method is obviously too time-consuming for practical use, and in addition small frictional effects might cause the beam to stop at other than its exact equilibrium position. Because of this, dynamic methods of determining the point of rest are used. The method most commonly described, which may be termed the "long swing method," consists in setting the beam in motion so that the pointer swing covers from 5 to 10 divisions on the scale, and then making a series of readings of the extreme points of the swings. An odd number of readings, from 3 to 5, are taken on one side, and an even number, from 2 to 4, are taken on the other side. The average of each of these two sets is taken, and the point of rest is the mean of these two values. For example, if the successive readings are a, b, c, d, e, f, and g (see Fig. 3), the point of rest would be

$$\text{P.R.} = \frac{\dfrac{a+c+e+g}{4} + \dfrac{b+d+f}{3}}{2}.$$

By taking an odd number of readings on one side, the error due to the decrease in the amplitude of successive swings (called the decrement) caused by friction and air resistance is eliminated. This is seen upon considering Fig. 3, where A, B, $C \cdots$ represent the swings of an ideal balance with no decrement, and a, b, $c \cdots$ the swings of a balance with a decrement K. The value of K can be assumed to be

[2] This is sometimes called the "zero point," because the pointer scales of balances were often calibrated from zero in the center to 10 divisions on each side; the term "zero point" is also sometimes used to designate the equilibrium position of the balance with zero load, and the "rest point" the equilibrium position of the loaded balance.

constant for the limited number of swings considered here, as its value is small in comparison to the amplitude of the swing. With no decrement it is obvious that the true point of rest would be the mean of the first two observations, thus:

$$\text{P.R.} = \frac{(A + B)}{2}.$$

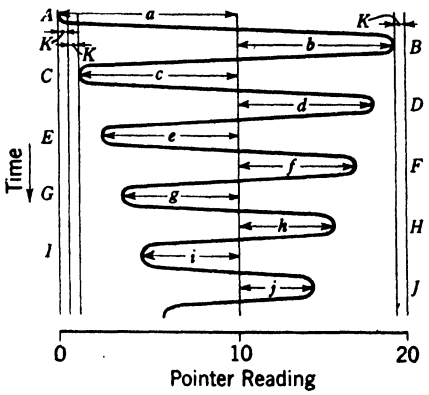

Fig. 3. The Effect of the Decrement on the Oscillation of a Balance.

The real observation, b, is equal to $B - K$; therefore $(A + B - K)/2$ differs from the true point of rest by $-K/2$. However, if two swings to the left and one to the right are taken, we have, for the ideal balance,

$$\text{P.R.} = \frac{\frac{A + C}{2} + B}{2},$$

and for the real observations,

$$\text{P.R.} = \frac{\frac{A + C + 2K}{2} + B - K}{2},$$

in which K is eliminated and the true point of rest obtained. The same treatment can be extended to a larger number of readings.

The method of long swings requires considerable time and computation, and in order to avoid this the so-called "short swing method" of determining the point of rest may be used with a precision usually well within the experimental limits desired. In this method the swing is limited to 1 or, at the most, 2 divisions, and the point of rest is determined by visually estimating the center of the pointer swing; for very precise work the extremes of one of the short swings may be recorded and the mean taken. As the pointer is moving much more slowly, the period of oscillation being constant, and as the decrement with such a short swing is hardly appreciable, the center can be very precisely placed.[3,4]

[3] For a discussion of the relative merits of the long and short swing methods see Wells, *J. Am. Chem. Soc.*, **42**, 411 (1920).

[4] Balances are now available which are provided with damping devices. These serve to bring the beam system to rest within 10 to 20 seconds and thus

Procedure I: DETERMINATION OF THE POINT OF REST. A. *Method of Long Swings.* Examine the balance to ascertain that it is in proper operating condition (Notes 1, 2). Release the pan rests by pushing in the button controlling them; this usually may be locked in by a slight turn. If the pans begin to swing, bring them to a stationary position by means of the pan rests. Now lower the beam by *very slowly* turning the beam-rest control in a counterclockwise direction as far as it will go (Note 3). By means of the rider control momentarily lower the rider to the beam near the end so that the pointer is caused to swing from 5 to 6 divisions to one side of the center. After one or two swings (Note 4) begin recording the successive extreme positions of the pointer, taking 5 such readings, three on one side and two on the other (Notes 5, 6, 7). Arrest the beam by means of the beam rest, *taking especial care that the beam is in a horizontal position* when it is lifted; then release the pan-rest control. From the readings so obtained calculate the point of rest of the empty balance (Note 8). Repeat the determination (Note 9).

Notes:

1. The balance should be situated in a position which is as free as possible from the corrosive fumes common to a chemical laboratory, from air movement, and from sudden changes in temperature, such as would be caused by an oven in the vicinity or by direct sunlight. Adequate illumination should be provided. The balance should be solidly mounted so as to avoid vibrations.

2. Before the balance is used, it should be examined to see that it is level (a leveling instrument is usually provided in the case), that the beam and pan arrests are operating smoothly, and that the "rider" is properly controlled by its mechanism throughout the entire range of the beam calibrations.

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effect a considerable saving of time in determining the point of rest. This damping is accomplished by air displacement or magnetically. In the first case cylinders which are closed at the top are suspended from the beam by the stirrups and move vertically inside cylinders closed at the bottom and supported in a fixed position by the central post. The two cylinders do not touch but fit sufficiently closely for the friction of the displaced air to give the desired damping. An adjustable vent allows the desired amount of damping to be obtained.

The magnetic damping is obtained by suspending an aluminum plate from the stirrup between the poles of a magnet which is supported by the balance post. The current induced by the vertical movement of this plate causes the damping.

Students should never attempt adjustments or repairs, but should report the condition to the instructor. The balance should be kept scrupulously clean at all times; any evidence of any material spilled on the pans or in the case, or of corrosion on the pans should be reported immediately. Even if apparently clean, the pans should be gently brushed off with a small soft camel's-hair brush (provided for that purpose only) before each series of weighings.

3. It cannot be too strongly emphasized that this release of the beam must be done with the utmost care, as by it the knife edges with their loads are brought into contact with the bearing plates. The operator of a balance can tell by the feel as the beam control is turned at what point the knife edges make contact and must use especial care to make this contact as gently as possible.

4. The first swings of the balance may be somewhat erratic; therefore it is preferable not to begin immediately recording the swings.

5. In order to avoid errors due to parallax the observer should seat himself squarely in front of the case and attempt to have the line of sight perpendicular to the scale as the reading is made.

6. See the discussion above for the reason for taking an odd number of readings, or "an even number on one side and an odd on the other"; seven or even nine readings may be taken if it is desired.

7. NOTEBOOKS. Because the recording of experimental data is of such fundamental importance, a few brief rules will be indicated: (1) A permanent bound notebook should be used and all data *immediately recorded in it in ink.* Pencil marks are not permanent, can be erased or altered, and may inspire doubt as to the integrity of the work. The use of loose scraps of paper is not to be tolerated. Original data are of more value than those which have been transcribed for the sake of neatness. (2) Date each entry. This is often of value in determining the time required for certain effects, in checking standard solutions, and in determining the sequence of experiments and may be of great value in research work leading to patent proceedings. (3) Make a complete record of the experiment. Before beginning, note the title and object of the experiment. Then record not only all the measurements made, but all experimental conditions, such as temperature, and so forth, however insignificant, that may in any way affect the results or conclusions. Many experiments have had to be repeated because some condition not considered worth noting was later found to influence the results. The method of procedure should be so clearly stated that another person could duplicate the results. Figures and diagrams of apparatus are extremely valuable and space-saving. Where a mass of data is to be taken, it is more easily comprehended and space is conserved if a tabular form is provided and the measurements entered directly therein. Clearly indicate the significance of all data; *do not rely on the memory to interpret them at some later time.* (4) Record **all** experiments; if they are later known to be faulty, they can be so labeled with an explanation of the causes or mistakes—such a record lends confidence in the notebook. (5) After finishing an experiment, record at once a summary of the results and any conclusions which can be drawn. This may save much time if it is necessary to refer to, or to interpret, the data at a later time.

8. In the recording of observations and measurements and in calculations involving these, attention should be paid to the proper use of "*significant*

figures." Significant figures are the numbers expressing the value of a measured quantity, and by convention the digits comprising the number are extended to, but not beyond, one digit whose value is doubtful. Thus, as the observation of the extreme of a swing is usually uncertain to approximately 0.2 of a division, it would be recorded to one decimal place and not beyond; an observation thought to be exactly ten would be recorded as 10.0, not merely 10, and not 10.00.

In calculations involving the multiplication or division of significant figures the principle to be kept in mind is that the percentage precision of the final resulting figure cannot be greater than that of the percentage precision of the least precise of the measurements entering into the calculation. As an example, in this procedure the calculated value of the point of rest cannot be extended to any such number as 10.152, as it would imply a precision obviously greater than that of the measurements on which it is based; the number should be rounded to 10.2. In discarding superfluous figures increase the last figure by one if the discarded figure is 5 or greater.

In adding or subtracting significant figures discard all figures occurring to the right of the term extending the least number of figures to the right relative to the decimal point. Thus, in adding the terms 24.6, 8.72, and 0.2564, each term should be rounded off to only one figure to the right of the decimal point; the sum would be 33.6.

9. The rest points obtained by a series of three or more such determinations should not show a maximum deviation of more than 0.2 of a division. A constant shift in the point of rest usually indicates uneven temperature conditions.

Procedure II: DETERMINATION OF THE POINT OF REST.

B. *Method of Short Swings.* Release the pan and beam arrests and, if necessary, set the beam in motion by momentarily touching it near the center with the rider so that a swing of not over 1 to 1.5 divisions is obtained (Note 1). Determine the point of rest by visually estimating the central point of these swings. Record this value, and without arresting the beam, repeat the determination by recording the extremes of a swing and taking the mean. Raise the beam and release the pan rests. Repeat the determination (Note 2).

Notes:

1. Usually, unless the point of rest is exactly at the center of the scale, a swing of from 0.5 to 1 division can be obtained without the use of the rider by carefully releasing the beam.

2. The values obtained by this method should be compared with those obtained by Method I. It is recommended that the discussion of the relative merits of the two methods by Wells, *J. Am. Chem. Soc.*, **42**, 411 (1920), be read. From the data obtained the analyst can draw his own conclusions as to the relative precision of the two methods and decide which method he is justified in using.

P. III. The Determination of the Sensitivity of a Balance

Discussion. The structural factors influencing the sensitivity of the balance have been discussed above. It is advantageous to know the sensitivity of the balance at various loads, because this knowledge enables one to estimate the weight to add or subtract in order to restore the original point of rest when making weighings, because it is useful in making weighings by the sensitivity method (see p. 14), and because it indicates the maximum load which the balance should carry. It is generally stated that a balance should not be made to carry an excess of weight over that which causes the sensitivity to decrease to 40 per cent of its maximum value; analytical balances are usually designed to carry a maximum of 100 or, for better instruments, 200 g on each pan. Obviously this criterion cannot be applied to the somewhat rare case in which a balance shows a continued increase in sensitivity with loading. A convenient sensitivity for making weighings to 0.1 mg is from 2 to 5 divisions per milligram.

Procedure III: DETERMINATION OF THE SENSITIVITY OF A BALANCE. Determine the point of rest of the empty balance, place upon one of the pans (Note 1) a 1-mg weight (or if a 1-mg weight is not provided in the set of weights being used, place the "rider" upon the division on the beam indicating 1 mg, Note 2), and again determine the point of rest. The number of scale divisions through which the pointer has been deflected is the sensitivity of the balance with zero load.

Repeat the determination with 10-, 20-, and 50-g loads on each pan (Note 3), and construct a curve by plotting the sensitivity as ordinate against the load as abscissa.

Notes:

1. In making weighings the object is usually placed on the left pan, since the manipulation of weights is more conveniently made upon the right pan.

2. Since balance beams are calibrated differently, care should be taken that the weight of the rider used should correspond to the value of the calibration directly above the terminal knife edge; the exact weight of the rider should also be checked.

3. The point of rest with a load may not agree with that of the empty balance, owing to inequality of length of the arms of the balance or small errors in the weights; if the pointer is deflected from the central portion of the scale with the heavier loads, it should be brought back by adjusting the rider.

Methods of Weighing

Discussion. The simplest method of weighing an object would be to determine the point of rest of the empty balance, then to place the object on one pan and, by means of adding weights and adjusting the rider, to restore the original point of rest. This is the method commonly used by chemists for routine work. In order to avoid having to adjust the weights to the exact mass of the unknown object, the method of "weighing by sensitivity" is often resorted to, especially when making precise weighings. In this method the weights are applied until the total is within 1 or 2 mg of the required amount and the point of rest determined. Then, if the original point of rest and the sensitivity of the balance are known, the weight to be added or subtracted in order to restore the original point of rest can be calculated. It is convenient in making weighings by this method to have the sensitivity expressed in milligrams per division of the pointer scale. Because the sensitivity of the balance may vary with the load, it is better practice for precise work to determine the sensitivity under the actual load conditions by again taking a point of rest after adding or subtracting a milligram from the load on the pan.[5,6]

Methods of Weighing Which Eliminate Errors Due to Unequal Arm Lengths. In the previous methods it has been assumed that when the original point of rest has been restored, the applied weights are equal to the weight of the object; this may or may not be a justifiable

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[5] The so-called "single deflection" method of weighing is frequently used for routine work where a saving of time is desired. In this method a weight is first applied to one arm of the balance (by means of the adjusting nut at the end of the beam or by adding a milligram weight to one pan). The beam is then lowered, the pan rests are released, and the position of the pointer at the limit of the first deflection is noted. An object is weighed by placing it on one pan and adding weights to the other until, upon releasing the beam as before, the pointer again reaches the same position at the extreme of its first swing.

This method requires that a balance with separate beam and pan controls be used; also that the pan controls be so adjusted that they impart no impulse to the pans when they are released. For a discussion of this method see Brinton, *J. Am. Chem. Soc.*, **41**, 1151 (1919).

[6] In order to expedite the weighing process the "chainomatic balance" has been developed. This balance eliminates the rider and uses in its place a fine gold chain, one end of which is supported by the beam and the other end by a support which can be raised or lowered by a control outside of the balance case, thus varying the fraction of the weight of the chain carried by the beam. In this way the rider and fractional weights up to 100 mg are replaced by the chain. The effective weight applied to the beam is read by means of a vernier scale.

assumption. When the balance reaches an equilibrium, the moments arising from the object and the applied weights are equal; that is,

$$Q \times L = R \times W,$$

where Q is the weight of the object, L is the length of the left arm, W is the applied weights, and R is the length of the right arm. Obviously, only when $L = R$ is the above assumption justified, and this may not be true within the desired experimental limits. Accordingly, for precise work, it is necessary either to determine the effect of this inequality and then correct for it, or to carry out the weighing in such manner that the effect is eliminated. The latter procedure is more commonly used and may be accomplished by either of two methods.

1. The Method of Substitution. This method, commonly called Borda's method, consists in placing the object on one pan and balancing it with any suitable material T (commonly called a *tare*), preferably weights from an old set, and then removing the object and balancing the tare with precise weights W. From the principle of moments, the following relation applies to the first weighing:

$$QL = RT,$$

and for the second,

$$WL = RT,$$

from which it is seen that L and R can be eliminated from the equations and that $Q = W$.

2. The Method of Transposition or Double Weighing. This method, commonly called Gauss' method, consists in placing the object Q on one pan and balancing it with weights W_1, and then transferring the object to the other pan and again balancing with weights W_2. For the first weighing,

$$QL = RW_1,$$

and for the second,

$$W_2L = RQ,$$

from which it is seen that

$$Q = \sqrt{W_1W_2},$$

and the true weight is the geometric mean of the observed weights. As the difference between W_1 and W_2 is relatively small, the arithmetical mean,

$$Q = \frac{W_1 + W_2}{2},$$

will give the true weight well within the desired experimental limits and is generally used. This latter method is usually more convenient, since it does not require an additional set of tare weights and is more generally used for precise weighings.

The Correction for Buoyancy

Discussion. A further assumption which has been made in the above methods was that the only force acting on the object and weights was that of gravity. Actually objects and weights are buoyed up by the weight of the air which they displace, and unless they are of the same density, this force will not be the same. Although the effect is so small that it can be neglected for most work, when calibrating volumetric vessels or carrying out weighings where unusual accuracy is desired, the correction for buoyancy must be made.

If W_o is the observed weight, then the weight *in vacuo*, W_v, will be $W_v = W_o + (V' - V'')d$, where V' and V'' are the volumes of the object and weights respectively, and d is the density of the air at the time of the weighing. However, $V' = W_v/d'$, and $V'' = W_o/d''$, where d' is the density of the object and d'' the density of the weights. However, as W_v differs from W_o by such a small amount, as an approximation $V' = W_o/d'$, and therefore

$$W_v = W_o + \left(\frac{W_o}{d'} - \frac{W_o}{d''}\right)d.$$

Although the density of the air varies with the barometric pressure, the temperature, the humidity, and the carbon dioxide content, it is usually sufficiently accurate to assume that 1 ml of air weighs 0.0012 g.

P. IV. The Calibration of a Set of Weights

Discussion. Unless they have been specifically certified by the makers or by the Bureau of Standards, or if they have been in previous use, weights cannot be relied upon for precise work until they have been calibrated. The method used for carrying out this calibration consists in principle in assuming a value for one of the smaller

weights, or the rider, and obtaining the value of all the other pieces in the set in terms of this arbitrary standard. These relative values may then be used where the absolute weight of the object is not necessary; however, in order to obtain absolute weighings (as, for instance, in calibrating volumetric vessels) it is necessary to compare one of the larger pieces with a piece of known value, usually one certified by the Bureau of Standards. An absolute value having been established for this piece, the values of the remaining ones can be calculated by means of the ratio of the absolute and relative values. In order to eliminate an accumulation of errors due to inequality of arm lengths the weighings should be made by substitution or by double weighing. The latter method avoids the use of a second set of weights, and the modification suggested by Weatherill[7] is particularly adapted for the calibration process. This method can be illustrated as follows: Suppose that the two pieces W_1 and W_2 are to be compared; W_1 is placed on the left pan and W_2 on the right and the point of rest determined. The pieces are exchanged, and the difference in weight, Δw, necessary to restore the first point of rest is determined. For the first point of rest

$$W_1L = RW_2,$$

and for the restored point of rest

$$W_2L = R(W_1 + \Delta w).$$

From this it is seen that

$$W_2 - W_1 = \frac{\Delta wR}{L + R},$$

and as Δw is small, it can be safely assumed that L and R are equal; therefore

$$W_2 - W_1 = \frac{\Delta w}{2}.$$

If an arbitrary value has been assigned to W_1, then $W_2 = W_1 + (\Delta w/2)$. If weight has to be added to W_1 to restore the first point of rest, Δw is positive; if weight has to be removed, Δw is negative.

This method is illustrated by the actual data taken in calibrating a set of weights and shown in Table I. The 0.005-g weight was taken as the arbitrary basis on which to obtain the relative values. The

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[7] Weatherill, *J. Am. Chem. Soc.*, **52**, 1938 (1930).

TABLE I

The Calibration of a Set of Weights

1 Face Value	2 Weights on Left Pan	3 Weights on Right Pan	4 Point of Rest	5 $\Delta w/2$ (mg)	6 Rel. Value (based on 5-mg wt.)	7 Absolute Value	8 Corr. (mg) (rounded)
0.005	0.005	rider	10.2		0.00500	0.00501	
rider	rider	0.005	9.1	−0.11	0.00489	0.00490	−0.1
0.01	0.005, rider	0.01	8.7				
	0.01	0.005, rider	10.5	+0.18	0.01007	0.01008	+0.1
0.01*	0.005, rider	0.01*	9.1				
	0.01*	0.005, rider	10.2	+0.11	0.01000	0.01002	
0.02	0.01, 0.01*	0.02	9.5				
	0.02	0.01, 0.01*	10.0	+0 05	0.02012	0.02015	+0.2
0.05	0.02 + Σ[a]	0.05	10.4				
	0.05	0.02 + Σ	8.8	−0.16	0.04992	0.04998	
0.1	0.05 + Σ	0.1	10.5				
	0.1	0.05 + Σ	8.9	−0.16	0.09984	0.09997	
0.1*	0.05 + Σ	0.1*	10.4				
	0.1*	0.05 + Σ	9.0	−0.14	0.09986	0.09999	
0.2	0.1, 0.1*	0.2	9.7				
	0.2	0.1, 0.1*	9.7	0	0.19970	0.19995	
0.5	0.2 + Σ	0.5	9.7				
	0.5	0.2 + Σ	9.4	−0.03	0.49937	0.50000	
1	0.5 + Σ	1	9.9				
	1	0.5 + Σ	9.1	−0.08	0.99869	0.99996	
1*	1	1*	9.7				
	1*	1	9.7	0	0.99869	0.99996	
1**	1	1**	9.7				
	1**	1	9.7	0	0.99869	0.99996	
2	1, 1*	2	6.7				
	2	1, 1*	12.4	+0.57	1.99795	2.00049	+0.5
5	2, 1, 1*, 1**	5	10.8				
	5	2, 1, 1*, 1**	7.4	−0.34	4.99368	5.00003	
10	5, 2, 1, 1*, 1**	10	10.1				
	10	5, 2, 1, 1*, 1**	6.3	−0.38	9.98732	10.00002	
10*	10	10*	7.7				
	10*	10	8.7	+0.10	9.98742	10.00012	+0.1
20	10, 10*	20	7.0				
	20	10, 10*	6.3	−0.07	19.97467	20.00007	+0.1
50	20 + Σ	50	4.7				
	50	20 + Σ	0.5	−0.42	49.93669	50.00019	+0.2
1	1 standard	1	9.8				
	1	1 standard	9.4	−0.04		0.99996	

[a] Σ indicates the sum of the smaller weights of the series, in this case the 0.01-, 0.01*-, 0.005-g weights and the rider.

sensitivity of the balance did not vary appreciably from 0.20 mg per division throughout the load applied. It should be noted that the arms of the balance used for obtaining this data were not exactly equal, the effect caused by this becoming quite appreciable at the heavier loads. Column 1 shows the face value of the weight being compared, columns 2 and 3 the weights on each pan, and column 4 the point of rest with the weights in the original and transposed positions. Column 5 shows $\Delta w/2$ (in milligrams), and in column 6 the values of the pieces on the basis of the 0.005-g weight are summed up. After comparing the 1-g piece with a Bureau of Standards 1-g weight, the absolute values of the other pieces are calculated by correcting each of the pieces by the ratio of the absolute weight to the relative weight, that is, 0.99996/0.99869, and the values shown in column 7 obtained.[8] For convenience in making weighings the value of the correction in milligrams to be applied to the face value of each weight to give its absolute weight has been rounded off and is shown in column 8.

Procedure IV: CALIBRATION OF A SET OF WEIGHTS. Examine the balance, brushing off the pans, and see that it is in proper condition. Examine the weights to be calibrated, noting if they have any dust or dirt sticking to them or if any pieces are corroded or tarnished (Note 1). Place the rider on the right arm exactly at the 5-mg calibration and the 0.005-g weight on the left pan and determine the point of rest (Note 2); place the rider on the left arm (Note 2) and the 5-mg weight on the right pan and again determine the point of rest (Note 3). Similarly compare the 10-mg weight with the 5-mg weight plus the rider, and continue

[8] The labor involved in the calculations required for the calibration can be greatly reduced as follows: In the data above we find that the relative value for the weight of face value 1 g is 0.99869, whereas the absolute value is 0.99996; therefore for this 1-g weight a correction of +0.00127 g has to be applied to the relative value in order to obtain the absolute value. As the relative values are consistent among themselves, the correction to be added to any other weight can be assumed to be +0.00127 g multiplied by the ratio of the face value of that weight to that of the 1-g weight; in the case above, the correction to be added to the relative value of the 0.5-g piece will be $+0.00127 \times 0.5/1$, which is 0.00063. The advantage of applying a ratio to the correction rather than to the relative value is that only the same number of significant figures have to be carried in the ratio as are necessary in the correction. For a discussion of the assumptions involved in the calibration process and a justification of the above method of procedure see the article by Frank H. Hurley, Jr., *J. Ind. Eng. Chem., Anal. Ed.*, **9**, 238 (1937).

until all the pieces of the set have been compared as indicated in Table I. Next obtain a standard weight (Note 4) and compare it with a piece of the same denomination from the set.

From the two points of rest obtained in comparing each piece calculate the $\Delta w/2$, referring to the curve obtained in P. III for the sensitivity with varying loads. From these values compute the relative values for the pieces on the basis of the 5-mg piece (or the 10-mg piece, if it is used). From the ratio of the *absolute value* (obtained by the comparison of a piece with the standard weight), and the *relative value* obtained for this same piece, calculate the absolute value for each piece of the set (Note 5). From these values calculate to 0.1 mg the correction to be applied to the face value of each piece in order to obtain its true value.

Notes:

1. Dust sticking to weights should be brushed off with a camel's-hair brush; if the weights appear dirty or corroded, the instructor should be notified. Dirt can be removed by rubbing the weights with a soft silk cloth or fine chamois skin. Weights that are corroded should be returned to the manufacturer for repair and adjustment. *Weights should never be touched with the hands.* Use the ivory- or bone-tipped forceps provided with the set; these forceps should not be used for any other purpose.

2. If the balance is equipped with a 10-mg rider, it can be compared with the 10-mg weight. If the left arm of the balance has no calibrations, the rider can be placed directly on the pan.

3. It is recommended that a tabular form similar to that shown in Table I be drawn in the notebook and the data taken directly in it. Only the weights and points of rest should be recorded while in the balance room; the remaining calculations can be completed subsequently.

4. Weights accompanied by a certificate as to their mass value can be obtained from the Bureau of Standards, or individual weights can be submitted to the Bureau for standardization. The fees are nominal.

The calculations involved in the calibration are somewhat shortened, the possibility of accidental error is reduced, and more accurate values are obtained for the heavier weights if two standard weights are available, a 1-g piece being used as a reference standard for the fractional weights and a 50-g piece for the heavier pieces.[9]

5. See footnote 8, p. 19, in regard to these calculations.

If only a 1-g standard weight is available, it is also to be noted that, having obtained the value of the 1-g weight by comparison with this standard 1-g piece, the absolute values for the larger pieces can be obtained by building up

[9] See Hopkins, Zinn, and Rogers, *J. Am. Chem. Soc.*, **42**, 2528 (1920), for suggestions in this regard.

directly from it; this method should be used to check those obtained from the relative values by the ratio calculated above.

General Rules for the Use of the Balance

1. Keep the balance case and pans clean. Brush off pans with camel's-hair brush before making a weighing.

2. Sit directly in front of the balance to avoid error from parallax.

3. Release the beam with a gradual steady motion.

4. Arrest the swing of the beam *only* when the pointer is at the center of the scale. *Always* raise the beam before leaving the balance. Do not leave weights or objects on pans after weighing. Keep the case closed.

5. Use only your own weights. Handle the weights with the forceps provided for that purpose; *never use your hands.*

6. Place weights and objects as near as possible to the center of the pan. Damp oscillation of the pans before determining the point of rest.

7. As a general rule, substances should not be placed directly upon the pans. *No liquids,* unless in stoppered bottles, are to be brought into the balance case.

8. Allow heated objects to cool to balance-room temperature before weighing.

9. Do not vigorously rub glass objects (possibly producing an electrostatic charge) just before weighing.

10. When making successive weighings use the same larger weights whenever possible.

11. Ascertain rated capacity of the balance, or determine it from the change in sensitivity, and do not exceed it.

12. Triple count the weights to avoid error; (1) count the weights on the pan; (2) count the spaces in the box; and (3) check the weights as they are removed from the pan.

13. Record weighings at once in your notebook. *Do not carry scraps or loose sheets of paper into the balance room.*

14. Report any injury to the balance to the instructor at once. *Do not attempt to make adjustments or repairs yourself.*

Volumetric Methods of Analysis

GENERAL DISCUSSION

Volumetric methods are used extensively in this system of analysis for estimating the amount of the constituents which have been detected. This is done because, if standard solutions are available, volumetric methods, in general, can be carried out much more rapidly and usually require less experience and special technique than gravimetric methods. For these reasons the first section of this book is devoted to a general discussion of volumetric methods and to the preparation and standardization of the solutions which are later required.

Volumetric methods differ from gravimetric methods in that the final *weighing* of a compound of definite percentage composition, which is the characteristic feature of gravimetric methods, is replaced by the *measurement of the volume* of a standard solution which reacts directly or indirectly with the substance being estimated. Thus, the amount of chloride in a sample of drinking water can be determined by titrating the sample with a standard silver nitrate solution by means of the precipitation reaction

$$Cl^- + Ag^+ = AgCl_{(s)},$$

or the amount of iron in an ore can be determined by a titration with a standard permanganate solution, the iron being first dissolved and reduced to the ferrous condition by suitable means. In this case the reaction is represented by the equation

$$5Fe^{++} + MnO_4^- + 8H^+ = 5Fe^{+++} + Mn^{++} + 4H_2O.$$

In order for a given reaction to be developed into a volumetric method, certain requirements must be met, namely:

1. The fundamental reaction involved, that is, the reaction between the standard solution and the titrated substance, must, when it reaches an equilibrium, be complete to within the desired precision. The equilibrium conditions can usually be predicted from available data such as solubility measurements, ionization constants, or potential values.

2. The reaction must proceed with practical rapidity. This "reaction rate" *cannot* be predicted from the equilibrium calculations and usually must be measured experimentally.

3. The reaction must be stoichiometric. That is, the reaction must proceed according to some definite equation, or equations, so that from the volume and concentration of the standard solution used the exact amount of the titrated substance present can be calculated. These criteria are not met by titrations involving "side reactions" or "induced reactions." An example of each of these follows: (a) The reaction between iodine and thiosulfate is assumed to proceed as follows:

$$I_2 + 2S_2O_3^- = 2I^- + S_4O_6^-;$$

however, if the titration is made in a solution which is slightly alkaline, part of the thiosulfate is oxidized to sulfate. (b) The reaction between stannous tin and permanganate is assumed to have the following stoichiometric equation:

$$2MnO_4^- + 5Sn^{++} + 16H^+ = 2Mn^{++} + 5Sn^{++++} + 8H_2O;$$

however, if the titration is made in the presence of air, the oxidation of stannous tin by oxygen is induced, and such a large error introduced that this particular determination is not practical. Often the existence and magnitude of these effects can be determined only by experiment.

4. Some means must be available for determining the completion of the titration. Various methods are available: (a) The titrating solution may have such a distinctive and intense color that a very slight excess becomes apparent (permanganate solutions); (b) indicators (substances which undergo a color change at the desired point) may be used; or (c) physical methods, such as observing the change in potential or conductance of the solution, are available. By these means the "end-point" of the titration is taken. This is to be distinguished from the "equivalence-point," which is the point at which an exactly equivalent amount of the titrating substance has been added. The error in the titration is measured by the difference between the equivalence-point and the end-point.

The imposition of the above requirements greatly limits the number of reactions upon which precise volumetric methods can be based.

Types of Volumetric Methods

The methods used in volumetric analyses may be divided into three general types, as follows:

I. Precipitation methods.

II. Oxidation and reduction methods.

III. Ionization methods (including neutralization, complex-ion, and un-ionized compound formation). This classification is based

upon the type of reaction taking place between the substance being titrated and the standard solution. With methods of the first type the completeness of the reaction is dependent upon the solubility of the precipitate formed, and the conditions obtaining at the equivalence-point usually can be calculated if solubility-product data are available. With methods of the second type the completeness of the reaction is dependent upon the potentials involved. Those of the third type are dependent upon the formation of un-ionized compounds, and, especially in neutralization reactions, upon the degree of ionization of the acids and bases involved. The ionization constants of these substances being available, calculation of the equilibrium conditions can be made. Specific examples of these general types will be discussed in detail in the subsequent procedures.

Concentration Units

Concentrations may be expressed in many different units. Therefore it is necessary to state definitely the conventions to be used hereafter in order to avoid confusion. Two general classifications are in use. First, *volume concentration*, which states the amount of any substance per unit of volume; and second, *mass* or *weight concentration*, which states the amount of any substance per unit of mass of the solvent or the solution. In volumetric analysis, interest is centered on volume measurements and volume concentrations, and the unit of volume is the *liter* (defined in Note 8 of P. V). In this book, volume concentrations will be expressed as **formal**, **molal**, or **normal**.

A **formal** solution contains 1 gram-formula weight of the stated compound per liter and states only the total amount of the substance present, not the specific molal or ionic species in which it may exist in the solution.

A **molal** solution contains 1 gram-molecular weight of the particular molecule or ion stated per liter.[1] As an example, a solution containing 12.006 g of sodium hydrosulfate ($NaHSO_4$) per liter is 0.1 formal in $NaHSO_4$, and, as, according to modern theories, the sodium hydrosulfate is completely ionized into sodium and hydrosulfate ions, the

[1] It should be pointed out that there is extensively used another convention in which the term **molar** is used to designate the moles of solute per liter of solution and **molal** the moles of solute per 1000 g of solvent; when this convention is used, the above distinction is not made between formal and molal concentrations. It is found that the use of molar to denote volume concentration and molal to denote weight concentration is confusing when used with normal to denote volume concentration. Also, it appears more definite to specify weight concentrations (which are not extensively used in volumetric work) by the terms "weight-formal" or "weight-molal," as the case may be.

sodium ion (Na^+) concentration is 0.1 molal. However, the hydrosulfate ion (HSO_4^-) is partly ionized into hydrogen (H^+) and sulfate ($SO_4^=$) ions, and according to measurements which have been made the solution is 0.034 molal in $SO_4^=$ and H^+ and 0.066 molal in HSO_4^-.

A **normal** solution contains 1 **gram-equivalent** weight per liter. A **gram equivalent** of a substance is that weight of it which, directly or indirectly, reacts with 1 gram-atomic weight (1.0081 g) of hydrogen. The same substance may have several equivalent weights, depending upon the reaction in which it is involved. Thus it may take part in precipitation or neutralization reactions (broadly termed **metathetical reactions**), or this same substance may enter into one or more oxidation and reduction reactions. As an illustration, iodic acid in either of the following reactions would have 1 equivalent per formula weight, and a solution which was 1 formal would likewise be 1 normal.

$$HIO_3 + OH^- = H_2O + IO_3^- \qquad \text{(Neutralization)} \qquad (1)$$

$$HIO_3 + Ag^+ = AgIO_{3(s)} + H^+ \qquad \text{(Precipitation)}^2 \qquad (2)$$

As an oxidizing agent in the reaction

$$IO_3^- + 3H_2S = I^- + 3S_{(s)} + 3H_2O, \qquad (3)$$

iodic acid would have 6 equivalents per formula weight and a normal solution would contain one sixth of a formula weight per liter.

However, in the reaction

$$IO_3^- + 5Fe^{++} + 6H^+ = \tfrac{1}{2}I_2 + 5Fe^{+++} + 3H_2O, \qquad (4)$$

it has only 5 equivalents per formula weight, and a normal solution would contain one fifth of a formula weight per liter, thus being 0.2 formal. It is therefore seen that the concentration of a normal solution is not uniquely specified, and that confusion is likely to result, unless the reaction for which the solution is to be used is also stated. Because of this fact objections have been raised to the use of this unit; however, in stoichiometric calculations the use of equivalents and of normal concentrations is of great convenience. Therefore throughout the procedures of this system reagents will be specified by their **normal** concentration except where confusion is likely to

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[2] In writing equations, solids will be indicated by the subscript (s) and gases by (g). In general, equations will be written in their ionic form (as above); this form is simpler to construct, and shows the fundamental changes taking place in the reaction and the effect of each ion or molecule upon the equilibrium of the reaction. If the principles involved in writing the ionic equations are understood, the completed equation can be readily constructed when this is desired for stoichiometric calculations.

result, in which case their formal concentration will be given. Molal concentrations will be used in mass-action considerations where it is desired to express the concentration of some particular species of ion or molecule as it exists in the solution.

Volume concentration is sometimes expressed as the weight of a given substance per unit of volume; this unit will not be used here.

Weight concentrations will be expressed in terms of grams of solute per 100 g of solution, or the weight per cent.

Formal and molal weight concentrations, although extensively used in thermodynamic calculations, will not be used here.

The Preparation of Standard Solutions

Discussion. Standard solutions for volumetric work can be prepared by two methods: First, directly, by weighing precisely the required amount of a pure substance, dissolving it, and diluting this solution at a definite temperature to an exactly known volume in a calibrated flask; or, second, by making the solution of approximately the concentration desired and then measuring the volume of it which reacts with a precisely weighed amount of some pure substance (called a *primary standard*), thus *standardizing* it. The first process is used when the substance from which the standard solution is made can be obtained in a high degree of purity, can be precisely weighed, and does not change upon being dissolved in water or when the solution is diluted (for example, react with the gases or traces of organic matter usually present even in distilled water). The second process is more frequently employed because many of the substances used for standard solutions are not readily obtained in a sufficiently pure form, or are not stable when first dissolved in distilled water.

PRECIPITATION METHODS OF VOLUMETRIC ANALYSIS

P. V. The Preparation of a Standard Silver Nitrate Solution

Discussion. As very pure silver nitrate can be prepared by recrystallization (or purchased), and as it can be dried and weighed (even fused at 220° to 225°) without change, provided organic matter, reducing gases, or hydrogen sulfide are avoided, standard solutions of silver nitrate are usually prepared by precisely weighing out the desired amount of the salt and then dissolving and diluting this to the

desired volume in a volumetric flask at a specified temperature. Such solutions are then stable, provided they are protected from organic matter, reducing gases, and also from light.

When the silver nitrate solution with its concentration precisely known is available, it can be used for standardizing other solutions which are not readily directly prepared.

Procedure V: PREPARATION OF A STANDARD SILVER NITRATE SOLUTION. Clean a weighing bottle, wipe it with a clean, dry, lintless towel (Note 1), dry it in an electric oven or by gently heating it with a burner, allow it to cool in a desiccator (Note 2), and weigh it to 0.01 g (Notes 3, 4). Weigh into the bottle approximately 17.0 g of silver nitrate (Note 5) of the highest purity obtainable, place the open bottle in a small beaker loosely covered with a watch glass, and heat for at least 2 hours in an electric oven at 105° to 110°C. (Note 6). Again cool in the desiccator and weigh. With the aid of a large-stem funnel carefully transfer the silver nitrate to a clean, calibrated 1-liter flask (Notes 7, 8), then rinse the weighing bottle out repeatedly with 5-ml portions of water (Notes 9, 10). Use a stirring rod to guide the solution from the bottle to the beaker and take care to avoid loss by spattering. Dissolve any silver nitrate crystals remaining on the funnel and fill the flask almost to the mark with water at room temperature (Note 11); so use the funnel as to avoid wetting the flask above the calibration mark. Finally, remove the funnel, being sure to rinse off any solution adhering to it; then with a dropper or pipet add water until the lower meniscus just coincides with the calibration mark. Any droplets of water spilled against the side of the flask above the calibration mark should be removed with filter paper before making this final adjustment. Stopper the flask and shake it vigorously until the contents are perfectly mixed (Note 12).

Transfer the solution to a clean ground-glass-stoppered bottle (Note 13), first rinsing it out with several small portions of the silver nitrate solution. Calculate the normality of the solution at the standard laboratory temperature (20°C.) and label the bottle (Note 14).

Notes:

1. After being cleaned and dried, a weighing bottle, or any other piece of apparatus which is to be *weighed precisely* (to 0.1 to 0.2 mg) should be han-

dled by means of a piece of paper, lintless cloth, or chamois skin folded around it. It is preferable not to handle such apparatus with the fingers, since they may be greasy or moist, and prolonged handling may raise the temperature of the apparatus sufficiently to cause an apparent decrease in weight. These effects would not be significant in the above case, where the object is to be weighed to only 0.01 g.

2. A desiccator is a glass container in which objects, especially crucibles, may be placed and allowed to cool in a dry atmosphere protected from dust, carbon dioxide, and the fumes common to a laboratory. A common type of desiccator is shown in Fig. 4. The desiccating agent most frequently used is anhydrous calcium chloride; for special purposes sulfuric acid or phosphorus pentoxide may be used. The desiccator should be opened only when necessary, closed as soon as possible, and kept tightly closed at all other times;[3] the desiccant should be replaced as soon as it begins to lose its efficiency. After being heated, an object should be allowed to cool from 20 to 30 minutes before it is weighed.

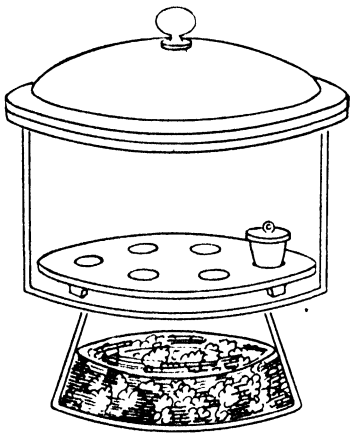

Fig. 4. Desiccator.

3. *Methods of weighing out samples.* Material prepared for analysis, primary standards, and similar substances are usually dried and kept in glass-stoppered weighing bottles. Samples may be weighed out from these by either of two general methods, here termed the "direct" and "difference" methods. By the direct method (used in this procedure) an empty weighing bottle, a watch glass, a piece of glazed paper, or any other suitable container is weighed, the desired amount of material from the weighing bottle transferred to it, and the weight of the container plus the material found. The material is usually transferred by holding the sample bottle over the weighed receiver, removing the stopper, and then tipping the bottle and slowly rotating it, holding the top close to or against the receiving vessel, until approximately the desired amount of material has been transferred. If an exact weight of sample is desired, material can be added or taken by means of a pointed steel spatula until this is obtained. In the above procedure time may be saved by drying the silver nitrate in a clean weighing bottle and then weighing it on a clean, dry, previously weighed watch glass. Care must be taken not to get any of the silver nitrate on the balance pans and not to lose any in the subsequent transfer.

In using the "difference" method, the weighing bottle containing dry material is first weighed, the desired amount of material transferred from it directly to the beaker or flask in which it is to be treated, and the weighing bottle closed and again weighed; the loss or "difference" in weight represents

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[3] Booth and McIntyre, *J. Ind. Eng. Chem., Anal. Ed.*, **8**, 148 (1936), give data showing the length of time required to dry the air in a desiccator.

the sample taken. The transfer of the material is accomplished by essentially the process described above, care being taken that all of the material leaving the bottle is caught in the beaker or flask. Since it is not good practice to return material from the receiving vessel (which may not be entirely dry or clean) to the sample vessel, it is not convenient to take exact sample weights by this method. Approximate sample weights can be taken by removing slightly less than the weight of the desired sample from the right pan and then intermittently removing material from the bottle until an approximate balance is again obtained; however, frequent removal and insertion of the stopper may cause loss of material by "dusting," especially with finely powdered dry material.

The direct method is usually more convenient where a large amount of material is to be weighed, presents less chance of loss of finely powdered material, and permits taking an exact sample weight; the "difference" method is more rapid where several successive weighings are to be made or where the sample is likely to absorb moisture during weighing, and permits weighing out the sample directly into the beaker in which it is to be treated.

4. The analyst should always keep in mind the precision to which measurements should be carried out. One is not justified in carrying most chemical analyses to a precision of greater than one part in a thousand or one tenth of one per cent; this limit is set by instrumental errors, by errors inherent in the methods involved, and in some cases by uncertainty in the atomic weights. This being true, it is obviously a waste of time to weigh out 17 g of silver nitrate to 0.0001 g, which would represent a precision of one part in 170,000, or approximately six ten-thousandths of one per cent. If the weighing is made precise to 0.01 g, it will be within the desired limits; obviously a sample of 0.17 g should be weighed precisely to 0.0001 g.

5. Directions are given for preparing a liter of the solution; if less than this is required, a smaller volume should be prepared. By approximately weighing out the amount of silver nitrate taken, no excess is dried, and the solution will be close to the desired normality. If it is desired to make the solution exactly 0.1 normal, small crystals of the dried salt can be removed or added by means of a clean, dry, pointed steel spatula until exactly 16.99 g of the nitrate are taken.

6. As silver compounds are easily decomposed by organic matter and reducing agents, the oven should be protected from dust and from reducing gases. Paper labels should not be used on articles placed in the drying oven, because the adhesive material used chars, giving off volatile reducing substances (tarry materials) which cause the reduction of silver compounds. Weighing bottles should be identified by marking with a pencil on the ground-glass seal around the stopper. Most commercial silver nitrate will darken slightly on being heated, but with the better grades this decomposition is not significant.

7. *The cleaning of volumetric apparatus.* The vessels used in volumetric measurements must be scrupulously clean. A vessel may be considered suitable for use when it is visually clean and when a solution drains from it *without leaving perceptible streaks or droplets on the surface.* The most common contaminant is a grease film. Glass apparatus for volumetric work often can be effectively cleaned by scouring it with soap powder and then rinsing it with distilled water; to economize with distilled water, beakers,

flasks, and so forth may be liberally rinsed with tap water and finally with a small portion of distilled water. Except when a resistant film of grease is encountered which cannot be removed by treatment with the soap solution, or when the construction of the vessel makes the use of soap powder ineffective, the use of the so-called "cleaning solution,"[4] while effective, is to be discouraged because of its corrosive nature and the difficulty with which it is completely removed from glass surfaces. When cleaning solution is used, it may be necessary to allow it to stand in the vessel for an hour or even overnight. More rapid action is frequently obtained by treating the vessel with 6 n. NaOH for 5 or 10 minutes and then following this with the cleaning solution. Calibrated vessels should not be heated if it can be avoided.

8. *The calibration and use of volumetric apparatus.* Volumetric vessels are usually calibrated either "to contain" (flasks) or "to deliver" (burets and pipets) a definite volume of solution at a stated temperature, and because of drainage an appreciable error will be made if they are used for other than the indicated purpose.

When using volumetric apparatus for precise work, care should be taken that the solution is at the temperature for which the vessel is calibrated or that the proper correction is made if working at a different temperature. Since there has been some confusion in regard to the units of volume and since glassware as often purchased is not precisely calibrated, all such apparatus should be checked before being used. This is usually done by finding the weight of water which such apparatus will contain or deliver, and converting this weight into the metric unit of capacity.[5]

As the actual calibration of apparatus is carried out at room temperatures and under atmospheric pressure, it is necessary to calculate the proper weight of water to be taken. As an example, if it is desired to calibrate a liter flask for use at 20°, it will be found by reference to a table showing the relative densities[6] of water at various temperatures that this volume of water would weigh 998.23 g *in vacuo*. The apparent weight of this mass of water in air of mean humidity and 760 mm pressure is 997.19 g. The calculation for temperatures other than the standard temperature of 20° can be similarly made, remembering that the average cubical coefficient of expansion (the increase in volume per unit of volume per degree centigrade) of glass is 0.000025. Flasks which are calibrated "to contain" are checked by weighing the clean dry flask on a balance of suitable capacity, carefully filling the flask with water of the proper temperature, taking care that there is no water above the calibration (as indicated in the procedure above), and again

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[4] Cleaning solution is made by adding 50 g of commercial sodium dichromate to 500 ml of commercial concentrated sulfuric acid.

[5] The liter is the metric unit of capacity and is defined as the volume occupied by 1000 g of pure water at the temperature of its maximum density and under a pressure of one atmosphere. One milliliter is not exactly the same as one cubic centimeter; the latter is derived from the unit of length and is the volume of a cube with an edge one centimeter in length; 1 ml is 1.000027 cc.

[6] The absolute density of water (or any other substance) in C. G. S. units is the mass per cubic centimeter. The relative density (or specific gravity) is the ratio of the mass to the mass of an equal volume of water at 4°C. Therefore, in order to obtain the mass of a given volume of water the absolute density must be used if the volume is in cubic centimeters, the relative density if the volume is in milliliters.

weighing.[7] Pipets and burets are calibrated "to deliver" and are checked by weighing the water obtained from them (Notes 3–6, P. VI). Reference books on quantitative analysis should be consulted for the details of these operations.

9. Two methods are used for transferring weighed material to a flask. If the material is finely ground, crystalline, and readily soluble, it may be transferred directly by means of a funnel as directed above. Any solid remaining in the funnel is readily dissolved by the water added. If the material is of an amorphous nature, tending to "lump" together, or is not readily soluble, it is advisable to transfer it first to a beaker where it can be more readily brought into solution (heated if necessary) and this solution then poured through the funnel into the flask. When a solution is being poured, it should always be guided by means of a stirring rod. This prevents the solution from spattering in the receiving vessel and from running down the outside of the vessel from which it is poured.

10. Stirring rods, droppers, and wash bottles are constantly used by the analyst, and an adequate supply should be available. It is recommended that these be made while the silver nitrate is being dried.

Make the stirring rods by cutting glass rod (3 to 4 mm in diameter) into lengths varying from 10 to 25 cm, and then heating both ends in a flame until they are well rounded and smooth (fire polished). If this is not done, they scratch the inside of vessels in which they are used; precipitates then tend to crystallize in these cracks, and are difficult to remove.

Droppers are made by heating and drawing glass tubing (6 to 8 mm inside diameter, 10 to 15 cm in length) to a capillary at one end and heating and enlarging the other end with the end of a file so that it holds a rubber nipple tightly. It should then be marked at the position from which it delivers 1 ml, and the number of drops per ml noted. Droppers are extremely useful for adding small volumes of reagents and for washing precipitates with small volumes of water.

Wash bottles are constructed from Florence flasks as indicated in Fig. 5. The flask should be of a resistance glass and the stopper and rubber tubing should be of the best grade rubber. The tip of the outlet tube should be gradually constricted until the desired stream of water is delivered. When designed for hot water the neck may be wrapped with asbestos cord or cork. For greater flexibility, the mouthpiece can be provided with a piece of rubber tubing 5 to 8 cm in length. A liter

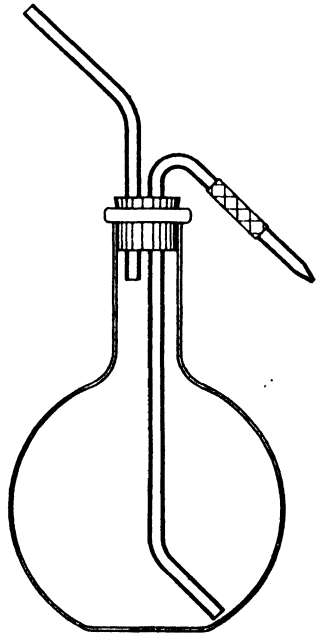

Fig. 5. Wash Bottle.

[7] When a number of flasks (or burets) are to be checked, calibrating bulbs (of the Morse-Blalock or Ostwald type) can be used to advantage. Directions for their use can be found in reference books on quantitative analysis.

flask is convenient for wash water, smaller flasks for special wash solutions.

11. The solution in the flask should be gently swirled as the water is added so that it is well mixed before the final adjustment of the meniscus is made. The solution of a solid or the mixing of solutions may result in an appreciable volume change.

12. One of the most common sources of error in volumetric analysis is the incomplete mixing of solutions following their preparation in volumetric flasks. Such solutions can be effectively mixed by swirling the solution, inverting, and again swirling, repeating this sequence at least ten times.

13. Solutions which are sensitive to light should be kept in bottles of brown glass or, if these are not available, in bottles which are covered with paper or painted with black lacquer.

14. All standard solutions, reagents, and solutions for analysis which are to be reserved for future use should be carefully labeled, dated, and, if for general use, initialed by the person preparing them.

P. VI. The Preparation and Standardization of a Thiocyanate Solution

Discussion. As both ammonium and potassium thiocyanate are somewhat hygroscopic, are too soluble to be readily purified by recrystallization, and cannot be easily dried, standard solutions of these substances are not usually prepared by direct weighing as was done with silver nitrate.[8] Solutions of approximately the desired concentration are therefore prepared and then standardized, usually against pure metallic silver or silver nitrate.

This standardization is accomplished by making use of the reactions involved in the so-called Volhard method for determining silver;[9] this titration is an example of a volumetric precipitation method. In carrying out this titration, a definite volume of the already prepared standard silver nitrate solution is pipeted out, some ferric nitrate is added as indicator, and the solution is titrated with the thiocyanate solution. As long as there is an appreciable amount of silver in the solution being titrated, the concentration of the thiocyanate remains so small, owing to the precipitation of silver thiocyanate, that no perceptible amount of the red compounds which thiocyanate forms with ferric iron (probably $Fe(SCN)_6^{=}$ and

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[8] Kolthoff and Lingane, *J. Am. Chem. Soc.*, **57**, 2126 (1935), have prepared KSCN suitable for use as a primary standard by recrystallization from water, drying over P_2O_5, and finally melting for a short time at 200°C. The dried material is not hygroscopic at a relative humidity of less than 45 per cent but deliquesces rapidly at relative humidities greater than 50 per cent.

[9] Charpentier, *Bull. Soc. Ing. Civ. France*, **135**, 325 (1870). Volhard, *J. Prakt. Chem.* (2), **9**, 217 (1874).

$Fe \cdot Fe(SCN)_6$) are formed.[10] As the amount of thiocyanate added becomes approximately equivalent to the silver present, further addition causes its concentration to rise very rapidly; this results in the formation of perceptible amounts of the red-colored compounds, giving the end-point.[11]

This change in the concentration of the silver and of the thiocyanate ions during the course of the titration can be predicted from the mass-action and solubility-product laws. It will be recalled that the mass-action law states that in the reaction between a molecules of substance A, b molecules of substance $B \cdots$, to form g molecules of G and h molecules of $H \cdots$, according to the equation

$$aA + bB + \cdots = gG + hH + \cdots,$$

when equilibrium is attained, the following relation will exist between the molal concentrations of the various molecules, $[A]$, $[B] \cdots$, $[G]$, $[H] \cdots$, namely:

$$\frac{[G]^g[H]^h \cdots}{[A]^a[B]^b \cdots} = K \text{ (at a given temperature).}$$

This equation is known as a **mass-action** or **equilibrium expression**, and K is known as the **equilibrium constant**.[12] The above type of

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[10] Schlessinger and Van Falkenburgh, *J. Am. Chem. Soc.*, **53**, 1212 (1931), cite experiments to show that with an excess of thiocyanate $Fe(SCN)_6^{=}$ is formed; with an excess of ferric iron the molecule $Fe \cdot Fe(SCN)_6$ predominates.

[11] Attention is again called to the distinction that should be made between the equivalence-point, which is the point at which an equivalent amount of the standard solution has been added, and the end-point, at which the titration is concluded. The latter is based upon some perceptible evidence, usually furnished by an indicator, that the desired reaction is completed. The agreement between these two points measures the accuracy of the titration.

[12] As an example of the conventions used in formulating mass-action expressions, consider the reaction previously mentioned (Equation 3, p 25):

$$IO_3^- + 3H_2S = I^- + 3S_{(s)} + 3H_2O.$$

The complete equilibrium expression for this reaction would be written as follows:

$$\frac{[I^-][S]^3[H_2O]^3}{[IO_3^-][H_2S]^3} = K'.$$

However, the concentration of the dissolved sulfur would always have a constant value (if the solution were saturated—that is, an equilibrium had been reached—with the solid sulfur) and, therefore, this term may be omitted from the expression and the value of K changed correspondingly; this omission is justified in writing mass-action expressions in all cases where the solution is kept saturated at a definite temperature with a pure solid substance. Next, the concentration of water in dilute aqueous solutions (0.1 formal or less) does

expression is applicable to equilibria between gases or substances in solutions, but is subject to increasing deviations as the reactants become more concentrated, especially in solutions of highly ionized substances. These deviations will be discussed later (p. 40). In considering the titration of thiocyanate with silver nitrate solution, it is seen that as soon as a precipitate of silver thiocyanate is produced, the equilibrium in the solution can be represented by the equation

$$AgSCN_{(s)} = Ag^+ + SCN^-$$

(it is assumed that silver thiocyanate, like most other salts, is completely ionized in dilute solutions), and therefore when equilibrium is attained (and the solution saturated, but not supersaturated, with solid AgSCN), the mass-action expression can be formulated:

$$[Ag^+][SCN^-] = K.$$

This expression states that in dilute solutions which are in equilibrium with solid AgSCN the product of the concentration of the two ions has a constant value at any given temperature; this is a statement of a general principle applicable to all slightly soluble salts, and the value of the ion-concentration product at saturation is commonly termed the solubility-product constant, and denoted as $K_{S.P.}$.[13] Using this solubility-product principle, the theoretical change in the thiocyanate and in the silver ion concentrations can be calculated for the course of a titration, and in Fig. 6 is shown the curve (labeled Ag^+) obtained by plotting the silver ion concentration, and the curve (labeled SCN^-) obtained by plotting the thiocyanate ion concentration, as the ratio of the equivalents of thiocyanate added to the equivalents of silver initially present is gradually increased. (For convenience it has been assumed that a 0.1 n. solution is titrated without volume change.) The changes in ionic concentrations

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not vary greatly (pure water being about 55.4 f. in H_2O at 20°); therefore for dilute solutions and for all except the most precise calculations, its concentration can be assumed to be constant, and it may also be omitted from the mass-action expression, the value of K again changing. The equilibrium expression for the above reaction therefore becomes

$$\frac{[I^-]}{[IO_3^-][H_2S]^3} = K.$$

[13] It is seen that the form of the solubility-product expression will differ in considering other types of salts; thus for lead chloride the equilibrium would be represented by the equation $PbCl_{2(s)} = Pb^{++} + 2Cl^-$; and the solubility product would have the form $[Pb^{++}][Cl^-]^2 = K_{S.P.}$

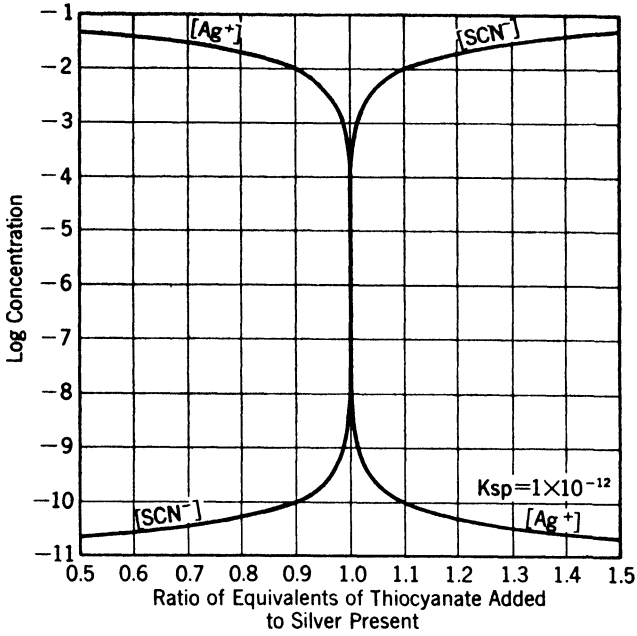

Fig. 6. Changes in Silver and Thiocyanate Ion Concentrations When Titrating Silver Nitrate with Potassium Thiocyanate.

occurring near the equivalence-point during the titration of silver ion with other ions forming slightly soluble salts are shown in Fig. 7.[14]

[14] As an example of the method of calculating these values, consider the case when the ratio of equivalents of thiocyanate to silver has the value 0.90. For simplicity assume that the volume remains constant throughout the titration. First, it is necessary to obtain the solubility product of silver thiocyanate. Upon looking up solubility data it will be found that the solubility of silver thiocyanate at 20°C. has been experimentally determined to be 10^{-6} formal; therefore, assuming complete ionization and neglecting any hydrolysis, the solubility product will be

$$[Ag^+][SCN^-] = K_{s.p.} = 10^{-12}.$$

If a tenth normal solution of silver nitrate is titrated with thiocyanate and the thiocyanate added until the ratio of the equivalents of thiocyanate (the negative ion) to the equivalents of silver nitrate initially present has the value 0.90, the concentration of the *excess* silver nitrate will be 0.01 (assuming that there has been no volume change), and the total concentration of the ion will be 0.01 plus an amount equal to the concentration of the thiocyanate ion remaining in solution or to 0.01 plus the molal solubility of silver thiocyanate in a solution in which the excess of silver ion is 0.01 molal. Substituting the unknown concentration of the thiocyanate ion in the solubility-product equation, there is obtained the expression

$$[Ag^+][SCN^-] = [0.01 + x][x] = 10^{-12}$$

By inspection it is seen that x must be small in comparison to 0.01 so that

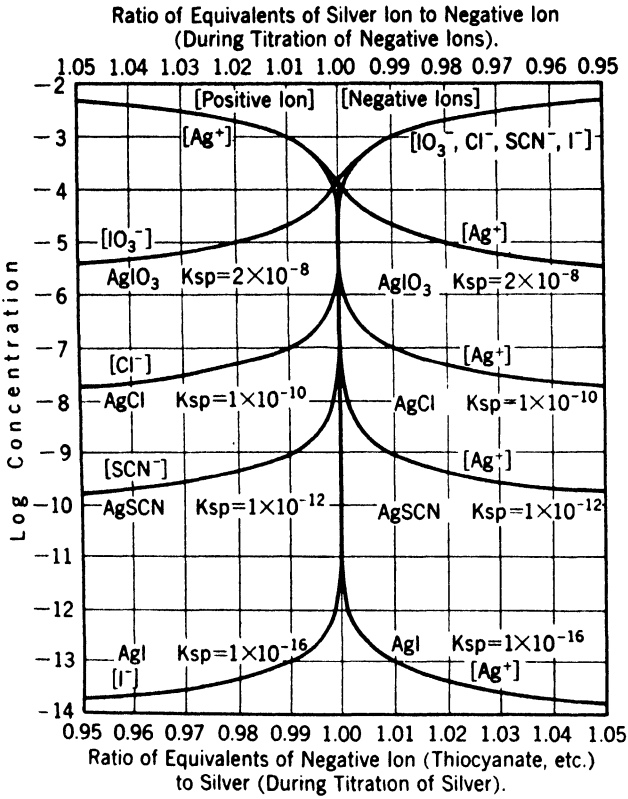

Fig. 7. Concentration Changes of Silver Ion and Various Negative Ions During Precipitation Titrations.

From the curve for the thiocyanate titration (which expresses the requirements of the solubility-product equation), it is seen that as the ratio of the equivalents of thiocyanate to silver is increased (as the titration with thiocyanate proceeds), the silver ion concentration decreases and the thiocyanate ion concentration increases until at the exact equivalence-point they are equal. It is to be noted that the rate of change of these concentrations with a given change in the

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the solution of the equation can be simplified by neglecting the additive term. It is desirable in solving mass-action equations that the exact expression be formulated and that methods of simplification then be considered. As will be shown later, deviations from the mass-action laws of from 1 to 5 per cent are to be expected even in dilute solutions; therefore greater exactness than this in solving such equations is not justified. Upon solving the above equation, there is obtained a value for x (or for the thiocyanate ion concentration) of 10^{-10} and for the total silver ion concentration of $(0.01 + x)$, or substantially 0.01. Values for other ratios of thiocyanate to silver can be similarly calculated, and the curves illustrated in Figs. 6 and 7 were constructed from such data.

ratio of equivalents of the ions present increases tremendously when this ratio approaches unity, or as the equivalence-point is approached. This rapid rate of change of concentration near the equivalence-point is of fundamental importance, as by the addition of a small amount of the standard solution (in this case the thiocyanate) there is produced such a large change in the ionic concentrations of the solution that some effect producing an end-point will take place (in this case the formation of a visible amount of the red compound). As will be observed later, this rapid change near the equivalence-point is an essential characteristic of all "titration curves" and one of the features which determine the precision of the method.

Consider now in this regard the titration of silver ion with thiocyanate ion in the presence of ferric ion. Experiments have shown that with the ferric nitrate 0.01 formal the color of the red compound can be detected when the concentration of the thiocyanate ion is between 1×10^{-5} and 2×10^{-5} formal. It is seen from Fig. 7 that at this point the ratio of thiocyanate to silver is between 1.001 and 1.002 and, therefore, results accurate to within 0.2 per cent should be obtained.[15]

From the curves shown in Fig. 7 for the titration of other silver salts it is seen that the position of the curves and the rate of change of the concentration of the ions involved near the equivalence-point is a characteristic of the solubility product of the salt. Thus if a titration were made of a salt with a solubility product of 2×10^{-8} (corresponding to that for silver iodate), the concentration of the anion would reach 1×10^{-5} when the ratio of the equivalents was only 0.98, and thus an error of as much as 2 per cent might result. In this regard it is to be remembered that one of the requirements which was set up for the use of a reaction as the basis of a precise volumetric method was that it should be quantitatively complete. Obviously, the more soluble the salt, the less complete its precipitation reaction. As will be observed later, it is a general feature of titration curves that the less complete the fundamental reaction, the less pronounced the inflection of the curve near the equivalence-point. It is also to be pointed out that these curves are characteristic of other di-ionic salts; for example, the curves for barium sulfate, $K_{S.P.} = 10^{-10}$, would coincide with those for AgCl.[16]

[15] This calculation neglects the amount of the $Fe(SCN)_6^{=}$ needed to give a visible color, but experiments have shown this to be of the order of 10^{-6} formal.

[16] $BaSO_4$ is not readily adapted to a volumetric precipitation process because its solutions tend to supersaturate, and thus the rate at which it attains an equilibrium is slow.

Summarizing these considerations with respect to the thiocyanate titration of silver, it is seen that the point at which the color appears, and the end-point is taken, depends upon the relative solubility of silver thiocyanate and the stability (or degree of dissociation) of the colored compound. If silver thiocyanate were much more soluble or the ferric thiocyanate compound much less ionized, the end-point would be taken before the equivalence-point; if the ferric thiocyanate compound were highly dissociated, it would require a larger concentration of thiocyanate to force the equilibrium

$$Fe^{+++} + 6SCN^- = Fe(SCN)_6^{---}$$

to the right and thus produce a perceptible color; the end-point would then occur after the equivalence-point. It is also to be seen from the foregoing discussion that the end-point can be shifted somewhat by varying the concentration of the ferric salt added as indicator; experimentally the relations are such that highly precise titrations can be made.

Experimental studies of this method have shown that there is a tendency for the silver thiocyanate precipitate which is first formed to collect, or, as such a process is termed, to adsorb[17] silver ions on its surface; therefore, unless the mixture is vigorously stirred, the first end-point obtained may be premature. In addition, the solution should be acid in order to repress the partial hydrolysis of the ferric ion, as the products of this hydrolysis impart a yellow color to the solution, making the end-point less easily detected. It should be cold, since ferric ion is more hydrolyzed in hot solutions and the $Fe(SCN)_6^{---}$ molecule is more dissociated; in addition, the thiocyanate ion is oxidized by nitric acid and by ferric ion at elevated temperatures.[18]

Other Indicators for Volumetric Precipitation Titrations. It has been seen above that there is an extremely rapid change in the concentration of both cation and anion near the equivalence-point in a precipitation reaction involving a slightly soluble precipitate, and, in the titration just discussed, the sudden increase in the anion (thiocyanate) concentration caused the appearance of the red color which was taken as the end-point. Obviously other effects which depend upon the cation or anion concentration could be used for the same purpose.

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[17] See "Gravimetric Methods," p. 119, for a discussion of the phenomena of adsorption.

[18] For an experimental study of this method, the article by Kolthoff and Lingane, *J. Am. Chem. Soc.*, **57**, 2126 (1935), should be consulted.

Thus in P. 95 the end-point of the titration of chloride with silver ion is obtained by adding a soluble chromate to the solution and noting the first appearance of a precipitate of silver chromate. As is seen in Fig. 7, when chloride ion is titrated with silver ion, the silver ion concentration remains very small until quite close to the equivalence-point, and then it rapidly rises. Because silver chromate is somewhat more soluble than silver chloride, no precipitation of the reddish silver chromate occurs until very close to the equivalence-point, and therefore a precise end-point determination can be made. A detailed discussion of this end-point is given in P. 95.

Adsorption indicators. It has been found that certain colored organic compounds tend to be adsorbed (see "Gravimetric Methods," p. 119) on the surface of precipitates and that the extent to which this adsorption takes place is greatly influenced by whether there is an excess of the precipitating anion or cation in the solution. As an example, fluorescein, which is a colored organic acid ($K_A = 10^{-8}$), is scarcely at all adsorbed on a silver halide or thiocyanate precipitate so long as there is an excess of halide or thiocyanate ion present (preferentially adsorbed). However, as soon as an excess of silver ion is added and the halide or thiocyanate concentration reduced, the fluorescein is thereupon strongly adsorbed. According to Kolthoff[19] and his associates, this may be due to an "exchange adsorption" which may be represented as follows:

$$\underset{\text{(Surface)}}{Ag^+SCN^-} + \text{Fluorescein}^- = \underset{\text{(Surface)}}{Ag^+\text{Fluorescein}^-} + SCN^-$$

In addition, upon being adsorbed, the fluorescein undergoes a pronounced change in color, so that this effect can be used to obtain an end-point.[20]

As fluorescein is a very weak acid, it is not useful in other than practically neutral solutions. Dichlorofluorescein and eosin are stronger acids and can be used in hydrogen ion concentrations as large as 10^{-3} molal.

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[19] Kolthoff and Larson, *J. Am. Chem. Soc.*, **56**, 1881 (1934); Kolthoff and Rosenblum, *J. Am. Chem. Soc.*, **56**, 1264, 1658 (1934).

[20] The detailed mechanism of the adsorption process and accompanying color change has been extensively investigated, especially by Fajans and his coworkers, who originated and developed the use of these indicators.

Fajans and Hassel, *Z. Electrochem.*, **29**, 495 (1923); Fajans and Steiner, *Z. physik. Chem.*, **125**, 309 (1927); Fajans and Wolff, *Z. anorg. allgem. Chem.*, **137**, 221 (1924); Hassel, *Kolloid Z.*, **34**, 304 (1924); Kolthoff, *Kolloid Z.*, **68**, 190 (1934).

For a review of the theories regarding the mechanism of the process and the factors affecting their application, see Kolthoff, *Chem. Rev.*, **16**, 87 (1935).

The end-point with such indicators is likely to be unsatisfactory with large concentrations of other ions present, since they may be preferentially adsorbed or cause coagulation of the precipitate before the end-point.

Because the ferric thiocyanate end-point for the silver-thiocyanate titration is so precise and can be used in acid solutions as well as in the presence of even high concentrations of many other anions and cations, it is a much more generally useful indicator for the titration of silver ion with thiocyanate than are adsorption indicators. Adsorption indicators are more useful in the titration of chloride with silver ion and are employed in an optional procedure in P. 95.

For a general discussion of the use of these indicators in other titrations see Kolthoff and Furman, *Volumetric Analysis*, Vol. II, p. 214, and Fajans, *Neuere Massanalytische Methoden*, Enke, 1935, pp. 161–207, 194–196.

Limitations to the Use of Concentrations in Mass-Action Expressions. In the preceding discussion it was stated that there were deviations from the mass-action law as the reacting substances became more concentrated, and application of the solubility-product law was restricted to relatively dilute solutions in predicting the accuracy of the thiocyanate-silver titration. It has been found that the mass-action law can be applied to solutions of *un-ionized* substances as concentrated as 1 formal with deviations not exceeding a few per cent, but that with solutions of highly ionized substances the deviations may become greater than this at concentrations as low as 0.01 formal. It is found that the "effective concentration" of a substance, that is, the concentration which should be substituted in a mass-action expression in order to express the effect which that substance exerts on the equilibrium in which it is involved, becomes progressively less the higher the total ion concentration of the solution. This effect is now explained on the basis of what is commonly called the "inter-ionic attraction theory." The principle postulates of this theory are (1) that most salts and the so-called strong acids and bases are practically completely ionized and (2) that the "effective concentration," or "activity," of these ions is decreased in solutions because of the mutual attraction of the opposite charges. The magnitude of this effect is dependent upon the total ionic concentration of the solution, the size and number of unit charges on the individual ions, the dielectric constant of the medium, and the temperature. In order to obtain the "effective concentration," or, as it is termed, "activity," a, to be used in mass-action expressions it is necessary to correct the

formal concentration, c, by an appropriate factor termed the **activity coefficient**, γ; thus $a = c\gamma$.

The activity coefficients of many substances have been experimentally derived (from vapor pressure, freezing point, and electromotive-force measurements), and in order to illustrate their magnitude the values for solutions of a few common electrolytes are shown in Table II. It is to be emphasized that these are the activity co-

TABLE II

ACTIVITY COEFFICIENTS OF VARIOUS ELECTROLYTES

Solution	Coefficient					
	0.001 f.	0.01 f.	0.05 f.	0.1 f.	1 f.	3 f.
HCl	0.98	0.92	0.86	0.81	0.82	1.4
KOH	0.98	0.92	0.84	0.80	0.65	0.70
KCl	0.98	0.92	0.84	0.80	0.75	
$AgNO_3$	0.97	0.90	0.78	0.72	0.40	

efficients of the electrolytes in pure solutions of the concentrations given, and that in the presence of other electrolytes the activity coefficients will have other values dependent upon the total ionic concentration of the solution and the valence type of the individual ions.

Because of the inter-ionic attraction effects discussed above, it is unsafe to make quantitative use of the mass-action law unless the total ionic concentrations are below approximately 0.01 formal or unless the activities, and not concentrations, are used. In Fig. 8 this effect is shown by plotting the solubility of thallous chloride against the equivalent concentration of various added salts. In this same figure there is shown by means of the dotted line the calculated solubility (assuming complete ionization) in the presence of salts having a common ion. The increased solubility in the presence of the salts with no common ion is to be noted, and especially the effect of the divalent sulfate ion, which, having a molal concentration only half that of the nitrate, causes a greater solubility increase. The more pronounced effect on the solubility of salts having divalent ions is shown in Fig. 9, where the solubility of silver sulfate in various salt solutions is similarly plotted. It is to be pointed out that thallous chloride and silver sulfate are moderately soluble salts and that the deviations due to inter-ionic attraction forces are relatively much more pronounced than those to be expected in dealing with dilute solutions containing slightly soluble salts such as silver chloride or silver thiocyanate.

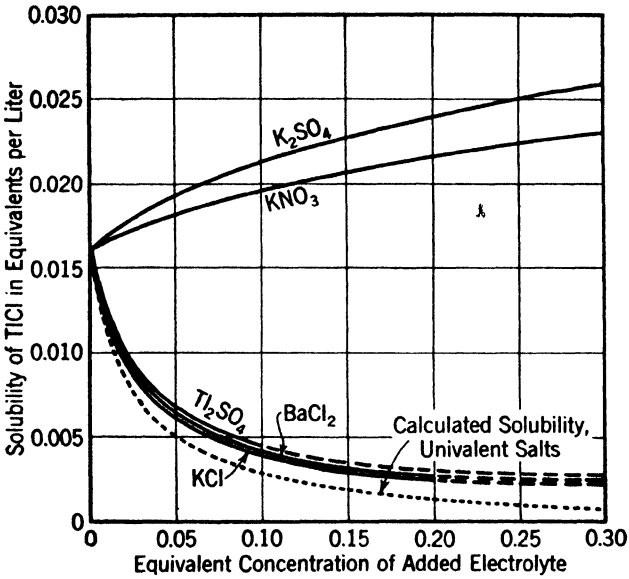

Fig. 8. The Solubility of Thallous Chloride in Various Salt Solutions. (Data from article by A. A. Noyes, *J. Am. Chem. Soc.*, **46**, 1107 (1924). Broken lines are extrapolated values.)

Summarizing, it is seen that the deviations to be expected when substituting concentrations in mass-action or solubility-product expressions may be relatively large unless the total ionic concentration of the solution is small (0.01 formal or less) and unless only univalent ions are present. Because the calculation of the activity coefficients of individual ions in complex solutions is too involved to be treated here, concentrations will be used in mass-action expressions, but it will be understood that except in extremely dilute solutions of simple electrolytes the results so obtained are of value only as an approximation of the effect to be expected.

Procedure VI: PREPARATION AND STANDARDIZATION OF A THIOCYANATE SOLUTION. Weigh out 8.0 g of ammonium thiocyanate (or 10.0 g of potassium thiocyanate) on a rough balance, dissolve it in water, dilute the solution to a liter (Note 1), transfer it to a clean ground-glass-stoppered bottle, and thoroughly mix the solution. Label the bottle.

Pipet three 25-ml portions of the silver nitrate solution into separate 200-ml flasks (Notes 2, 3), add to each of these 10 ml of chloride-free 6 n. HNO_3, 3 ml of chloride-free 1 n. $Fe(NO_3)_3$ solution, and 25 ml of water. Fill a buret (Notes 4, 5) with the thiocyanate solution and draw the

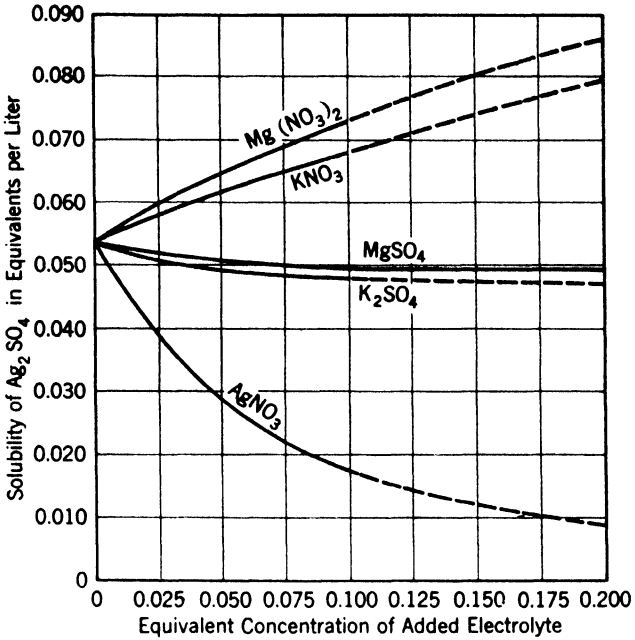

Fig. 9. The Solubility of Silver Sulfate in Solutions of Various Salts. (Data from article by A. A. Noyes, *J. Am. Chem. Soc.*, **46**, 1107 (1924). Broken lines are extrapolated values.)

meniscus down to the zero mark (Note 6); allow 30 seconds for drainage, again adjust the meniscus to the mark, and remove any hanging drop from the tip. Swirl the silver nitrate solution and add the thiocyanate to it until the first perceptible pink color is produced which remains permanent upon vigorously shaking the mixture for 30 seconds (Note 7). After allowing time for drainage, read the buret, and *immediately record this data in ink in a permanent notebook.* Similarly titrate the other portions of silver nitrate. From the normality of the silver nitrate solution and the volumes of silver nitrate and thiocyanate used, calculate the normality of the thiocyanate solution (Note 8).

Notes:

1. As the solution is to be subsequently standardized, this dilution does not have to be precisely made, and may be done in a 1-liter graduated cylinder.

2. Standard solutions containing nonvolatile compounds should not be poured from storage bottles, since the solution adhering to the neck of the bottle evaporates and the residue may fall back into the bottle when the stopper is withdrawn. If such solutions are to be used frequently, some type of delivery tube should be arranged. For occasional use the solution may be removed by means of a clean dry pipet. When not in use, the tops of

the bottles should be protected from dust, and so forth, by inverting over them small beakers.

3. When measuring a solution with a pipet, the sequence of operations is as follows: (1) Draw a small portion of the solution into the cleaned pipet (the pipet should be dry on the outside, should have been carefully drained, and suction should be applied as it is first immersed in a solution in order to avoid possible contamination or dilution of standard solutions) and wet the entire surface of the pipet; discard this solution, and repeat the operation (the pipet should be again cleaned if streaks or droplets are left on draining). (2) Draw the liquid into the pipet slightly above the calibration mark. (3) Wipe off any liquid adhering to the outside of the lower stem. (4) Holding the pipet vertically, allow the solution to escape very slowly (by regulating the pressure of the finger on the top of the pipet) until the lower meniscus of the solution just reaches the calibration mark. (5) While maintaining the column of liquid in this position carefully touch the tip of the pipet against a glass surface. (6) Allow the solution to run into the desired vessel, holding the pipet vertically with the tip sufficiently close to the receiving surface to prevent spattering. (7) Fifteen seconds after continuous flow has ceased, lightly touch the tip of the pipet against the wet side of the receiving vessel. It is not precise technique to blow out the portion remaining in the tip.

The tip of the pipet should be so constricted by the manufacturer that the time of outflow is not less than the minimum specified by the United States Bureau of Standards,[21] or serious errors from drainage effects may result. The minimum outflow time for 10- and 50-ml pipets is 20 and 30 seconds, respectively.

Before being used for precise work, the calibration of a pipet should be checked by delivering water of a known temperature from it into a previously weighed weighing bottle or light-weight conical flask closed by means of a watch glass. The volume delivered by the pipet can be calculated from the vacuum weight of water thus obtained and from the relative density.

4. Burets are of two types (see Fig. 10), those with glass stopcocks (Geissler), and those fitted with a connection of rubber tubing between the buret proper and the glass tip (Mohr). The flow is controlled in the latter type by means of pinch or screw clamps or by glass beads in the tubing. The Mohr type is not to be used for highly precise work. Such burets are less expensive and are convenient for use with alkaline solutions (which cause glass stopcocks to stick if left in contact with them) and for less precise work with other solutions which do not attack rubber (iodine or permanganate solutions should not be so used). Glass stopcocks should be lubricated by means of vaseline, or if there is a tendency to leakage, with stopcock grease, which can be prepared or purchased. Before applying the grease, the stopcock should be dried and only a minimum amount of lubricant applied, or it is likely to collect in the tip and cause stoppage during a titration.

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[21] The specifications as to outflow times, tolerances, and so forth, for volumetric glassware can be found in United States Bureau of Standards Circular No. 9, 1916.

5. Before being used, the buret should be cleaned with a buret brush and soap powder or cleaning solution and then thoroughly rinsed with water; it should then drain without leaving any streaks or droplets. Before filling it with the thiocyanate solution it should be rinsed several times with small portions of the thiocyanate, care being taken that the tip is flushed out and that no air bubbles remain around the stopcock.

6. When reading a buret, one should take care that the line of sight is perpendicular to the buret. This can be done by lining up the front and back calibration mark (these marks should extend completely around the buret at each milliliter) or by encircling the buret just below the meniscus with a piece of paper and sighting across the top of this. With other than opaque solutions the lowest meniscus should be read. As the position of this meniscus may vary with the position of the liquid and the lighting, it is an aid to darken it by encircling the buret just below the meniscus with a strip of darkened paper or piece of black rubber tubing, while a white card or piece of filter paper held back of this makes a contrasting background on which to view the darkened meniscus. A piece of white cardboard with the lower half blackened, preferably with india ink, is also quite satisfactory.

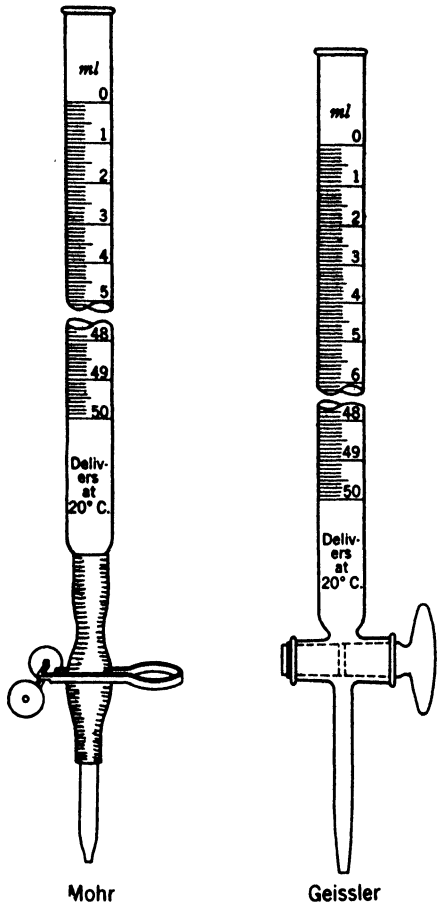

Fig. 10. Types of Burets.

If solutions are withdrawn from burets too rapidly, errors may result, since it has been shown[22] that drainage is considerable and continues for a long period of time. The tip of the buret should be so constructed that a 50-ml buret does not empty in less than 120 seconds; if it is found that the rate of outflow is greater than this, it should be restricted by the stopcock. With this rate of delivery the buret can be read immediately with very little drainage error; however, as an additional safeguard, it is recommended that a fixed interval of 30 seconds be adopted. Do not allow the buret to stand for any considerably longer period of time before making the reading, since errors from leakage or drainage may then become significant.

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[22] Stott, *Volumetric Glassware*, Witherby (London), 1928, pp. 109–125.

Before being used for precise measurements, the calibrations of a buret should be checked as follows: The clean buret is filled with water at the proper temperature, the water drawn down to within 0.02 to 0.03 ml of the zero mark, 30 seconds allowed for drainage, and the meniscus then carefully adjusted to the zero mark. The tip of the buret is then touched with a glass surface to remove the hanging drop. The water is then slowly drawn out into a weighed weighing bottle (or light-weight conical flask covered with a small watch glass) until it is just above the 5-ml (or 10-ml) mark (20 to 30 seconds should be required for the delivery), and after 30 seconds the meniscus again exactly adjusted and the tip of the buret touched against the inside surface of the weighing bottle. The container and water are then weighed. It is convenient, but not necessary, that the meniscus be stopped exactly on the unit mark; the buret should be read to 0.01 ml and the water weighed to 0.01 g. The interval from 5 to 10 ml (or from 10 to 20 ml) is similarly checked, and so on, until the length of the buret is covered. From the weights and temperature of the water the corresponding volumes are calculated. Should any portion of the buret show an abnormal error, it can be calibrated for each milliliter interval. It is convenient in using the buret to have a plot of the corrections as abscissae against the volumes as ordinates.

7. When unknown amounts of silver are titrated, the approach to the end-point is shown by the slower disappearance of the local red color caused by each drop of thiocyanate. As mentioned in the discussion, this is partly due to adsorption of silver on the precipitate, and the mixture should be vigorously shaken so that this may be removed. At this stage of the titration the thiocyanate should be added by allowing only a fraction of a drop to form on the tip of the buret, removing this, and adding it to the solution by means of a stirring rod. Also, when near the end of a titration, the inside walls of the flask, or other titration vessel, should always be washed down by means of a jet of water from the wash bottle; any of the standard solution, or of the solution being titrated, adhering thereto is thus recovered. When very precise measurements are desired, an "end-point correction" should be made. This is done by titrating the thiocyanate solution into a solution of the same volume as that at the end-point of the titration, and also containing the same amount of acid and ferric nitrate, until a color matching that used for the end-point is obtained. This volume is subtracted from the volume used in the titration.

8. Properly carried out, these titrations should give results which agree to within 2 parts in a thousand.

The Applications of Precipitation Methods

Volumetric precipitation methods are used most extensively for determining the anions which form insoluble silver salts (see P. 114 and P. 141 for a list of these salts). These may be determined either (1) by direct titration, using suitable indicators, or (2) by adding an excess of a standard silver solution and titrating this excess in the presence of the precipitate; sometimes a preliminary filtration may be necessary. Other metallic ions that form insoluble salts with these anions may be determined indirectly. Discussions of

these methods will be found in P. 22, "The Estimation of Silver"; P. 95, "The Indirect Estimation of Sodium"; P. 27, "The Indirect Estimation of Bismuth"; P. 122, "The Estimation of Sulfide"; P. 123, "The Estimation of Cyanide"; and P. 148, "The Estimation of Chloride." The estimation of silver discussed in P. 23 and of mercury in P. 45 are examples of methods which should not be classified as precipitation methods (the principle reactions being carried to completion because of ionization effects) but which because of their similarity to certain precipitation methods are frequently grouped with them.

OXIDATION AND REDUCTION METHODS OF VOLUMETRIC ANALYSIS

General Principles of Oxidation and Reduction (Electronic) Reactions

Discussion. Oxidation and reduction reactions may be defined as those in which there is a transfer of electrons from some ion or compound (called the reducing agent) to some other ion or compound (called the oxidizing agent), and thus may be more concisely termed **electron-transfer**, or for brevity, **electronic** reactions. Thus, electrons are readily removed from metallic zinc or from bipositive tin,

$$Zn = Zn^{++} + 2E^-$$

$$Sn^{++} = Sn^{++++} + 2E^-$$

and, therefore, metallic zinc and solutions of stannous tin are classed as reducing agents. On the other hand, chlorine, tripositive cobalt, and permanganate ion in an acid solution very readily take up electrons,

$$2Cl^- = Cl_2 + 2E^-$$

$$Co^{++} = Co^{+++} + E^-$$

$$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5E^-$$

and are classed as oxidizing agents. Also, there are other reactions of intermediate nature, such as

$$Fe^{++} = Fe^{+++} + E^-$$

$$Ag = Ag^+ + E^-$$

$$H_3AsO_3 + H_2O = H_3AsO_4 + 2H^+ + 2E^-$$

which can be made to proceed in either direction with comparative ease, depending upon whether these substances are brought into reaction with more reducing or more oxidizing compounds. As all of these reactions involve electrons,[23] it would seem that this tendency to give off or take up electrons would give rise to an electrical potential, and such is the case. Thus if a zinc rod is immersed in a beaker of water, there is a tendency for the zinc atoms to ionize and pass into the solution as zinc ions. This process cannot proceed to an appreciable extent, since the electrons remaining in the zinc develop an opposing potential on the rod which checks the process, the rod becoming thereby an electrode. Similarly, if we pass chlorine gas into a separate beaker of water, there is a tendency for the elementary chlorine to take up electrons and form chloride ions, but if there are no substances present with available electrons, the reaction cannot proceed to an appreciable extent. If an inert conducting metal, such as platinum, is immersed in the solution, there is a tendency for the chlorine to draw electrons from it; and this results, as was the case with the zinc rod, in the production of a potential on the platinum, which likewise becomes an electrode. This potential will be opposite in sign to that on the zinc, where there was a tendency for electrons to accumulate. Thus we have two electrodes with potentials of opposite sign, and it would seem that if they were suitably connected in an electrical circuit, a flow of electrons, or an electrical current, would take place. There would be thus produced an electrical **cell,** and each electrode and the solution of the substances involved in the production of its potential would constitute a **half-cell.**

If only the two **electrodes** were connected, by means of any suitable conductor (usually a copper wire), a flow of electrons would take place momentarily; however, at the zinc electrode positive ions, Zn^{++}, would accumulate; at the platinum electrode negative ions, Cl^{-}, would accumulate, and these accumulated charges would check the further flow of electrons. If, however, some means of transfer of these charges between the two solutions is provided, a continuous current can flow. This is accomplished experimentally by connecting the two solutions by means of a "**salt bridge,**" which is usually an inverted **U**-tube dipping into each solution and filled with a solution of an electrolyte. This permits the migration of positive ions

[23] The definition that oxidation-reduction reactions involve a transfer of electrons does not exclude non-ionic reactions such as $S + O_2 = SO_2$, for it seems reasonable to assume that the valence electrons of the sulfur are more closely associated with the oxygen atoms in the sulfur dioxide molecule.

to the chloride-chlorine **half-cell** and of negative ions to the zinc–zinc ion **half-cell.** If the two electrodes are now connected, there will be obtained a finite and continuous current flow, electrons passing from the zinc electrode to the platinum electrode, positive ions being produced in the zinc–zinc ion half-cell, negative ions in the chloride-chlorine half-cell, and a transfer of ions taking place through the salt bridge. The electromotive force, or potential of the complete cell, will be determined primarily by the potentials arising at the two electrodes (small potentials are also developed at the junctions of unlike solutions). These potentials will be determined by the inherent tendency of the substances involved to take up or give off electrons, in this case, of the reactions $Zn = Zn^{++} + 2E^-$ and $2Cl^- = Cl_2 + 2E^-$ to take place, and by the concentrations of each of the substances involved in these half-cell reactions. As any two of the illustrative electron reactions first mentioned above can be similarly used to construct a complete cell, it is seen that all of these equations represent essentially the reactions taking place at suitable electrodes or are what are termed **half-cell** reactions. If some one of these half-cells is assumed to have a definite potential value when the ions involved are at definite concentrations, the value of any other can be measured by combining it with this reference half-cell and then experimentally measuring the electromotive force of this completed cell. The reference half-cell thus used is the so-called hydrogen electrode,

$$H_2 \text{ (g, 1 atm.)} = 2H^+ \text{ (unit activity)} + 2E^-,$$

which is arbitrarily given the value zero. The more important of these electronic reactions with the values of these potentials in volts when all of the reactants are present in unit activity, that is, when the gases are at 1 atmosphere and the ions or soluble compounds at 1 molal activity, have been collected in Table II of the Appendix; and these values are referred to as their **molal reduction potentials.**

These molal potentials are often of little practical value, and may be misleading, when one attempts to predict from them the behavior of oxidizing and reducing agents in the relatively concentrated salt and acid solutions encountered in analytical chemistry. As an example, Huey and Tartar[24] pointed out that the value -0.154v, which they calculated for the molal potential of the reaction

$$Sn^{++} = Sn^{++++} + 2E^-,$$

represents the potential of an electrode in a neutral solution where

[24] Huey and Tartar, *J. Am. Chem. Soc.*, **56**, 2585 (1934).

these ions were at unit activity and where no hydrolysis or complex-ion formation was involved. Because of the pronounced acidic character of stannic tin and the impossibility of obtaining stable solutions except where complex ions exist, such a molal potential has very little physical significance. Because of such cases, there also have been collected with this table of molal potentials the potential values for certain of these reactions when the concentrations of the substances involved are 1 formal; these values are designated as **formal potentials.** These formal potentials could be calculated from the molal potentials (or the reverse) if there were available adequate data for the hydrolysis constants, for the dissociation constants of any complex ions which may be formed, and, finally, for the activity coefficients of the reactants in these relatively concentrated solutions. Since such data are usually inadequate, it is advantageous to have the experimentally measured *formal* potentials.

According to the convention adopted here, a positive sign to the potential indicates that with respect to the reference hydrogen half-cell the tendency is for the half-cell reaction to proceed to the right, that is, to give up electrons; and a negative sign indicates a tendency for the reaction to proceed to the left.

The Effect of Concentrations on Potentials. The potential at other than unit pressures or concentrations (activities) can be calculated by the Nernst equation, which is most useful in the form

$$E = E_0 - \frac{0.059}{n} \log_{10} Q \qquad \text{at } 25°\text{C.},$$

where E is the calculated or observed potential, E_0 is the molal (or formal) potential, and Q is the product of the activities of the substances on the right-hand side of the half-cell equation divided by the product of the activities of the substances on the left-hand side of that equation, each activity having as an exponent the coefficient of the substances in the equation; n is the number of electrons involved in the equation (the number of faradays of electricity produced by the reaction); and 0.059 is a numerical constant which varies with the absolute temperature, being 0.058 at 18°C. Qualitatively, it is thus seen that the potential of a half-cell is changed approximately $0.06/n$ by a tenfold change in the value of Q.

This effect of the concentration on the potential set up by the ions involved in a half-cell reaction and the use of the above equation is shown by considering the case of the silver–silver ion half-cell,

$$\mathrm{Ag} = \mathrm{Ag}^+ + \mathrm{E}^-; \qquad E_0 = -0.799 \text{ v.}$$

This moderately large negative value indicates that silver ion should show oxidizing tendencies and, in fact, should act as a better oxidizing agent than ferric ion, as the ferrous-ferric potential has the more positive value, namely,

$$Fe^{++} = Fe^{+++} + E^{-}; \qquad E_0 = -0.782 \text{ v.}$$

As a matter of experiment, if silver ion is added in excess to a ferrous sulfate solution, there will be a partial reduction of the silver ion to metallic silver, and an equivalent amount of ferric sulfate will be produced. However, if to a solution of silver ion there is added thiocyanate until the thiocyanate ion activity is 1 molal, the concentration of the silver ion is reduced to 2×10^{-12} ($K_{S.P.}$ AgSCN being 2×10^{-12}) and the silver-silver ion potential becomes

$$E = -0.799 - \frac{0.059}{1} \log 2 \times 10^{-12} = -0.109 \text{ v.}$$

It is worthy of note that this value should represent the molal potential for the reaction[25]

$$Ag + .SCN^{-} = AgSCN_{(s)} + E^{-}; \qquad E_0 = -0.109 \text{ v.}$$

It is now seen that metallic silver in the presence of thiocyanate ion should reduce ferric iron, and a quantitative method has been proposed for so reducing ferric solutions preliminary to titrating them with standard permanganate solutions.[26] In this method the thiocyanate ion concentration is made approximately 0.01 molal, so that the silver-silver ion potential becomes -0.227 v. As, under equilibrium conditions, there can be only one potential value obtaining in a given solution, other oxidizing or reducing agents present in this solution must have their concentrations so changed as to have this same potential value. Therefore, the ratio of ferric to ferrous iron can be obtained by substitution in the Nernst equation as follows:

$$-0.227 = -0.782 - \frac{0.059}{1} \log \frac{[Fe^{+++}]}{[Fe^{++}]},$$

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[25] As the result of recent measurements, Pearce and Smith, *J. Am. Chem. Soc.*, **59**, 2063 (1937), have calculated for this potential the value -0.095 v; the discrepancy probably arises from the value of the solubility product used above.

[26] Edgar and Kemp, *J. Am. Chem. Soc.*, **40**, 777 (1918).

which gives the ratio $[Fe^{+++}]/[Fe^{++}]$ the value 3.9×10^{-10}. It is thus seen that only 3.9×10^{-8} per cent of the ferric iron should remain unreduced.

As an example of the use of this same equation in calculating the conditions existing at the end-point of an electronic reaction, consider the calculation of the potential of a solution 10^{-3} molal in Mn^{++}, 1×10^{-5} molal in MnO_4^-, and 1 molal in H^+; these concentrations approximate those which would exist at the end of a permanganate titration. Substituting in the Nernst equation, we have

$$E = -1.45 - \frac{0.059}{5} \log \frac{(1 \times 10^{-5})(1)^8}{(10^{-3})} = -1.426.$$

One can now calculate what the ratio of ferric iron to ferrous iron would be under these conditions, and thereby predict how completely ferrous iron would be oxidized when titrated by a permanganate solution. Again simply substituting

$$-1.426 = -0.782 - \frac{0.059}{1} \log \frac{[Fe^{+++}]}{[Fe^{++}]},$$

we obtain

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = 8.2 \times 10^{10}.$$

This indicates, as is found experimentally, that the reaction would be complete well within the usual analytical limits. The possibility that the rate at which the reaction proceeds is too slow for it to be of practical use is not precluded.

The Calculation of Equilibrium Constants from Potential Values. The potential of a complete reaction, that is, of a cell, can be obtained by subtracting two half-cells,[27] thus:

$Mn^{++} + 4H_2O$	$= MnO_4^- + 8H^+ + 5E^-$		-1.45
$5Fe^{++}$	$= 5Fe^{+++} +$	$5E^-$	-0.782
$Mn^{++} + 4H_2O + 5Fe^{+++}$	$= MnO_4^- + 8H^+ + 5Fe^{++}$		-0.67

The relatively large negative value for the molal cell potential, $E_0 = -0.67$, indicates that the reaction as written should proceed

[27] It should be noted that in adding or subtracting half-cell reactions it is permissible to multiply the constituents on each side of a half-cell equation without changing the value of the potential; the potential is independent of the amount of electricity which is involved.

quantitatively from right to left. Similarly, by subtracting the Nernst equations for two half-cells, the potential of the cell reaction can be obtained in terms of the equilibrium constant for the reaction; thus in the above case

$$E_1 = E_{0_{[Mn^{++}, MnO_4^-]}} - \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{++}]}$$

and

$$E_2 = E_{0_{[Fe^{++}, Fe^{+++}]}} - \frac{0.059}{1} \log \frac{[Fe^{+++}]}{[Fe^{++}]}.$$

Subtracting,

$$E_1 - E_2 = E_{0_{[Mn^{++}, MnO_4^-]}} - E_{0_{[Fe^{++}, Fe^{+++}]}} - \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8[Fe^{++}]^5}{[Mn^{++}][Fe^{+++}]^5}.$$

When the reaction reaches equilibrium, E_1 must equal E_2, and therefore $E_1 - E_2 = 0$, and the potential of the cell (E) is zero. Therefore the following simple expression is obtained for calculating the equilibrium constant from the molal potentials:

$$E_{0_{(Mn^{++}, MnO_4^-)}} - E_{0_{(Fe^{++}, Fe^{+++})}} = E_{0_{(cell)}} = \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8[Fe^{++}]^5}{[Mn^{++}[[Fe^{+++}]^5}$$

$$= \frac{0.059}{n} \log K.$$

In the above case K has the value 10^{-57}. It is thus seen that if molal potential values are available, predictions can be made as to the completeness of any reaction it is desired to use. It is to be emphasized again that such predictions refer to equilibrium conditions only and that no predictions can be made therefrom as to the rate at which these equilibrium conditions will be attained.

Permanganate Methods of Volumetric Analysis

Discussion. Standard solutions of permanganate are extensively used in volumetric oxidation and reduction reactions. This is due, first, to the large negative value, −1.45 v, of the manganous ion–permanganate potential, and, as a result, the pronounced oxidizing tendency of that reaction; second, to the intense color of the compound which enables it to serve as its own indicator; and third, to

the fact that, properly prepared and kept, permanganate solutions are stable over long periods of time.

In the discussion to P. VI, there was given a series of curves showing the calculated changes in the concentrations of the ions involved during the titrations of a soluble silver salt with various anions which form insoluble silver salts. In these curves the predominant feature was the very rapid change in the concentrations of the silver ion and of the anion near the equivalence-point, and it was pointed out that these large concentration changes could be

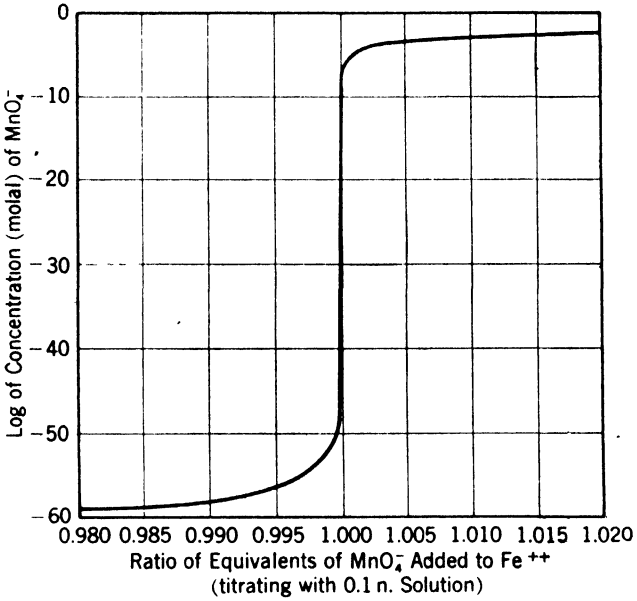

Fig. 11. Changes in Permanganate Ion Concentration During the Titration of a Ferrous Salt Solution.

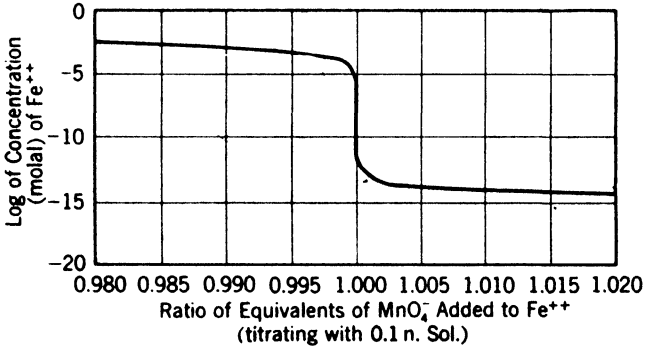

Fig. 12. Changes in Ferrous Ion Concentration During Titration with Permanganate.

used to cause some effect which would indicate the end-point of the reaction. This same principle is illustrated in Fig. 11, where the changes in the permanganate concentration during the titration of ferrous iron with permanganate have been calculated and are shown as a function of the ratio of the two substances present. It is noted that as long as there is an appreciable amount of ferrous iron present, the concentration of the permanganate is practically negligible, but that near the equivalence-point there is a very rapid rise in the permanganate concentration which causes its color to become visible; therefore, the appearance of this color can be taken as the end-point of the titration. It would also be possible to determine the end-point by testing for the ferrous ion; for, as is seen by Fig. 12, its concentration very rapidly decreases to a negligible quantity near the equivalence-point.[28]

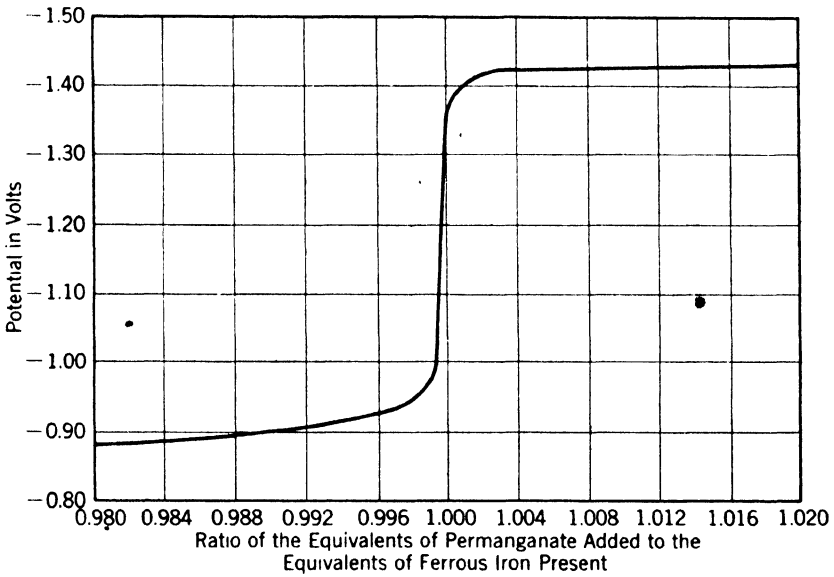

Fig. 13. The Potential Change During the Titration of Ferrous Ion with Permanganate.

Change of Potential During a Titration and Potentiometric Titrations. In Fig. 13 there has been plotted for the same reaction, not the

[28] This method is used in the so-called Penny method for titrating ferrous iron with standard dichromate solution (which is not so intensely colored as to be used as its own indicator) by removing a drop of the titrated solution and adding it to a drop of potassium ferricyanide solution. As long as there is an appreciable concentration of ferrous iron present, a blue coloration is obtained. For the details of the titration see Treadwell-Hall, *Analytical Chemistry*, Vol. II, Quantitative, 7th Ed., p. 549 A.

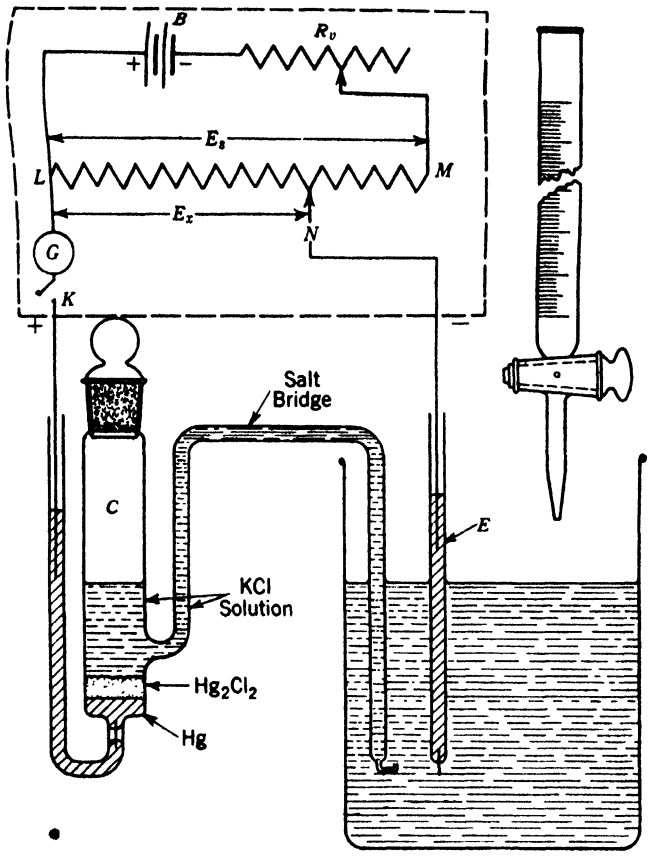

Fig. 14. Principles of Potentiometric Titrations. *B*—battery of constant e.m.f.; *LM*—uniform slide curve resistance; *N*—sliding contact; R_v—variable resistance; *G*—galvanometer; *K*—tapping key switch; *C*—calomel electrode; *E*—platinum-wire indicator electrode.

Explanation of method: Within the broken lines are shown the essential features of the potentiometer method of measuring an unknown electromotive force. The battery *B* is connected through a variable resistance to the terminals of the uniform slide wire resistance *LM*, and should maintain a constant potential drop through this resistance; this potential drop can be properly adjusted for the electromotive force to be measured by the variable resistance R_v. The cell whose unknown electromotive force is to be measured is connected as shown. In this case this cell is composed of the reference calomel electrode and the platinum electrode, which assumes the potential set up by the constituents in the titrated solution. As thus connected, the unknown electromotive force tends to send a current through the slide wire in a direction opposite to that of the battery, and, in making a measurement, the sliding contact *N* is adjusted until a position is found at which no current exists in the galvanometer circuit as evidenced by no deflection of the galvanometer, *G*, being obtained upon closing the tapping key, *K*. At this point the opposing electromotive forces through the resistance are equal. As the ratio of the lengths, *LN/LM*, is equal to the ratio of the resistances of these two lengths and to the potential drop across them, it is seen that if the potential drop

across LM has been fixed at a definite value, E_s, the unknown potential drop, E_x, across LN can be found; that is,

$$E_x = E_s \frac{LN}{LM}.$$

By this means no current need be drawn from the unknown cell as the measurement is made; this avoids polarization effects, which would result if the cell were directly connected to a voltmeter.

As the electromotive force of the reference calomel half-cell is constant, the change during the course of a titration of the measured electromotive force, E_x, represents the change in the potential of the solution in which the platinum indicator electrode is immersed. By the substitution of a reference standard cell of known electromotive force in place of the measured cell the electromotive, E_s, can be accurately determined, and thus a measurement of the actual value of E_x can be obtained; this is the basis of the electrical method of determining the molal and formal potential values.

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concentration of the ions, but the existing potential as a function of the ratio of the equivalents of the oxidizing and reducing substances present. As would be predicted, since the potential is a function of the ion concentrations, it is again seen that the rate of change of the potential is much greater near the equivalence-point. This fact is the basis of the electrometric method of determining the end-point, in which the potential set up by the ions or compounds present in the solution is experimentally measured by suitable means at frequent intervals during the course of the titration, and a curve similar to those of Fig. 7 obtained, from which the end-point can be determined. The principle of the method used in making these potential measurements is shown in Fig. 14 and the accompanying explanatory material. A more complete treatment of this subject will be found in textbooks of quantitative analysis or in special reference books dealing with this subject, such as Kolthoff and Furman, *Potentiometric Titrations*, 2nd Ed., Wiley and Sons (1931), and Kolthoff, *pH and Electrotitrations*, Wiley and Sons (1931).

The Effect of Reaction Rate on Titrations. It has been mentioned above that it is not proper to attempt to predict how rapidly a reaction will proceed from calculations of the equilibrium conditions. In general it is necessary to determine by experiment the effect which rate phenomena may have upon a given reaction or method. This factor of rate is of peculiar importance in permanganate titrations. Referring to the table of molal potentials, it is seen that there are three reactions, which might be involved in such titrations, namely,

$$MnO_{2(s)} + 2H_2O = MnO_4^- + 4H^+ + 3E^- \quad -1.59 \quad (1)$$

$$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5E^- \quad -1.45 \quad (2)$$

$$Mn^{++} + 2H_2O = MnO_{2(s)} + 4H^+ + 2E^- \quad -1.24 \quad (3)$$

It is desired in titrating a reducing agent with a standard permanganate solution that the reaction proceed from right to left according to Equation 2 and not according to Equation 1, with the resultant formation of manganese dioxide. As the hydrogen ion concentration enters to the eighth power in the equilibrium expression for Equation 2, it would be expected that as long as an excess of the reducing agent was present and an acid solution was maintained, no appreciable amount of manganese dioxide would be formed. However, as the end-point is approached and a perceptible excess of permanganate ion is added to the manganous ion in the solution, it might be expected that Reaction 1 would proceed to the left, forcing Reaction 3 to the right according to the reaction

$$3Mn^{++} + 2MnO_4^- + 2H_2O = 5MnO_{2(s)} + 4H^+, \qquad (4)$$

and, by the methods illustrated above, it is calculated that the equilibrium expression for this reaction has an exceedingly small constant, thus,

$$\frac{[Mn^{++}]^3[MnO_4^-]^2}{[H^+]^4} = 10^{-36}.$$

By substituting reasonable values for the manganous ion concentration at the end of a titration and for the permanganate ion concentration necessary to give a perceptible end-point, it can be calculated that the hydrogen ion concentration would have to be raised to an impracticable value in order to prevent the precipitation of manganese dioxide. Therefore if it were not for the fortunate fact that the rate of the reaction shown by Equation 4 is very slow, the permanganate end-point could not be used without the formation of a manganese dioxide precipitate. Experimentally it is found that unless the hydrogen ion concentration is kept above approximately 0.5 molal, such a precipitate is likely to form as the end-point is approached. There are also certain methods which are carried out in neutral solutions in which the permanganate is reduced only to hydrated manganese dioxide. Such titrations are to be avoided, if possible, because of the difficulty of detecting the end-point color in the presence of the precipitate. Rate effects are also an important factor in permanganate titrations which are carried out in hydrochloric acid solutions; again it would be predicted that chloride would be oxidized by permanganate, but the rate at which this takes place is so slow that, by properly controlling the conditions, such

titrations are experimentally possible. An extended discussion of these effects is given in P. 53*A*.

P. VII. The Preparation of a Permanganate Solution

Discussion. It has already been stated that, if properly prepared and stored, permanganate solutions are stable over long periods of time; however, it is not practical to prepare standard solutions of permanganate by direct weighing. Even the best grades commercially obtainable almost invariably contain some manganese dioxide which has been formed on the surface, and, although it is possible by elaborate means to prepare a very pure product, the distilled water used for the solution usually has sufficient reducing gases or organic material in it to cause the production of some manganese dioxide upon standing. This manganese dioxide then serves as a catalytic agent for the further decomposition of the permanganate, and such solutions rapidly decrease in strength, especially if they are exposed to light. Therefore, it is customary to prepare the solution, to heat it, or allow it to stand until all reducing substances in the water are oxidized, and then to filter the solution through asbestos or sintered-glass filters into the storage bottle. Thereafter the solution must be protected from light and from contact with dust, organic matter, or reducing gases.

Procedure VII: PREPARATION OF A PERMANGANATE SOLUTION. Weigh out 3.2 g of the best grade of $KMnO_4$ obtainable (Note 1), transfer it to a large beaker, add 1 liter of water, and heat the solution to boiling, stirring the mixture until the crystals have dissolved. Cover the solution with a clock glass and keep it just boiling for 15 minutes. Allow the solution to cool (Note 2) and filter it through a layer of asbestos supported on a wad of glass wool in a glass funnel (Note 3). Collect the solution in a ground-glass-stoppered bottle (Note 13, P. V) which has just been cleaned with cleaning solution, rinsed with distilled water, and drained. Swirl the solution, without wetting the neck of the bottle, until it is thoroughly mixed (Note 4).

Notes:

1. Even though the solution is later to be standardized, it is an advantage to use a good grade of $KMnO_4$, as it is less likely to contain substances which will later cause a slow reduction of the permanganate and the formation of MnO_2.

2. If time is available, the solution should be kept hot, preferably on a

water bath for an hour, or left to stand overnight. In this way slowly oxidized organic substances are more effectively removed.

3. A sintered-glass filter should be used if available. In any case the filter should be cleaned with cleaning solution and thoroughly rinsed first with distilled water and then with a small portion of the permanganate solution.

4. It is desirable that the neck and stopper of the bottle be not wet with the permanganate, since this then evaporates, and a deposit of $KMnO_4$ and MnO_2 results, which on again opening the bottle may fall into the solution. For this reason, when filling a buret, the solution should not be poured, but a clean dry pipet used (see Note 2, P. VI).

P. VIII. The Standardization of Permanganate Solutions

Discussion. *Primary standards.* A substance which is directly weighed and used for the standardization of a solution is called a "primary standard"; for very precise work it is preferable that a solution be thus directly standardized rather than compared with another standard solution.

A primary standard should meet certain qualifications, namely:

1. It should be a pure substance. It may be an elementary substance such as iodine, copper, or iron; or it may be a compound such as sodium oxalate, arsenious oxide, or potassium iodate; but it must be capable of purification, usually by recrystallization or sublimation, to a definitely known composition.

2. It should be stable. Hydrated substances, while frequently used, are not preferred, since they are difficult to free of extraneous moisture and are prone to change their moisture content upon storage. Compounds subject to surface oxidation ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, Fe wire) or reduction ($KMnO_4$) are to be avoided if possible.

3. It should not be hygroscopic. Difficulty in storage and in weighing is likely with such materials.

4. It should react stoichiometrically. Complex apparatus or special technique should not be required in order to make the reaction stoichiometric. A particular standard may be useful for only one solution of a general class. Thus arsenious oxide is an excellent reducing agent for the standardization of iodine solutions, but presents specific difficulties if used for standardizing permanganate.

5. It should have a large equivalent weight. It is desirable that the weight required for a titration should be so large that the weighing errors will be small relative to the other errors involved in the standardization.

The standardization of permanganate solutions against sodium oxalate. The primary standards which have been most commonly used for permanganate solutions are ferrous ammonium sulfate

($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$), oxalic acid ($H_2C_2O_4 \cdot 2H_2O$), iron wire, and sodium oxalate ($Na_2C_2O_4$). Of these, the latter most nearly fulfills the qualifications listed above,[29] and therefore its use as a standard for permanganate solutions will be considered in detail.

It was pointed out in the general discussion of volumetric methods that in order for a given reaction to be used as the basis for a precise method it must (1) be quantitatively complete, (2) proceed with reasonable rapidity, (3) be stoichiometric, and (4) there must be some practical means of determining the end-point.

The first of these requirements is satisfactorily met by sodium oxalate, since, from an equilibrium point of view, the reaction between permanganate and oxalate is quantitatively complete. This reaction, when taking place in an acid solution, is represented by the equation[30]

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{++} + 10CO_2 + 8H_2O,$$

[29] Sodium oxalate for standardization purposes can be obtained from the United States Bureau of Standards.

[30] The principles involved in constructing equations for electronic reactions are aptly illustrated by the permanganate reactions, which have been considered. These principles are as follows: First, there must be known the initial and final oxidation states of the reducing and of the oxidizing agents involved. From this the unit change of each can be noted; and, as the total change for the two substances must be equal, the proper coefficient for each substance can be determined. Following this, if any of the substances involved are oxygen compounds, it is usually necessary to include the proper amount of hydrogen ion, hydroxyl ion, or water, as the case may be. As an illustration, consider the equation

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O.$$

To construct this it must first be known: (1) that the reaction is to take place in an acid solution, (2) that permanganate under such conditions is reduced to bipositive manganese, and (3) that ferrous ion is oxidized only to the tripositive ion; the oxidizing and reducing substances can then be properly balanced. The hydrogen ion needed to combine with the oxygen of the permanganate is then readily seen.

The reaction between permanganate and oxalate in acid solutions given above, although showing the initial and final products, contains an example of a compound, namely, the oxalic acid molecule, where there may be doubt as to the oxidation state of one or more of the atoms involved. In such a case recourse is had to the principle that in a compound the sum of the positive oxidation numbers must be equal to the sum of the negative oxidation numbers of all the atoms present. Therefore, since the oxidation states of the hydrogen and oxygen atoms are known, it is seen that the average oxidation state of the carbon atoms is +3. (There are compounds in which atoms of the same element may exist in different oxidation states; in such cases the above rule gives only the average oxidation state.) As the final product of the oxidation of the oxalate is carbon dioxide, in which the carbon is quadripositive, two oxidation equivalents are required for each mole of oxalate. Knowing this fact, the equation can be balanced.

and is, moreover, an example of what is called an *irreversible* reaction, since it has not been found possible experimentally to cause the reduction of carbon dioxide to oxalate. The second requirement is not so satisfactorily fulfilled, since the rate of the reaction between oxalate ion or oxalic acid and permanganate is somewhat slow at room temperature, and it is necessary to heat the solution in order to cause the reaction to proceed to completion at a practical rate. It will be found experimentally that the first portion of the permanganate added will be decolorized very slowly even at 90°C., but that thereafter it disappears more rapidly. This is due to the fact that manganous ion catalyzes the reaction; and since it is one of the products, the reaction proceeds more rapidly as soon as an appreciable amount of the permanganate has been reduced. This is an example of an *auto-catalytic* reaction, that is, one which is catalyzed by one of the products of the reaction.

A small amount of manganous ion could be added before beginning the titration; however, this is not advised, as the initial delay is slight, and after the first one or two drops the reaction proceeds quite rapidly. The mechanism of this reaction and its catalysis is very complicated and, although extensively investigated, is not yet entirely clear.[31]

In very general terms it seems that, as stated, the reaction between oxalate or oxalic acid and permanganate is quite slow, but that if manganous ion is present, it can be oxidized by permanganate to the tri- or quadripositive state and that this in turn can rapidly oxidize the oxalate. This simple picture is complicated by the formation of complex compounds between the various manganese ions and oxalate ion, and the possible formation from the oxalate of unstable oxidation products, such as the ion CO_2^-. These considerations are extensively treated in the references cited.

The question of the stoichiometric nature of the reaction has been exhaustively studied by McBride[32] and more recently by Fowler and Bright.[33] In considering the titration, it is evident that errors can arise from the following sources: (1) As oxalic acid is readily sublimed, it is possible that it might be lost from a hot acid solution

[31] Skrabal, *Z. anorg. allgem. Chem.*, **42**, 1 (1904); Launer, *J. Am. Chem. Soc.*, **54**, 2597 (1932); Launer and Yost, *J. Am. Chem. Soc.*, **56**, 2571 (1934); Fessenden and Redman, *J. Am. Chem. Soc.*, **57**, 2246 (1935); Lidwell and Bell, *J. Chem. Soc.*, **1935**, 1303; Polissar, *J. Am. Chem. Soc.*, **58**, 1372 (1936).

[32] McBride, *J. Am. Chem. Soc.*, **34**, 393 (1912).

[33] Fowler and Bright, *J. Research Natl. Bur. of Stnds.*, **15**, 493 (1935).

during the titration. (2) It is known that oxalate solutions are not stable when kept in glass for considerable periods of time and that oxalic acid is decomposed by sulfuric acid in concentrated solutions, so that an appreciable decomposition of the oxalate might occur. (3) It has been shown that oxalate solutions in the presence of manganous ions are slowly oxidized by atmospheric oxygen, and it is entirely possible that, as is known to happen in other cases, this reaction might be further induced during the permanganate-oxalate reaction. (4) As permanganate is known to be unstable in hot acid solutions, decomposition may occur during the course of the titration. (5) The oxalate might not be completely oxidized by the permanganate at the end-point, or products other than carbon dioxide, such as hydrogen peroxide, might result from the oxidation reaction. (6) The permanganate might not be completely reduced to manganous ion at the end-point, compounds of tri- or quadripositive manganese remaining in the solution.

In order to determine the existence and magnitude of these possible effects experiments were made by McBride in which one factor was varied and, insofar as possible, all the other variables were kept constant. In this manner the effect of (1) temperature, (2) acidity, (3) volume of titrated solution, (4) rate of addition of the permanganate, (5) rate of stirring of the solution, (6) allowing the solution to stand at an elevated temperature before titrating, (7) the absence or presence of oxygen during the titration, and (8) the concentration of manganous ion were studied. For the details of these experiments one should consult the original article, but the results can be summarized as follows: There was no appreciable volatilization, decomposition, or air oxidation of the oxalate in solutions approximately 1 normal in sulfuric acid even at elevated temperatures. There was no evidence of an appreciable error due to incomplete oxidation of the oxalate. There was some evidence of error due to decomposition of the permanganate, with apparent loss of oxygen, but the magnitude of this effect was small, and, by proper control of the conditions of the titration, results which were reproducible, that is, precise, to 0.2 per cent were obtained.

As the result of his experiments, McBride recommended that the titration be carried out slowly, at relatively high temperatures (60° to 90°) and with continuous and vigorous stirring. These conditions, if closely regulated, gave very reproducible results, but it was later found that there was a tendency for these values to give

permanganate titers[34] from 0.1 to even 0.4 per cent too high. Fowler and Bright (*loc. cit.*) subsequently investigated this effect and are inclined to attribute it in part (but not wholly, as it could not be entirely eliminated by working under oxygen-free conditions) to peroxide formation, which may be represented as follows:

$$O_2 + H_2C_2O_4 = H_2O_2 + 2CO_2. \quad (1)$$

If the peroxide then decomposes,

$$2H_2O_2 = 2H_2O + O_2, \quad (2)$$

before it is oxidized by permanganate, too little permanganate is consumed, and a high normality for the permanganate is obtained; the slower the rate of titration the greater the opportunity for the peroxide to decompose. Several investigators have found evidence of peroxide formation during the permanganate-oxalate reaction, and Kolthoff[35] has shown that this increases with increase in temperature and manganous ion concentration.

As a result of their investigation of this positive error Fowler and Bright have found that it can be almost entirely eliminated if most of the permanganate is added rapidly at room temperature and the solution then heated to 55° to 60° before obtaining the end-point. In order to increase the rate of the reaction at room temperature, the initial concentration of the sulfuric acid present was increased from about 0.7 n. (as recommended by McBride) to about 1.8 n. An end-point correction is made by matching the permanganate color in another beaker containing the same amount of hot water and of acid. Under these conditions (which are provided for in the following procedure) the stoichiometric error should not exceed 0.1 per cent, and if weight burets are used, the instrumental errors should also be less than that value.

The determination of the end-point of the titration is simplified because the color of the permanganate ion is so intense that no additional indicator is required. The end-point is consistent, and, if the proper end-point correction is made, it is highly precise.

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[34] The titer of a solution may be defined as the concentration expressed in grams per milliliter. The titer is usually determined by titration and may refer to the weight of a given substance contained in, or that will react with, a milliliter of the solution. This convention may be used to advantage where a standard solution is to be used primarily for the determination of a single substance; the titer is then given as the grams of that substance reacting with 1 milliliter of the solution.

[35] Kolthoff, *Z. anal. Chem.*, **64**, 185 (1925).

Bray[36] found that if the titration is carried out under certain conditions, the end-point correction could not be precisely made by matching the color of the titrated solution, because of the presence of some incompletely reduced manganese compounds. However, McBride showed that at temperatures above 60°C. and by slow addition of the permanganate near the end-point this effect could be reduced to within the usual experimental limits.

Procedure VIII: STANDARDIZATION OF A PERMANGANATE SOLUTION AGAINST SODIUM OXALATE. Transfer about 1 g of $Na_2C_2O_4$ (Note 1) to a weighing bottle and dry the material at 110° to 200°C. for 1 hour (Note 2). Weigh out 0.25- to 0.30-g portions (Note 3) of the oxalate into each of three 400-ml beakers. Fill a clean buret with permanganate solution (Note 5, P. VI). Add to the oxalate in the first beaker 250 ml of 1.8 n. H_2SO_4 (12.5 ml of 36 n. diluted to 250 ml) which has been previously boiled for 10 to 15 minutes and then cooled to 27 ± 3°C. Gently stir until the oxalate has dissolved; a thermometer may be used to advantage. Add 90 to 95 per cent of the calculated volume of the permanganate at a rate of 25 to 35 ml per minute while stirring slowly (Note 4) and let the solution stand until the pink color disappears (usually about 45 seconds). Heat to 55° to 60°C. (Note 5), and then continue adding the permanganate at such a rate that no permanganate color persists in any part of the solution. As the end-point is approached, each drop must be allowed to decolorize before the next is added, and finally part drops should be transferred from the tip of the buret to the solution with the stirring rod (or thermometer). Keep the solution between 55° and 60°C. The end-point should be taken when the faintest perceptible pink color which persists is obtained, viewing the solution against a white background. Immediately after the end-point is obtained, add to 300 ml of 1.8 n. H_2SO_4 (which should have been previously boiled and then cooled to 55° to 60°) sufficient permanganate to match the color in the titrated solution; subtract this volume from that used in the titration (Note 6). Similarly titrate the other two samples and calculate the normality of the permanganate (Note 7).

[36] W. C. Bray, *J. Am. Chem. Soc.*, **32**, 1204 (1910).

Notes:

1. Sodium oxalate obtained from the Bureau of Standards or of a special grade for standardization purposes should be used.

2. Sodium oxalate can be heated to 240°C. without decomposition. It is not hygroscopic, however, and 1 hour at 100°C. will usually suffice to dry the material. It may be weighed without danger of absorption of moisture from the air.

3. The size of the sample should be such that at least 35 ml of the permanganate are used in the titration, thus reducing the percentage error caused by the uncertainty in reading the buret. The size is limited by the fact that it is undesirable to have to refill the buret, thus introducing the uncertainty of two additional buret readings. The approximate value of the permanganate should be known so that most of the required volume can be added before heating the solution; if desired, a preliminary titration can be run in a hot solution.

4. The permanganate should be added directly to the solution and not allowed to flow down the side of the beaker, since this is likely to result in the formation of a film of MnO_2 on the glass. Any permanganate spattering onto the side of the vessel should be washed down immediately.

5. This part of the titration is advantageously carried out with the beaker on an electric hot plate or over a low burner. The buret can be protected from heat and condensation of moisture by inserting the tip tightly through a piece of cardboard; the latter then acts as a shield.

6. This correction usually amounts to 0.03 to 0.05 ml of 0.1 n. $KMnO_4$.

7. By this method even inexperienced analysts should obtain results that check to at least 2 parts in 1000.

P. IX. The Preparation and Standardization of Ferrous Sulfate Solutions

Discussion. The application of permanganate methods can be extended to the determination of certain oxidizing agents if a standard solution of a reducing agent which reacts stoichiometrically with permanganate is available. The process consists in adding an excess of the reducing agent to the oxidizing agent to be determined and then titrating the excess with permanganate; the reducing agent most frequently used for this purpose is ferrous sulfate. As has been shown in the general discussion of electronic reactions, ferrous iron and permanganate react quantitatively, and, furthermore, the reaction is both rapid and stoichiometric.

Neutral ferrous solutions are rapidly oxidized by the oxygen of the air, and the ferric ion then hydrolyzes, with the resultant precipitation of ferric hydroxide. Hydrochloric acid solutions of ferrous salts are so rapidly oxidized as to be unsatisfactory standard solutions, and, in addition, the presence of chloride may be objectionable; sulfuric acid solutions are so slowly oxidized that they can be satis-

factorily used. However, for precise work, ferrous sulfate solutions should be standardized daily unless they are kept under an inert atmosphere, such as carbon dioxide or nitrogen.

Procedure IX: PREPARATION OF A FERROUS SULFATE SOLUTION. Add 28 g of finely crushed $FeSO_4 \cdot 7H_2O$ (or 40 g of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) to 100 ml of 6 n. H_2SO_4 and 400 ml of water and stir the mixture until the crystals dissolve. Dilute the solution to a liter, mix it thoroughly and transfer it to a ground-glass-stoppered bottle.

STANDARDIZATION OF A FERROUS SULFATE SOLUTION. Pipet 25 ml of the ferrous sulfate solution into a 200-ml flask containing 10 ml of 6 n. H_2SO_4 and 75 ml of water. Titrate this solution with the permanganate solution until the first perceptible pink color is obtained when viewing the solution against a white background (Note 1).

Notes:

1. The appearance of the pink color is most sensitively detected by comparing the titrated solution with an equal volume of acid and water in a similar flask. After obtaining the end-point, permanganate should be added to the comparison solution until its color matches that of the titrated solution. The volume of permanganate thus used should be subtracted from that used in the titration.

The Applications of Permanganate Methods

Permanganate methods are used in this system of analysis for the estimation of cadmium (P. 30), zinc (P. 62), strontium (P. 85), calcium (P. 87), for the optional estimation of iron (P. 53 A), and for the optional estimation of manganese (P. 72); they are also used in the analysis of the acidic constituents for the estimation of ferrocyanide (P. 133) and oxalate (P. 166 and P. 87). Other constituents that are frequently determined by titrations involving permanganate or ferrous sulfate solutions are antimony, manganese, and peroxide.

IODOMETRIC METHODS OF VOLUMETRIC ANALYSIS

Discussion. *General principles.* The molal potential of the reaction $2I^- = I_2 + 2E^-$ is only -0.53 v, and therefore it would appear that iodine might be used as an oxidizing agent for a considerable number of compounds which are positive to it in the Table of Reduction Potentials, and that, similarly, iodide ion might be used to reduce a considerable number of compounds which are negative to it in that series. It is because both of these conditions can be quantitatively realized that iodometric methods are so extensively used in volumetric analysis. For the first-mentioned type of reaction a standard solution of iodine is used. The second type usually involves the addition of an excess of a soluble iodide to the oxidizing substance to be determined, whereby an equivalent amount of iodine is set free; this iodine is then titrated with a standard solution of thiosulfate.[37] This latter reaction may be represented as

$$I_2 + 2S_2O_3^= = 2I^- + S_4O_6^=,$$

and is almost unique, since most other oxidizing agents convert thiosulfate at least partially to sulfate, and, in fact, some sulfate will be formed by iodine if the solution is at all alkaline. This is apparently due to the fact that iodine reacts with hydroxyl ion,

$$I_2 + OH^- = HIO + I^-,$$

and that the hypoiodous acid thus formed tends to oxidize thiosulfate to sulfate. Because of this same reaction of iodine with hydroxyl ion and the subsequent decomposition of the hypoiodite to iodate,

$$3IO^- = 2I^- + IO_3^-,$$

iodine cannot be used as an oxidizing agent in solutions in which the hydrogen ion concentration is less than approximately 10^{-9}.

Determination of the end-point of iodometric titrations. Several methods are available for determining the end-point of iodometric reactions. First, in the absence of other colored ions, the color of the iodine itself (or more properly of the tri-iodide ion, I_3^-, which iodine forms with iodide) can be detected in daylight when its concentration is as small as 3×10^{-5} normal, and therefore it can be titrated to within one drop of one-tenth normal thiosulfate. Secondly, the purple to violet color which iodine gives in organic solvents (such as

[37] Methods of the first type, involving the use of a standard solution of iodine, are sometimes designated as "iodimetric" methods, and those of the second type—where iodine is liberated and titrated with thiosulfate—as "iodometric" methods; this convention will not be used here.

carbon tetrachloride, chloroform, or benzene) is so intense that, by shaking a small amount of one of these with the solution being titrated and noting when this color disappears, a very satisfactory, although not so convenient, end-point can be obtained. In most cases, another almost unique reaction of iodine is made use of, namely, the fact that tri-iodide forms with starch an intensely colored blue compound, the exact nature of which is not certain, although it is generally thought to be an adsorption compound. This color is so intense that solutions 1 to 2×10^{-5} n. in iodine and at least 4×10^{-5} n. in iodide give an easily visible blue color. The intensity of the color decreases with less than this concentration of iodide, and is more pronounced in slightly acid than in neutral solutions; above 25°C. it is markedly decreased. The color is also somewhat dependent upon the presence of other salts, changing to purple or brownish in concentrated solutions.

P. X. The Preparation of Iodine Solutions

Discussion. Iodine is so slightly soluble in water, 1.34×10^{-3} moles per liter at 25°C., and has such an appreciable vapor pressure, that advantage has to be taken of the increased solubility caused by the presence of iodide in preparing the standard solutions. This effect is due to the reaction

$$I_2 + I^- = I_3^-,$$

which tends to proceed to the right, as is shown by the value for the equilibrium expression, thus:

$$\frac{[I_3^-]}{[I_2][I^-]} = 7.1 \times 10^2 \text{ at } 25°C.$$

Experiments have shown that in solutions containing approximately 2 to 3 per cent by weight of potassium iodide, tenth normal solutions of iodine do not rapidly lose iodine if the proper precautions are observed. The container should be kept stoppered except when withdrawing solution, and this should be done as rapidly as possible. The solution should be protected from dust and from reducing gases. Also, since the reaction

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O$$

is induced by light, the storage bottle should be covered or kept in a dark place.

Procedure X: PREPARATION OF AN IODINE SOLUTION. Weigh out into a liter flask or graduated cylinder 25 g of

potassium iodide (Note 1) and dissolve it in 25 to 30 ml (not more) of water (Note 2). Weigh into a weighing bottle 12.7 g of iodine (Note 3), add this to the potassium iodide solution, and shake the mixture until the iodine is completely dissolved (see Note 2). *Slowly* add sufficient distilled water to the solution to make the volume 1 liter, swirling the solution as the water is added. Transfer the solution to a ground-glass-stoppered bottle (Note 13, P. V), taking care that no iodine has remained undissolved.

Notes:

1. The KI should be free from iodate and carbonate. The first would react with the iodide when the solution was acidified, and the latter would by hydrolysis cause the solution to become alkaline, which would tend to convert the iodine into iodate and iodide. Iodate is tested for by dissolving 1 g of the KI in 10 ml of water, and adding 1 ml of 6 n. H_2SO_4; no iodine color should develop in 30 seconds. A similar solution, 1 g KI in 10 ml of water, should not give an alkaline reaction with phenolphthalein.

2. Iodine dissolves very slowly in dilute iodide solutions, and for this reason the iodine should be first *completely* dissolved in the concentrated KI solution. The solution of the iodine in the concentrated KI should not be rapidly diluted, or iodine will be reprecipitated; this falls to the bottom of the bottle and may not dissolve for days.

3. The weight of iodine taken need not be exact. Iodine should be brought into balance cases only in stoppered vessels; its vapors are corrosive.

P. XI. The Preparation of Starch Solutions

Discussion. The nature of the starch-iodine blue color and the sensitivity with which it can be detected have been mentioned in the general discussion of iodometric processes.

The indicator solution can be prepared from potato, arrowroot, or rice starch. These starches are composed of two main products, β-amylose, which is the so-called soluble starch, and α-amylose, which is quite insoluble. When the relatively insoluble starch grains are subjected to boiling water, they burst, and upon standing (or centrifuging) the α-amylose and other insoluble material settles out and can be eliminated by decanting off the clearer portion of the solution. This is desirable, since iodine forms with α-amylose reddish-colored compounds which are not as readily decolorized as is the blue compound; cornstarch contains a much higher percentage of α-amylose and should not be used.

If not kept sterile, starch solutions decompose within a few days, because of bacterial action, and the decomposition products are

likely to consume an appreciable amount of iodine as well as form a reddish color. Similar products are formed by the hydrolysis of starch in acid solutions, but this reaction is not sufficiently rapid to cause trouble in titration unless the acid concentration is greater than 3 to 4 normal or the titration is unduly prolonged. The above effects are accelerated and the starch is likely to be coagulated if it is introduced into a concentrated iodine solution; consequently, the indicator is always withheld from the titrated solution until the iodine color becomes uncertain.

Procedure XI: PREPARATION OF A STARCH SOLUTION. Place 2 g of powdered starch (potato, rice, or arrowroot) and 20 to 30 ml of cold water in a mortar, rub them into a thin paste, and pour this slowly into 500 ml of boiling water, stirring constantly. Heat the mixture just to boiling for 15 to 20 minutes, allow to stand overnight, and then decant the clear liquid into 100-ml bottles. Place these in boiling water, insert soft rubber stoppers loosely, and heat for 2 hours; finally insert the stoppers firmly and allow the solution to cool (Notes 1, 2).

Notes:

1. The preparation keeps indefinitely in the sterile stoppered bottles, but decomposes rapidly when opened; this is indicated in use by the appearance of a reddish or brown color which persists after the disappearance of the blue color.

2. So-called "soluble starch" may be purchased and is more convenient to prepare. As specimens vary in sensitivity they should be tested before use. Solutions are prepared as follows: Mix 1 g of the starch to a thin paste with cold water and pour into 200 ml of boiling water. Prepare the solution only as it is needed.

P. XII. The Standardization of Iodine Solutions

Discussion. *The reaction between arsenious acid and iodine.* The primary standard most suited for the standardization of an iodine solution is arsenious oxide. This substance can be purified by recrystallization from hot 6 n. hydrochloric acid and then by sublimation; however, it is more practical to purchase it from the Bureau of Standards. The method used in the standardization depends upon the oxidation in a neutral solution of the arsenious acid, formed in dissolving the arsenious oxide, to arsenic acid by means of a standard iodine solution. The reaction is of sufficient theoretical interest to be considered in detail.

The equilibrium constant for the reaction

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 3I^- + 2H^+ \qquad (1)$$

has the value 7×10^{-2}, and, consequently, the reaction can be forced in either direction by controlling the hydrogen ion concentration. When an aqueous arsenious acid solution is titrated with iodine, the reaction is incomplete if the acid formed by the reaction is allowed to accumulate in the solution; in an alkaline solution iodine reacts with hydroxyl ion,

$$I_3^- + OH^- = 2I^- + HIO, \qquad (2)$$

causing an excess of iodine to be consumed before the starch-iodine end-point is obtained. Therefore, the conditions under which the reaction can be made the basis of a precise iodometric method are limited but can be approximately calculated as follows:[38] In order to calculate the upper limit for the hydrogen ion concentration let it be assumed (1) that the final volume will be 200 ml, (2) that 5 milliequivalents of arsenious acid are to be titrated, (3) that the standard iodine solution is 0.05 formal in iodine (I_2), and 0.15 formal in potassium iodide, and (4) that an accuracy of 0.001 per cent is desired; this small value is arbitrarily taken to insure a reasonable factor of safety.

Since 50 ml of the iodine solution will be used, the final iodide concentration will be 0.0625 molal; to give the accuracy desired the ratio of the concentration of H_3AsO_3 to H_3AsO_4[39] will have to be 10^{-5}, and, if the minimum detectable starch-iodine color is used as the end-point, the concentration of the tri-iodide ion may be as low as 2×10^{-7} molal. (This value was experimentally found by Washburn.) Substituting these values in the equilibrium expression for Reaction 1, it is found that the maximum hydrogen ion concentration is 2.4×10^{-5}.

The factor limiting the lowest hydrogen ion concentration permissible is the reaction

$$I_3^- + OH^- = HIO + 2I^-.$$

Since the equilibrium constant of this reaction has been calculated to be 1.3×10^2, and since the final iodide and tri-iodide ion concentrations are essentially the same as in the above calculation, and since, in order to obtain the assumed accuracy, not over 0.001 per cent of the

[38] These conditions have been calculated and experimentally studied by Washburn, *J. Am. Chem. Soc.*, **30**, 31 (1908); it is recommended that reference be made to this article.

[39] More exactly, the ratio of H_3AsO_3 to $H_3AsO_4 + H_3AsO_3$.

iodine used can be converted into HIO, the final concentration of this substance should not exceed 1.25×10^{-7} molal. From these values the hydroxyl ion concentration is calculated to be 1.9×10^{-5}, corresponding to a hydrogen ion concentration of 5.3×10^{-10} molal. Therefore, from an equilibrium point of view, if the hydrogen ion concentration is controlled between the limits 2.4×10^{-5} and 5.3×10^{-10}, it would appear that the reaction could be made the basis of an accurate volumetric method. The *rate* of the reaction has not been considered in these calculations, and experimentally it has been found that it is better to adjust the hydrogen ion concentration nearer to the lower limit, since in more acid solutions the rate at which the iodine is removed by the arsenious acid becomes so slow as to make the titration quite tedious.

Buffer Solutions. Some means now has to be provided by which the hydrogen ion concentration of the solution can be automatically controlled within this favorable range. In any solution containing an acid and its salt the hydrogen ion concentration is determined by the ionization constant of the acid and the ratio of the molal concentration of the un-ionized acid to that of the salt, thus:

$$[H^+] = K_A \frac{[HA]}{[A^-]}.$$

Therefore, if, first, an acid with a constant having a value close to that of the desired hydrogen ion concentration is selected and, second, relatively large amounts of both the acid and the salt are provided, the hydrogen ion concentration of the solution will be fixed and, furthermore, will be little changed by addition or formation of either acid or base. Such a solution is said to be "buffered." It is desirable that the constant of the acid be approximately equal to the desired hydrogen ion concentration; this permits a ratio of acid to salt of near unity and provides the most effective buffering action against either acid or base for a given amount of the buffering material. For the present case, acids which will not be oxidized by iodine or reduced by iodide and having constants near the value desired (approximately 10^{-7}) are dihydrophosphoric acid ($H_2PO_4^-$, $K_A = 2 \times 10^{-7}$) and carbonic acid (H_2CO_3, $K_A = 3 \times 10^{-7}$); these acids and their salts were experimentally found to be satisfactory by Washburn (*loc. cit.*). By adding sodium hydrocarbonate ($NaHCO_3$) to an acid solution, carbonic acid is set free, and since the solubility of carbon dioxide in water has a fixed value at a given temperature, the concentration of the carbonic acid (H_2CO_3) in a solution saturated with carbon dioxide is fixed. Thus by neutralizing an acid solution

with hydrocarbonate, and then adding a definite amount in excess, the solution is buffered at a value determined by the excess of hydrocarbonate added. The molal concentration of carbonic acid [H_2CO_3] in a solution saturated at atmospheric pressure at 20°C. with carbon dioxide is 3.4×10^{-2}; therefore, if a sufficient excess of hydrocarbonate is added to make its molal concentration about 0.34, the hydrogen ion concentration would be 3×10^{-8} molal. Since during the titration of 5 milli-equivalents of arsenious acid 5 milli-equivalents of acid are set free, this would cause the hydrocarbonate concentration to decrease to 0.315 molal, and the hydrogen ion concentration would be increased proportionally to 3.2×10^{-8} molal, approximately a 7½ per cent change. If the same amount of acid is added to 200 ml of pure water, the hydrogen ion concentration would change from 10^{-7} to 2.5×10^{-2}, a 200,000-fold change. If carbon dioxide were continuously passed through the hydrocarbonate solution, it would also be "buffered" against a decrease in the hydrogen ion concentration, for the addition of 5 milli-equivalents of hydroxyl ion would result merely in the hydrocarbonate ion concentration increasing to 0.365 molal, and proportionally decreasing the hydrogen ion concentration to $2.8_7 \times 10^{-8}$—again only a 7½ per cent change as compared with one of 200,000-fold if the hydroxyl ion were added to a pure water solution.

It is obvious that in any solution containing a base and its salt similar considerations apply, thus:

$$[OH^-] = K_B \frac{[BOH]}{[B^+]}.$$

Therefore, when it is desired to "buffer" a solution to a basic range, a base with the proper ionization constant and its salt can be used effectively.

Buffer solutions are of such great importance in analytical, commercial, and biological processes that they have been discussed at some length here; the principles relating to them may be summarized from the practical side by recalling that in order to "buffer" a solution effectively two important considerations should be observed: First, an acid (or base) should be selected whose constant is of the same order of magnitude as that of the hydrogen (or hydroxyl) ion concentration at which it is desired to maintain the solution, since for a given total amount of acid and salt the buffering is most effective when the ratio of acid to salt is unity. Second, the amount of the buffer material provided must be large in comparison to the amount of hydrogen or hydroxyl ion which may be formed.

In this standardization sodium hydrocarbonate is used as the buffering agent, and, as has been shown by Washburn, a high order of precision is attainable.

Procedure XII: THE STANDARDIZATION OF AN IODINE SOLUTION AGAINST ARSENIOUS OXIDE. Dry approximately 0.6 g of As_2O_3 (Note 1) at 100° to 105°C. for 1 hour and weigh out 0.2-g portions into each of three 500-ml flasks (Note 2). Dissolve the solid in 2 ml of 6 n. NaOH and 10 ml of water, warming if necessary (Note 3). Dilute with 2 ml of water, add 2 drops of phenolphthalein indicator solution, carefully add 6 n. HCl until the red color disappears, and then add 1 ml in excess (Note 4). Cool the solution (Note 5) and, while inclining the flask, add (in small portions as long as vigorous effervescence occurs) 4 g of solid $NaHCO_3$; rinse the side of the flask. Add 5 ml of starch indicator and titrate with the iodine solution (Note 6), swirling the solution gently but not vigorously shaking it (Note 7), until the first purple or blue color is obtained which persists for 30 seconds (Notes 8, 9). Similarly titrate the remaining portions of As_2O_3 and calculate the normality of the iodine solution (Note 10).

Notes:

1. As_2O_3 for standardization purposes can be purchased from the Bureau of Standards, and it is recommended that this be used for highly accurate work; it is not hygroscopic and need not be dried unless extreme accuracy is desired or it has been exposed to considerable moisture. Since As_2O_3 sublimes at somewhat higher temperatures, it can be dried by being left over sulfuric acid in a desiccator for 12 hours.

Commercial material often contains chloride, sulfide, and water. The product may be purified by dissolving 40 g in 50 ml of hot 12 n. HCl, adding 50 ml of hot water, filtering out any residue, and then adding 50 ml more water and cooling in ice. The crystals are filtered out and washed with ice water until free of chloride. Sublime this product from a casserole onto a round-bottom flask.[40]

2. Weighing out three or more separate samples of arsenious oxide can be avoided by preparing a stock solution in a volumetric flask and taking aliquot portions of this with a pipet. A 250-ml flask and a 50-ml pipet are convenient for this purpose. If they have not been calibrated, a relative calibration is entirely satisfactory, as in this case it is desired only that an exactly known fraction of the total be taken. Such a calibration is made as follows:

Clean and dry a 250-ml volumetric flask. (To dry the flask, and similar apparatus, rinse it with several small portions of alcohol,

[40] See Chapin, *J. Ind. Eng. Chem.*, **10**, 522 (1918), for a discussion of the preparation of pure As_2O_3.

invert it, insert a glass tube almost to the bottom, attach the tube to a vacuum line and draw air through it. Compressed air is not as desirable, since it is likely to contain oily material picked up from the pumps.) Carefully deliver 5 pipets of water (Note 3, P. VI) into the flask and mark the position of the meniscus (a small gummed label may be used).

To prepare the arsenious acid solution precisely weigh out about 1 g of As_2O_3 into a small beaker, dissolve it in 5 to 10 ml of 6 n. NaOH, and transfer the solution to the 250-ml flask with the aid of a funnel. Wash out the beaker with repeated portions of water and dilute the solution to the calibration mark (see Note 9, P. V). Mix the solution (see Notes 11, 12, P. V), pipet 50 ml into a 500-ml flask, and treat as directed in the foregoing procedure. The solution should be used at once, since alkaline arsenite solutions are slowly oxidized; neutral solutions are quite stable.

3. Arsenious oxide is only moderately soluble in water, and the dry powder may dissolve slowly even in the sodium hydroxide solution.

4. The additional acid is added in order to saturate the solution with CO_2 when the hydrocarbonate is added. A solution saturated with this gas is desired for the purpose mentioned in the discussion.

5. The solution should be cooled to avoid loss of CO_2, to decrease the tendency for the reaction of the iodine to form hypoiodite, and to avoid the decrease in the sensitivity of the starch color which takes place above 25°C.

6. Iodine solutions should not be used in Mohr-type burets.

7. It is desirable that the solution remain saturated with CO_2 until the completion of the titration (see the discussion). Because of this, the titration is carried out in conical flasks, not open beakers, and the solution should not be shaken more than is necessary to cause mixing. If a tank or generator of CO_2 is available, it is more effective to keep a very slow stream of the gas passing through the solution, or a few drops of hydrochloric acid can be added just before taking the end-point.

8. Most starch preparations will show a transitory purplish tinge, which can be taken as the end-point. This color will be caused by a small fraction of a drop of iodine and should be followed immediately by a clear blue. It should not be confused with the more stable brown or reddish color given by decomposed starch solutions.

9. Overrunning the end-point should be avoided by noting the rate of disappearance of the local color caused by each drop of iodine. The inside of the flask should be rinsed down just before taking the final end-point. Should the end-point be slightly overrun, the solution can be back-titrated to the absence of color by means of a standard thiosulfate solution.

A common procedure which allows rapid titration of a solution without overruning the end-point is to reserve a small fraction of the solution and add it after a rapid titration to a preliminary end-point. This can be done by drawing up a small portion of the solution into a long "dropper" and leaving this in the solution until the preliminary end-point is obtained. The reserved portion is then expelled, the dropper flushed out with the titrated solution, the end-point obtained, and the dropper again flushed out..

10. Results obtained by this method should agree to within 0.2 per cent.

P. XIII. The Preparation of Thiosulfate Solutions

Discussion. As has been stated, iodometric methods can be divided into two general classes: (1) those in which a reducing agent is oxidized by a standard iodine solution, and (2) those in which an oxidizing agent is estimated by allowing it to react with an excess of iodide and then titrating the iodine set free with a standard reducing agent—almost invariably sodium thiosulfate. This substance is used because it reacts stoichiometrically with iodine and because its solutions are relatively stable with respect to the oxygen of the air. This is not true of most other standard reducing solutions, such as stannous chloride and titanous sulfate, which can be used to reduce iodine quantitatively.

Anhydrous sodium thiosulfate is too hygroscopic for use as a primary standard and although the pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) can be prepared in a high degree of purity by repeated recrystallizations from water and drying under carefully controlled conditions, this preparation is not justified because of some uncertainty as to the stability of the solution, especially when first prepared. Numerous explanations have been advanced as to the causes of the instability of thiosulfate solutions. It was originally suggested that, since thiosulfate is decomposed by acid, the effect was due to carbon dioxide present in the water, the reaction being

$$S_2O_3^{=} + H_2CO_3 = HSO_3^{-} + HCO_3^{-} + S,$$

and it was assumed that the solution would become stable after the carbon dioxide had been exhausted. However, since sulfite in neutral solution will reduce two equivalents of iodine, such solutions should increase in normality, which is not generally observed. Furthermore, as hydrosulfurous acid is stronger than carbonic acid, it would seem that the carbonic acid would be regenerated and serve merely as a catalyst for the decomposition of the thiosulfate; as a matter of experiment, thiosulfate solutions have been found to be relatively stable in the presence of carbon dioxide.

It has also been assumed that traces of metallic ions in the water catalyzed the air oxidation of thiosulfate. Thus, although the potential of the reaction

$$2H_2O = O_2 + 4H^+ + 4E^-$$

would indicate that it should oxidize thiosulfate quite completely, actually the rate of the reaction is such that it has been found that

solutions saturated with oxygen are very little affected.[41] However, if a trace of copper salt is present, it may react with thiosulfate as follows:

$$2S_2O_3^{=} + 2Cu^{++} = 2Cu^{+} + S_4O_6^{=}.$$

The cuprous ion is then oxidized by oxygen,

$$2Cu^{+} + \tfrac{1}{2}O_2 + H_2O = 2Cu^{++} + 2OH^{-},$$

and thus the oxidation of the thiosulfate continues as long as oxygen is present.[42]

More recent investigations[43] have shown that the major cause of the instability of thiosulfate solutions is sulfur-consuming bacteria, and that sterile solutions are quite stable; slightly alkaline solutions (H^+ concentrations of from 10^{-8} to 10^{-9}) seem to inhibit this bacterial action. Numerous experiments have confirmed the fact that 0.1 normal solutions which are prepared from freshly boiled water to which has been added 100 mg of sodium carbonate per liter and which are protected from bacterial infection are subject to very little change and may be used as soon as prepared.

It is assumed in iodometric methods that the equation

$$I_2 + 2S_2O_3^{=} = 2I^{-} + S_4O_6^{=}$$

represents quantitatively the reaction between thiosulfate and iodine. However, under certain conditions sulfate may be formed,

$$4I_2 + S_2O_3^{=} + 10OH^{-} = 2SO_4^{=} + 8I^{-} + 5H_2O,$$

and, as is indicated, its formation is favored by hydroxyl ion. It is generally assumed that the mechanism of this reaction involves the formation of hypoiodite, according to the reaction

$$I_2 + OH^{-} = HIO + I^{-},$$

since hypoiodite is known to oxidize thiosulfate to sulfate, as follows:

$$4HIO + S_2O_3^{=} + 6OH^{-} = 2SO_4^{=} + 4I^{-} + 5H_2O.$$

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[41] Kilpatrick and Kilpatrick, *J. Am. Chem. Soc.*, **45**, 2132 (1923).

[42] This is an example of "homogeneous catalysis," inasmuch as only one phase is present. Heterogeneous catalysis is usually assumed to take place because of an increase in the activity of the reactants at some surface.

[43] Kilpatrick and Kilpatrick, *loc. cit.*; Mayr, *Z. anal. Chem.*, **68**, 274 (1926).

Experimentally, it is found that acid or even neutral solutions, 0.1 n. in iodine, may be titrated with thiosulfate or into thiosulfate precisely, the order of the titration not affecting the results. With more dilute iodine solutions, where the hydrolysis into hypoiodite is more pronounced, and with solutions which may be slightly basic, containing, for example, an excess of bicarbonate and not being saturated with CO_2, the iodine should be titrated into the thiosulfate. When titrated in this order, the rate of reduction of the iodine is so rapid that hydrolysis and subsequent sulfate formation does not take place to an appreciable extent. Under no conditions should the hydrogen ion concentration be less than 10^{-9} during an iodometric titration.

It is an easily verified fact that the addition of a thiosulfate solution to even a dilute acid solution will cause decomposition of the thiosulfate with precipitation of sulfur,

$$S_2O_3^{=} + 2H^+ = H_2SO_3 + S_{(s)},$$

the precipitate of sulfur appearing after an interval of time which depends upon the concentration of the acid. Since this H_2SO_3 may react with iodine or may escape from the solution as SO_2, in one case increasing and in the other case decreasing the iodine equivalence of the solution, it is proper to question the use of thiosulfate in acid solutions. As a matter of experiment, thiosulfate solutions may be titrated into iodine solutions which are as concentrated in acid as 3 to 4 n. if the solution is effectively stirred during the addition of the thiosulfate; the rate of oxidation of the thiosulfate by iodine is so rapid that no appreciable decomposition of the thiosulfate takes place. Thiosulfate solutions should not be acidified before being titrated. Practically, in the vast majority of cases, the thiosulfate will be titrated into acid solutions of iodine. Since sodium carbonate (or sodium hydroxide) is often added to thiosulfate solutions, it is preferable to acidify neutral iodine solutions slightly before titrating them.

Procedure XIII: PREPARATION OF A THIOSULFATE SOLUTION. Boil somewhat more than 1 liter of distilled water in a flask for 5 minutes, cover the flask, and allow the water to cool. Weigh out 25 g of $Na_2S_2O_3 \cdot 5H_2O$ and 0.1 g of Na_2CO_3, dissolve them in the freshly boiled water, and dilute the solution in a graduated cylinder to 1 liter. Transfer the solution to a clean ground-glass-stoppered bottle (Note 1).

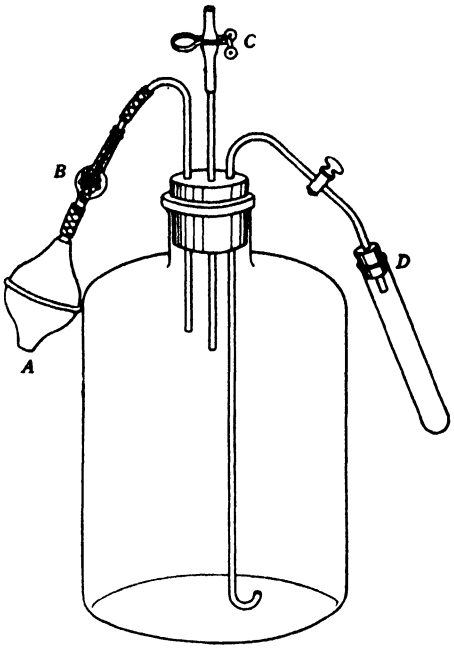

Fig. 15. Storage Bottle for Standard Solutions.

Notes:

1. If a large volume of solution is prepared, the storage bottle should be fitted with a siphon tube and the inlet tube provided with a soda-lime tube packed with sterile cotton. Since most of the solution may be lost should the rubber or glass stopcock of the siphon tube begin to leak, a convenient modification of this arrangement is shown in Fig. 15.

A is an atomizer bulb; *B* is a soda-lime bulb packed with sterile cotton; *C* is a relief tube fitted with a pinch clamp; *D* is a guard tube fitted over the outlet and containing a small volume of the standard solution in order to prevent evaporation. By removing *D* and pumping with *A*, solution is forced out as needed. The flow may be quickly stopped by releasing the pinch clamp at *C*. The relief tube may be eliminated by providing a stopcock on the outlet tube as shown.

P. XIV. The Standardization of Thiosulfate Solutions

Discussion. Various methods are available for the standardization of thiosulfate solutions. Since those solutions are always titrated against iodine solutions, the fundamental primary standard is iodine. While pure iodine can be readily prepared, it has such a relatively high vapor pressure that the weighing and transferring of it to the solution for titration requires a special technique; therefore this method is not generally recommended. Recourse is made to other primary standards, oxidizing agents, which when treated with an excess of iodide are capable of producing an equivalent amount of iodine in solution. Among these should be mentioned potassium iodate, potassium bromate, and potassium dichromate. While the first two are capable of very exact results, potassium dichromate is more commonly available, has a higher equivalent weight, and, as its solutions are useful for other purposes, is given preference here.

The reaction between iodide and dichromate, to give iodine and tripositive chromium, illustrates several of the factors which have to be considered in developing iodometric methods. In an alkaline solution iodine will oxidize tripositive chromium to chromate, while in an acid solution (10^{-4} molal or greater in hydrogen ion) iodide is quantitatively oxidized by chromate. However, at this low acid concentration, the rate of the oxidation is too slow for it to be of practical use. Experimentally, it has been found[44] that if the hydrogen ion concentration is greater than 0.2 molal and the iodide concentration greater than 0.05 molal, the oxidation is quantitatively complete in 5 minutes.

If the hydrogen ion concentration is much greater than 0.4 molal, another effect—one which has to be considered in all iodometric titrations made in acid solutions—becomes appreciable, namely, the so-called "oxygen error." As was true with thiosulfate, the potential of the oxygen half-cell is such that oxygen would be expected to oxidize iodide quite completely according to the reaction

$$O_2 + 4I^- + 4H^+ = 2I_2 + 2H_2O.$$

However, the rate of this reaction is so slow that iodide solutions with the hydrogen ion concentration as high as 0.4 molal can stand in contact with the air for periods up to 10 minutes without appreciable oxidation. Unfortunately, the reaction is induced by the presence of light and catalyzed by various ions, such as those of copper. Furthermore, the reaction may be caused to proceed more rapidly, or, as it is commonly called, "induced," during the course of another oxidation-reduction reaction. In the case of the dichromate-iodide reaction, it is found that if the hydrogen ion concentration is greater than about 0.4 molal, the above oxygen-iodide-hydrogen ion reaction is caused to proceed to an appreciable extent, is "induced," during the reaction between the iodide and chromate. It was experimentally found by Vosburgh and by Bray and Miller (*loc. cit.*) that this effect varied with the iodide concentration and even with the order of mixing of the iodide and dichromate, being greater when the dichromate was added to the iodide and acid than when the iodide was added to the dichromate and acid; these articles should be consulted for further details.

It is obvious that thiosulfate solutions can also be standardized against previously standardized iodine solutions, or, by a method

[44] Vosburgh, *J. Am. Chem. Soc.*, **44**, 2120 (1922); Bray and Miller, *ibid.*, **46**, 2204 (1924).

similar to the procedure below, against standard solutions of potassium permanganate, these latter serving as "secondary standards." In general, secondary standards are not recommended, since they involve the possibility of error in an additional set of volumetric measurements and in changes in the standard solutions. However, the accuracy with which the standardization of permanganate against oxalate and of thiosulfate against permanganate can be carried out makes this an exceptional case, and if a recently standardized permanganate solution is available, the saving in time will justify its use for all except the most exact work. Because of these facts, a brief procedure for the method is included in the notes. Bray and Miller have studied the method and shown that results obtained by it agree with other methods of standardization to within 0.1 per cent.

Procedure XIV: THE STANDARDIZATION OF A THIOSULFATE SOLUTION AGAINST POTASSIUM DICHROMATE. Precisely weigh out about 2 g of dry $K_2Cr_2O_7$ (Note 1), transfer to a 500-ml volumetric flask which has been calibrated against a 50-ml pipet (Note 2, P. XII), dissolve the crystals, and dilute with water to the mark. Mix the solution.

Pipet 50 ml of the $K_2Cr_2O_7$ solution into a 500-ml flask. Dissolve 3 g of KI in 50 ml of water, add to it 5 ml of 6 n. HCl (Note 2), and immediately add this to the dichromate solution. Gently swirl the solution once (Note 3), then close the flask with a watch glass, and allow it to stand in a dark place for 5 minutes. Dilute the solution with 300 ml of water, washing down the sides of the flask, and, while swirling the solution slowly, titrate with the thiosulfate solution. When the yellow color of the iodine becomes indistinct (Note 4), add 5 ml of starch solution and slowly titrate to the disappearance of the blue color of the starch. Repeat the titration with two other portions of the $K_2Cr_2O_7$ solution and calculate the normality of the thiosulfate solution (Note 5).

Notes:

1. As the best grades of $K_2Cr_2O_7$ often contain CrO_3, the salt should be purified by recrystallization from distilled water, the first portion of the crystals to appear being discarded; contamination from dust should be carefully avoided. The crystals should be dried to constant weight at 180° to 200°C.

2. On adding the HCl to the iodide, no iodine color should develop; otherwise there is indicated the presence of iodate or, rarely, of oxidizing agents, usually chlorine, in the acid. If this cannot be avoided, a correction should be made by dissolving another portion of KI in the same volume of water and acid and titrating it with thiosulfate. This is preferable to reducing the iodine with thiosulfate before adding the solution to the dichromate, as a slight excess of thiosulfate may be added, and as this, as well as the tetrathionate, may be oxidized to sulfate by the dichromate. The acidified iodide solution should not be allowed to stand for any prolonged length of time, or oxidation by the air will take place.

3. Iodine solutions should not be violently shaken in conical flasks or allowed to stand in open vessels, or loss of iodine vapor will occur. Thus, it has been found[45] that upon swirling gently for 1 minute approximately 30 ml of 0.1 n. iodine in 4 per cent KI solution in a 250-ml flask that about 0.2 per cent of the iodine was lost. Stoppering the flask did not appreciably reduce the loss. Upon leaving 50 ml of the same solution in an open beaker for 15 minutes, a loss of 0.9 per cent was found.

4. The titration should be continued without starch until the yellowish tinge of the iodine can no longer be detected with certainty. This is somewhat difficult in this case because of the green color due to the chromic ion present, but this color is so reduced by the dilution of the solution that there is no excuse for adding the starch until within 0.2 to 0.3 ml of the end-point. It is to be noted also that the final end-point will be a change from the starch blue to a green; however, the change caused by even half a drop of 0.1 n. thiosulfate is so distinct that it can be easily detected.

5. The thiosulfate solution can be standardized against a previously standardized iodine solution as follows:

> Pipet 25 ml of the iodine solution into a large conical flask containing 1 g of KI dissolved in 100 ml of water and then add to the solution 1 ml of 6 n. $HC_2H_3O_2$. Titrate with the thiosulfate solution until the iodine color becomes indistinct and then add 5 ml of starch and titrate slowly, with part drops, to disappearance of the color.

The iodide is added to prevent possible loss of iodine from the dilute solution; the acetic acid is added because of the sodium carbonate present in the standard sodium thiosulfate solution.

The thiosulfate solution can also be standardized against the standard permanganate solution as follows:

> Pipet 25 ml of the permanganate solution into 400 ml of water containing 3 g of KI and 2 ml of 6 n. H_2SO_4. After 1 minute titrate the solution with thiosulfate as directed in the above titration of the iodine solution.

The equilibrium and rate of the above reaction are so favorable that precise results are obtained as long as sufficient acid is added to provide for that used in the reaction; as much as 60 milli-equivalents may be present without harmful results.[46] It is obvious that the standardization of the thiosulfate by the three methods given should give consistent results, and if the solutions are available it is recommended that this check be made.

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[45] Rice, Kilpatrick, and Lemkin, *J. Am. Chem. Soc.*, **45**, 1362 (1923)

[46] Bray and Miller, *loc. cit.*

The Applications of Iodometric Methods

Iodometric methods are used in this system of analysis for the estimation of lead (P. 25), copper (P. 28), arsenic (P. 43), antimony (P. 47), tin (P. 49), iron (P. 53), cobalt (P. 66), manganese (P. 72), chromium (P. 75), barium (P. 83), magnesium (P. 89), ferricyanide (P. 134), iodide (P. 144), bromide (P. 147), and arsenate (P. 163). Other constituents that are often determined by iodometric methods are the elementary halogens and their oxygen acids (except perchlorate), peroxide, sulfide, and sulfite.

The Use of Standard Solutions of Other Oxidizing Agents in Volumetric Analysis

Potassium Dichromate. Standard solutions of potassium dichromate offer the advantages that they can be directly prepared by weighing the salt and diluting to volume, and that they are extremely stable. Dichromate solutions formerly were extensively used for the titration of ferrous salts in hydrochloric acid solutions, where the titration with permanganate is troublesome. Dichromate solutions have the disadvantage that the color of the chromate is not sufficiently intense for it to be used to obtain the end-point of the titration (especially in the presence of the green chromic ion which is the reduction product), and, therefore, some form of an indicator has to be used, or the end-point obtained potentiometrically.

Ceric Sulfate. The use of ceric sulfate, $Ce(SO_4)_2$, solutions has been developed somewhat recently by Willard and Young[47] and by Furman and various associates.[48] The solutions are readily prepared by dissolving ceric ammonium sulfate, which can be obtained commercially, in dilute sulfuric acid solutions; however, the solid is not sufficiently pure for the direct preparation of standard solutions. The $Ce^{III} = Ce^{IV} + E^-$ potential has been determined by Kunz[49]

[47] Willard and Young, *J. Am. Chem. Soc.*, **50**, 1322, 1334, 1368, 1376, 1379 (1928); **51**, 139, 149 (1929); **52**, 36, 132, 553, 557 (1930).

[48] Furman *et al.*, *J. Am. Chem. Soc.*, **50**, 755, 1675, (1928); **51**, 1128, 1449 (1929); **52**, 1443, 2347 (1930); **53**, 1283, 2561 (1931).

[49] Kunz, *J. Am. Chem. Soc.*, **53**, 98 (1931).

to be −1.44 v in sulfuric acid solutions, which places it between permanganate and dichromate as an oxidizing agent. Ceric sulfate solutions offer the advantages that they can be used for the titration of ferrous salts in hydrochloric acid solutions, that they are relatively stable, that there are no intermediate oxidation stages (as with permanganate), and that the cerous salts give colorless solutions. Ceric salt solutions are somewhat more intensely orange-yellow colored than are dichromate solutions of the same normal concentration, but the color is not sufficiently intense for it to be used for determining the end-point in highly precise titrations. Details of the preparation and use of standard solutions of ceric sulfate can be found in the newer text and reference books on quantitative analysis.[50]

Potassium Iodate. Standard iodate solutions are used almost exclusively with the iodine monochloride end-point, which is discussed below in connection with the subject of potential indicators.

The Use of Oxidation-Reduction (Potential) Indicators in Volumetric Analysis

Discussion. As has been stated, solutions of dichromate and ceric salts are not sufficiently colored to serve as their own indicators, and this fact formerly required the use of outside indicators or of potentiometric titrations when these solutions were employed. To eliminate this disadvantage, the use of oxidation-reduction, or potential, indicators has been developed. A potential indicator may be defined as any substance which changes from a colorless to a colored form, or from one color to another, when it is oxidized or reduced.

The theory of these indicators can be illustrated by considering first the use of an inorganic compound in such a capacity. If iodine in hydrochloric acid solutions is treated with an oxidizing agent, a reaction which can be represented as follows takes place:

$$I_2 + 2Cl^- = 2ICl + 2E^-. \qquad (1)$$

It has been shown that, in hydrochloric acid solutions, iodine monochloride is largely combined with chloride ion as follows:[51]

$$ICl + Cl^- = ICl_2^-. \qquad (2)$$

[50] The G. Frederick Smith Chemical Company, 867 McKinley Avenue, Columbus, Ohio, has compiled a booklet on the applications of ceric sulfate solutions to volumetric analysis which also contains a complete bibliography of the literature on this subject.

[51] Philbrick, *J. Am. Chem. Soc.*, **56**, 1257 (1934).

Therefore the equation for the reaction is more adequately expressed as

$$I_2 + 4Cl^- = 2ICl_2^- + 2E, \qquad (3)$$

and the value of the formal potential in 4 f. hydrochloric acid has been found to have the value -1.05 v.[52] As has been mentioned previously, very low concentrations of iodine (in the absence of iodide, less than 10^{-5} f.) can be detected in aqueous solutions by the use of organic solvents (such as carbon tetrachloride); also, iodine monochloride in hydrochloric acid solutions has only a faint yellowish color and is not extracted by these solvents from hydrochloric acid solutions. Therefore, when the reaction represented by Equation 3 takes place, the iodine color disappears from the solution (or the carbon tetrachloride) and only a very pale yellowish color remains. Now suppose that one desired to titrate a solution of ferrous iron in 4 f. hydrochloric acid—under which conditions it would be difficult to obtain a permanent permanganate end-point because of the reduction of permanganate by this high concentration of hydrochloric acid. The iodine–iodine monochloride potential given above indicates that if a small amount of an iodine monochloride solution were added to the ferrous solution, it would be largely reduced to iodine, which would impart its characteristic color to the solution. The difference between the formal iodine–iodine monochloride potential (-1.05 v in 4 f. HCl) and the formal ferrous-ferric potential (-0.70 v in 1 f. HCl and probably more positive in 4 f. HCl) indicates that if the solution were now titrated with permanganate (or, in fact, with any other powerful oxidizing agent), substantially all of the ferrous iron would be oxidized to ferric before a large fraction of the iodine was re-oxidized to iodine monochloride; also that the disappearance of the iodine color could be taken to indicate the completion of the titration.

The reactions taking place if permanganate is used are as follows:

(1) Addition of the iodine monochloride to the ferrous solution:

$$2Fe^{++} + 2ICl_2^- = 2Fe^{+++} + I_2 + 4Cl^-.$$

(2) Oxidation of the remaining ferrous iron by the permanganate:

$$MnO_4^- + 5Fe^{++} + 8H^+ = Mn^{++} + 5Fe^{+++} + 4H_2O.$$

(3) Oxidation of the iodine to iodine monochloride by the permanganate:

$$2MnO_4^- + 5I_2 + 16H^+ + 20Cl^- = 2Mn^{++} + 10ICl_2^- + 8H_2O.$$

[52] Unpublished experiments by J. S. Edwards.

It is to be noted that, since the indicator is added as iodine monochloride and exists in that form at the end-point, the titration is independent of the amount of indicator added; if the indicator were added as iodine, the amount added would have to be so small as to be negligible in comparison with the permanganate used in the titration, or a correction for the amount added would be necessary.

The agreement of the end-point with the equivalence-point obtained by using this indicator can be predicted by means of the following calculations: When within 0.2 per cent of the equivalence-point, the ratio of the equivalents of permanganate added to the ferrous iron present has the value 0.998, and the ratio of ferric iron to ferrous iron will be 0.998/0.002. By use of the Nernst equation the potential existing at that point in the titration can be calculated as follows: Since the titration is made in 4 f. hydrochloric acid, the formal ferrous-ferric potential in 4 f. hydrochloric acid should be used for the E_0 value; since this is not available, the formal potential in 1 f. HCl (−0.700 v) will give more nearly correct values than the molal potential (−0.782). Therefore the desired potential is

$$E = E_0 - 0.059 \log \frac{[Fe^{+++}]}{[Fe^{++}]} = -0.700 - 0.059 \log \frac{0.998}{0.002} = -0.859.$$

If the indicator is added in such an amount as to make the solution initially 10^{-4} f. in iodine (which is more than the amount needed to detect the iodine color easily), there can be calculated from the equation

$$E = E_0 - \frac{0.059}{2} \log \frac{[ICl_2^-]^2}{[I_2][Cl^-]^4}$$

that the molal ratio of the concentration of iodine to iodine monochloride will be 0.87 (assuming the solution to be 4 f. in HCl). Therefore the iodine color will still be plainly visible in the solution. When the ratio of permanganate to ferrous iron is 1.002, the molal ratio of permanganate to manganous ion will be 0.002/1.000, and if the hydrogen ion concentration is assumed to be 4 molal, calculations similar to those above will show that the potential existing is approximately −1.50 v, and that then the ratio of iodine to iodine monochloride will be 4.8×10^{-22}. It is thus seen that 0.2 per cent before the equivalence-point of the titration the indicator exists largely as iodine, but that before 0.2 per cent excess of permanganate has been added, it has been substantially all converted to the iodine monochloride. Therefore a sharp and precise end-point should be obtained.

This so-called iodine monochloride end-point is the basis of an extensive series of methods in which the titrations are carried out in 2 to 6 f. hydrochloric acid, and various reducing substances are titrated with standard oxidizing solutions, such as potassium iodate, permanganate, or ceric sulfate.[53]

It should also be noted that iodine could be used as a potential indicator for the titration of a strong reducing agent, such as stannous tin, with standard oxidizing solutions. In this case, the small amount of iodine added as the indicator would be reduced to iodide by the stannous tin, and the end-point would be obtained when the remainder of the stannous tin has been oxidized by the standard oxidizing solution and the appearance of iodine color is observed. Thus iodine (or its compounds) can be used as a potential indicator for two different potential ranges, one corresponding to the oxidation of iodide ion to iodine and the other to the oxidation of iodine to iodine monochloride.

With the exception of the iodine monochloride end-point, inorganic substances have not been extensively used as potential indicators. However, there are many organic compounds which are capable of being oxidized and reduced and with which processes there is associated an appearance, disappearance, or change of color; such compounds are therefore capable of being used as potential indicators. Many such compounds are not of practical value because (1) the color change is not sufficiently pronounced; (2) they are often so easily oxidized as to be of no value for most titrations; and (3) the oxidation-reduction reaction may not be readily reversible, one of the oxidation stages reacting only slowly or being further changed by excess of the titrating reagent.

Although these organic compounds are usually of rather complicated structure, the reaction taking place can be represented as

$$\mathrm{In_{Red}} = \mathrm{In_{Ox}} + n\mathrm{E}^{-},$$

and for a large majority of the organic compounds so used n is 2. Therefore if the value of the molal potential of the indicator is known, the value of the ratio of the oxidized to the reduced form can be calculated for any point in the course of an oxidation-reduction titration, thus:

$$E = E_{0_{\mathrm{In}}} - \frac{0.059}{n} \log \frac{\mathrm{In_{Ox}}}{\mathrm{In_{Red}}}.$$

[53] See Jamieson, *Volumetric Iodate Methods*, Chem. Cat. Co., 1926, for a compilation of the methods using standard iodate solutions. For a study of the conditions under which the iodine monochloride end-point can be applied to titrations with other oxidizing agents see Swift, *J. Am. Chem. Soc.*, **52**, 894 (1930).

It is seen that the same principles which were discussed in connection with the use of the iodine–iodine monochloride end-point can be applied to these substances. Potential indicators which have been extensively used are the following: (1) Diphenylamine, which is colorless in the reduced form and violet in the oxidized form, the transition range occurring close to −0.76 v. This indicator has been extensively used for the titration of ferrous salts with dichromate.[54] It is necessary that phosphoric acid be present (which, by forming an un-ionized compound with the ferric iron, gives a more positive and therefore less oxidizing potential at the equivalence-point) or the transition is somewhat sluggish and premature. It is not a strictly reversible reaction. (2) Diphenylamine sulphonic acid[55] turns a reddish-violet color at about −0.83 v. It therefore gives a sharper end-point in the titration of ferrous salts in the absence of phosphoric acid and in addition is more soluble in aqueous solutions than is diphenylamine. (3) Orthophenanthroline ferrous complex[56] has been extensively used with ceric sulfate solutions. It is red in the reduced form and very pale blue when oxidized. The transition occurs at a potential of about −1.2 v—too high to be used very satisfactorily with dichromate solutions.

NEUTRALIZATION (AND DISPLACEMENT) METHODS OF VOLUMETRIC ANALYSIS

General Discussion. *Neutralization Reactions.* For the purposes of this discussion only neutralization in aqueous solutions will be considered, and the classical definition will be used, namely, that the characteristic feature of neutralization methods is the reaction of hydrogen ions with hydroxyl ions to form un-ionized water,[57]

$$H^+ + OH^- = H_2O.$$

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[54] Knop, *J. Am. Chem. Soc.*, **46**, 263 (1924).

[55] Sorver and Kolthoff, *J. Am. Chem. Soc.*, **53**, 2902, 2906 (1931); Willard and Young, *Ind. Eng. Chem., Anal. Ed.*, **5**, 154 (1933).

[56] Walden, Hammett, and Chapman, *J. Am. Chem. Soc.*, **55**, 2649 (1933).

[57] For simplicity of presentation the hydrogen ion will be written as above even though it exists as H_3O^+ in aqueous solutions. It is also felt that neutralization reactions in nonaqueous solutions are not as yet of sufficient analytical importance to warrant a more generalized treatment of the subject at this place. The article "Modern Conception of Acids and Bases" by N. F. Hall, *J. Chem. Ed.*, **7**, 782 (1930), is recommended to those wishing a preliminary treatment of this topic; references to more detailed treatments are given in the article.

The equilibrium expression $[H^+][OH^-]/[H_2O] = K_w$, which can be written $[H^+][OH^-] = K_w$ (since in dilute solutions the concentration of the un-ionized water is practically constant), has for K_w, called the ionization constant for water, the value at 20°C. of 1.0×10^{-14}. If the equation for the reaction of a "strong" acid, that is, one which is highly ionized (such as hydrochloric, nitric, and the first hydrogen of sulfuric acid), with a strong base (such as sodium or potassium hydroxide) is written ionically

$$H^+A^- + B^+OH^- = HOH + B^+A^-,$$

it is seen that the equilibrium expression for the reaction reduces to the form of the reciprocal of that for the ionization constant of water. Therefore the constant for such a neutralization reaction, (K_n), has the value 10^{14}, which shows that the reaction is complete well within the usual measurements of quantitative analysis.

When a weak acid reacts with a strong base, the reaction can be represented as follows:

$$HA + B^+OH^- = H_2O + B^+A^-.$$

If ionization of the salt is assumed to be complete, the equilibrium expression for this reaction has the form

$$\frac{[A^-]}{[HA][OH^-]} = K_n.$$

Here it is obvious that not only the ionization constant for water $[H^+][OH^-] = K_w$ but also that of the acid $[H^+][A^-]/[HA] = K_A$ has a determining effect on the completeness of the reaction and on the value of K_n. By combining these last two expressions, thus eliminating $[H^+]$, there is obtained the neutralization expression above,

$$\frac{[A^-]}{[HA][OH^-]} = \frac{K_A}{K_w} = K_n.$$

This shows that K_n for the reaction of a weak acid with a strong base is equal to the constant for the acid divided by the constant for water. It is therefore obvious that such reactions will not be as quantitative as those between strong acids and bases, and the completeness of such reactions will vary with the strength of the acid. Similar considerations will show that K_n for the reaction between a weak base and a strong acid will be given by K_B/K_w.

For the reaction of a weak acid and a weak base, $HA + BOH = H_2O + B^+A^-$, the equilibrium expression is

$$\frac{[B^+][A^-]}{[HA][BOH]} = K_n.$$

Here the constant for water, K_w, for the acid, K_A, and for the base, K_B, are all involved, and by properly combining the corresponding expressions it will be seen that the neutralization expression is

$$\frac{[B^+][A^-]}{[HA][BOH]} = \frac{K_A K_B}{K_w} = K_n.$$

From this it is seen that the reaction of even moderately weak acids and bases will not proceed to completion.

The Hydrolysis of Salts in Aqueous Solutions. In the foregoing considerations the reactions have been considered as taking place from left to right as written and have been termed *neutralizations*. It is obvious that, especially for those cases where the reaction is incomplete in this direction, if we start with the products on the right side of the equation, namely, a salt and water, then the reaction will proceed to the left until an equilibrium is set up which satisfies the equilibrium constant. Such reactions are termed **hydrolysis** reactions, and from the considerations given above it is clear why the hydrolysis of salts occurs, and how, when the constants for the acids and bases involved are known, the extent of such reactions can be predicted, and the equilibrium conditions calculated.

Since the value of the ionization constant for water (K_w) changes much more rapidly with temperature than does that of most acids and bases, K_w being 0.11×10^{-14} at 0°C. and 48×10^{-14} at 100°C., it is seen that at higher temperatures neutralization will be less complete and hydrolysis correspondingly greater.

The Changes in Hydrogen and Hydroxyl Ion Concentrations during Neutralization Titrations. Analytically, the factor of most importance during the course of a neutralization titration is the change in the hydrogen ion concentration of the solution, because it is this change which enables the end-point to be determined. This hydrogen ion concentration can be calculated for any point during the titration involving a strong acid and base from the excess of either the acid or base present (if it is assumed that they are completely ionized and that the activity is equal to the concentration). At the equivalence-point

$$[H^+] = [OH^-] = 10^{-7} \text{ molal (at 20°C.)},$$

and the solution is said to be neutral. In these strong acid–strong base titrations the hydrogen ion concentration changes very rapidly with the addition of acid or base, especially near the equivalence-point. This is shown in Fig. 16 by the curves labeled "Strong Acids" and "Strong Bases." In this figure there are shown the

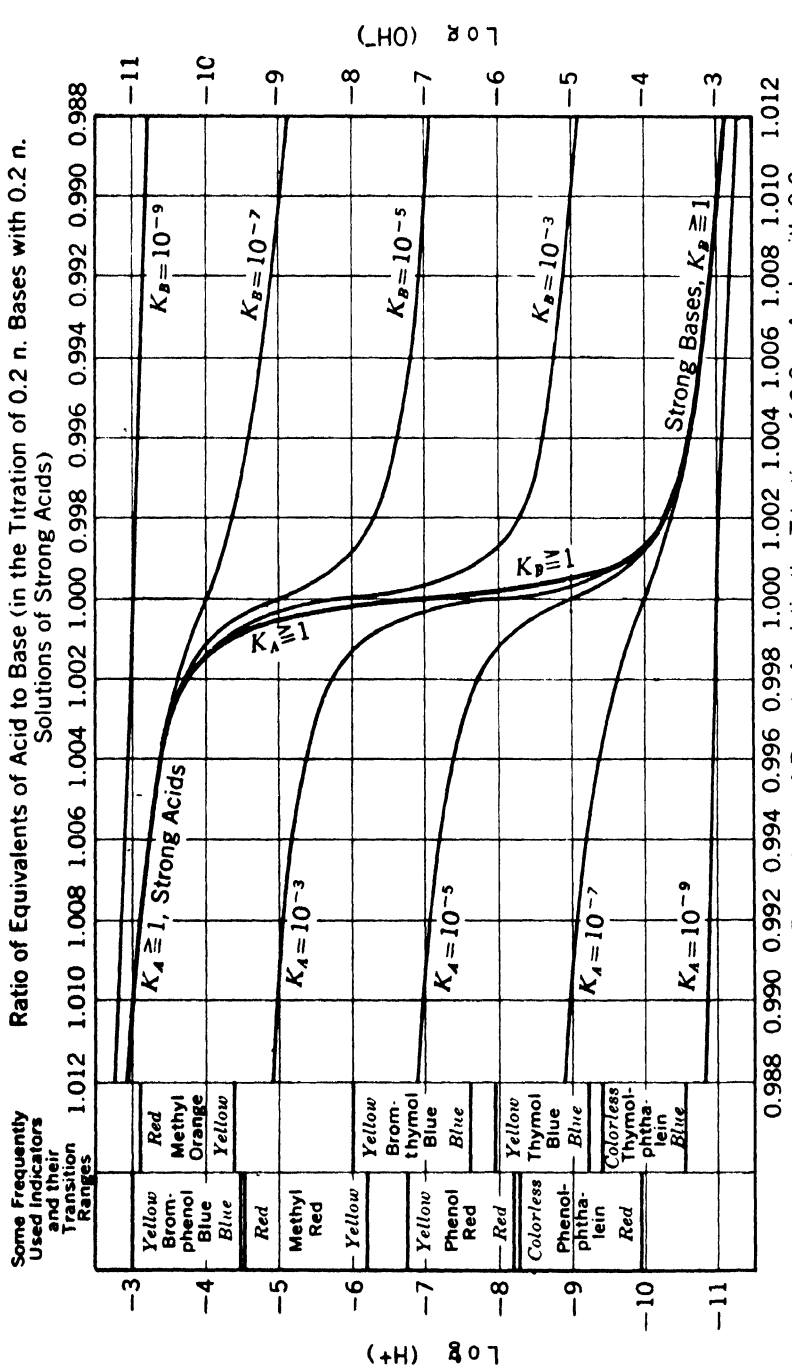

Fig. 16. Hydrogen and Hydroxyl Ion Concentration Changes During Neutralization (and Displacement) Titrations. Indicator Transition Ranges.

changes in the $[H^+]$ and $[OH^-]$ plotted logarithmically as a function of the ratio of acid to base during the course of titrations with acids and bases of various strengths.[58] The similarity of these curves to the titration curves for precipitation and for oxidation and reduction reactions is to be noted.

The calculation of the hydrogen ion concentrations at various points during the titration of a weak acid with a strong base is not so simple; as an example consider the titration of acetic acid ($K_A = 1.8 \times 10^{-5}$ at 25°C.) with sodium hydroxide. The equation for the reaction is

$$HC_2H_3O_2 + OH^- = C_2H_3O_2^- + H_2O,$$

and the equilibrium expression is

$$\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2][OH^-]} = \frac{1.8 \times 10^{-5}}{10^{-14}} = 1.8 \times 10^9.$$

If it is assumed that 100 ml of 0.2 n. $HC_2H_3O_2$ were taken and that to it has been added 99 ml of 0.2 n. NaOH, and if it is further assumed that the reaction has proceeded to completion, it is seen that the excess of $HC_2H_3O_2$ would be $0.2 \times 1/199$ molal, and that the concentration of the acetate formed would be $0.2 \times 99/199$ molal. However, since the reaction between the acid and hydroxide is incomplete, there will be a certain amount of hydroxyl ion remaining in the solution. If the molal concentration of this hydroxyl ion is represented by x, the molal concentration of $HC_2H_3O_2$ will be $0.2 \times 1/199 + x$ and that of the $C_2H_3O_2^-$ will be $0.2 \times 99/199 - x$. Assuming, as an approximation, that x is negligible in comparison with these values and solving, it is found that the $[OH^-]$ is equal to 5.5×10^{-8} and the $[H^+] = 1.8 \times 10^{-7}$.[59]

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[58] In plotting these curves it has been more practical to use, rather than the concentrations, the logarithms of these concentrations. The same is also true in many of the calculations involved in the determination and use of hydrogen ion concentrations. This has led to the convention of designating the hydrogen ion concentration of a solution by a quantity called the pH and defined by the equation $p\text{H} = \log 1/[H^+] = -\log[H^+]$. (Rigorously, the hydrogen ion activity rather than the concentration should be specified.) Thus it is seen that for solutions in which the hydrogen ion concentrations are 10^{-7} and 5×10^{-7} respectively, the pH values are 7 and 6.3. As the use of pH values has become quite widespread, their significance should be clearly comprehended.

[59] A much simpler approximate solution is obtained by noting that as long as an appreciable excess of $HC_2H_3O_2$ is present (as long as $HC_2H_3O_2$ in the

At the equivalence-point it is more convenient to consider the problem as one of hydrolysis, as the solution is the same as one containing an equivalent amount of salt dissolved in water. In this case the formal concentration of the $C_2H_3O_2^-$ is $0.2 \times 100/200$, and the molal concentration of the $HC_2H_3O_2$ is equal to that of the $[OH^-]$. If this is represented by x, the molal concentration of $C_2H_3O_2^-$ is $0.1 - x$, and the approximations used above give the $[OH^-]$ as 7.5×10^{-6} and the $[H^+]$ as 1.3×10^{-9}. This value shows that at the equivalence-point of this titration the solution has already become distinctly alkaline.

It is thus seen that the hydrogen ion concentration can be calculated for frequent intervals during the course of a titration and that curves similar to the titration curves for other types of reactions can be constructed from these data. This has been done and is shown in Fig. 16, where the $[H^+]$ at any point during the titration of acids with various ionization constants with strong bases, and of bases with various ionization constants with strong acids, can be approximated by means of the curves which are shown. These curves are calculated for 0.2 n. solutions; in general the error will be less when using more concentrated and greater with more dilute standard solutions. The case for the titration of weak acids with weak bases will not be considered as it is relatively unimportant in analytical work, due to the incompleteness of these reactions and to the consequent relatively slow rate of change of the $[H^+]$ during the titration.

The hydrogen electrode. So far we have considered only the course of the reaction during the neutralization titration without reference to possible means of determining the end-point. It was seen in the discussion of oxidation-reduction titrations that the end-point could be determined potentiometrically by inserting in the solution an inert conducting electrode and measuring the change in potential during the course of the titration. In the absence of other strongly oxidizing or reducing systems it is possible to do the same thing in a

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above equation is large in comparison to x), the $[H^+]$ can be calculated from the familiar relation

$$[H^+] = K_A \frac{[HA]}{[A^-]}.$$

Also, as there is a ratio of the concentrations, the $[H^+]$ is approximately independent of the volume or dilution.

neutralization titration by saturating the solution with hydrogen gas at constant pressure and measuring the potential of the reaction

$$H_2 = 2H^+ + 2E^-$$

during the course of the titration. Also, as the molal potential of this reaction is known, it is possible to determine the hydrogen ion concentration in the solution if the pressure of the hydrogen gas is maintained at the same known value—this is the principle and procedure used in the determination of hydrogen ion concentrations or *p*H by means of the so-called "hydrogen electrode."[60]

Neutralization indicators. Potentiometric titrations of neutralization reactions are to be avoided if possible, since the electrode is usually slow to reach an equilibrium and considerable time is required. The end-point is most frequently obtained by the use of organic compounds called neutralization indicators, which for the present can be considered as weak acids, possessing the distinguishing characteristic that the free acid exhibits a different color from that of the basic ion; thus they show a color change upon being neutralized. Assuming them to be simple acids, the ionization of these indicators can be represented as

$$HIn = H^+ + In^-, \qquad (1)$$

and the conventional mass-action expression formulated:

$$\frac{[H^+][In^-]}{[HIn]} = K_{In}. \qquad (2)$$

Here K_{In} is the ionization constant of the indicator acid, or, as it is more commonly termed, the **indicator constant.** It is seen that the color which the indicator exhibits will be determined by the fraction of the indicator which has been converted to the salt or basic (In^-) form (red with phenolphthalein) and the fraction remaining in the acidic (HIn) form (colorless with phenolphthalein). Thus if we have a solution in which the indicator is c formal and we let x be

[60] The electrical equipment used is essentially the same as that outlined in the method for making potentiometric titrations. Instead of the straight piece of platinum wire used there as the inert electrode, it is necessary to use a metallic electrode, usually platinum which has been coated with an amorphous deposit of that metal; such a surface more quickly reaches an equilibrium with the hydrogen gas. Some device must also be provided for keeping the electrode and the solution immediately surrounding it saturated with the hydrogen gas at a constant pressure.

the fraction converted into the basic form, then cx is the molal concentration of In^- and $c[1 - x]$ that of the HIn, and we obtain

$$\frac{[H^+](x)}{1 - x} = K_{In},$$

which is the conventional form of the indicator equation. From this it is apparent that the indicator is 50 per cent transformed when the hydrogen ion concentration—hereafter indicated for brevity as the $[H^+]$—is equal to the value of K_{In} ; also that if the $[H^+]$ of the solution is known and the fraction of the indicator transformed determined (for example, by colorimetric measurements), then K_{In} can be calculated; or, that knowing K_{In} and determining x, the $[H^+]$ of a solution can be determined.[61]

From the foregoing it is seen that an indicator changes in color when the $[H^+]$ of the solution changes through such a range that a sufficient fraction of the indicator is converted from one form to the other to result in a color change visible to the eye. The percentage

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[61] The mechanism of the color change of indicators is not as simple as has been assumed above, but usually involves equilibria which can be represented as follows:

$$HIn' = HIn'' \quad \text{and} \quad HIn'' = H^+ + In'',$$

where HIn' (with phenolphthalein) would represent the colorless acid, and this would be in equilibrium in an acid solution with HIn'', the colored form. This latter is present in only small amount but being more highly ionized is converted into its salt (In''^-, colored) upon addition of base. It is seen that combining the mass-action expressions

$$\frac{[HIn'']}{[HIn']} = K_1 \quad \text{and} \quad \frac{[H^+][In''^-]}{[HIn'']} = K_2$$

gives an expression, namely,

$$\frac{[H^+][In''^-]}{[HIn']} = K_1K_2 = K_{In},$$

in which, as long as HIn'' and In' are small in comparison to HIn' and In'', the total indicator in the acid form can be substituted for the HIn' and that in the basic form for In''^-, and that thus it is justifiable to treat indicators as though they were simple acids. It is also apparent that even though the indicator be a base, $InOH = In^+ + OH^-$, the ionization expression

$$\frac{[In^+][OH^-]}{[InOH]} = K_B$$

can be combined with that for water $[H^+][OH^-] = K_w$ to give

$$\frac{[InOH][H^+]}{[In^+]} = \frac{K_w}{K_B} = K_{In},$$

which again gives the relation between the basic and acidic forms in terms of the $[H^+]$.

conversion necessary to cause a visual color change depends upon the specific nature of the indicator, and whether the change is from colorless to a colored form, or from one color to another. In general the human eye cannot detect the presence of less than 10 per cent of one form of an indicator in the presence of the other, and, therefore, the transition range of most indicators extends over approximately two *p*H units. However, by titrating to either the acid or basic color of an indicator, this *p*H interval can be restricted to approximately either half of the transition range; by using a reference solution containing the same volume of solution and indicator (and approximately the same amount of salts or of other compounds as are present in the titrated solution at the equivalence-point), the *p*H of the titrated solution at the end-point can be adjusted to within a few tenths of a *p*H unit. In Fig. 16 is shown not only the change in (H^+) during the titration of various acids and bases but also the so-called "transition ranges" of several of the more common indicators. Therefore, by the use of this table it is possible to select for use in titrations those indicators which will give color changes near the equivalence-point of the titration. Thus it is seen that any of the indicators listed can be so used as to give a color change within 0.2 per cent of the equivalence-point in titrating strong acids with strong bases, but that such is not the case when titrating weak acids with strong bases or weak bases with strong acids. The transition ranges of indicators are shifted somewhat by changes in (1) temperature, (2) the ionic concentration of the solution (this is usually termed the "salt effect"), and (3) the solvent (for example, by the addition of alcohol to the solution). Usually the magnitudes of these effects are not such as to cause serious errors in titrations, but they are of importance in the use of indicators to determine the hydrogen ion concentration of a solution.[62] The selection of the proper indicator for specific titrations will be taken up in more detail in the following procedures.

The Preparation of Standard Solutions of Acids and Bases

General discussion. It is desirable that, unless intended for some specific purpose, the acids and bases to be used as standard solutions in neutralization methods should possess certain general qualifica-

[62] For a discussion of these effects and of the indicator method of determining hydrogen ion concentrations see Kolthoff, "The Colorimetric and Potentiometric Determination of *p*H," John Wiley and Sons, 1931; Clark, "The Determination of Hydrogen Ions," 3rd ed., Williams and Wilkins, 1928.

tions, as follows: (1) They should be highly ionized, for, as has been mentioned, if the titration of a weak base with a weak acid is attempted, the rate of change of the hydrogen ion concentration near the equivalence-point is likely to be so slow as to prevent a precise determination of the end-point. (2) They should be so soluble that solutions as concentrated as half normal and in some cases even 1 normal can be prepared. (3) They should form soluble salts, since the formation of a precipitate during the titration may obscure the end-point, or the precipitate may adsorb the indicators. (4) They should be stable compounds. Oxidizing or reducing agents, besides being affected by the possible presence of extraneous material (such as dust, organic matter, or even the oxygen of the air) are likely to react with the indicators, many of which are unstable with respect to oxidation or reduction, being decomposed or converted into colorless compounds. Volatile compounds, such as ammonia, are difficult to preserve in storage without elaborate precautions. Substances which rapidly attack glass containers also require special apparatus in storage.

No one acid or base meets all of the above qualifications. Sulfuric acid, which is nonvolatile, forms insoluble salts with alkaline-earth hydroxides; nitric acid, although relatively stable when cold and dilute, may act as an oxidizing agent in hot solutions or may contain traces of nitrous acid, which reacts with certain indicators, notably methyl orange and methyl red. Perchloric acid is a strong acid, is nonvolatile, is stable toward reduction in dilute solutions, but is expensive, and the potassium and ammonium salts are only moderately soluble. Although hydrogen chloride is a gas, it is so highly ionized in aqueous solutions that its partial pressure from even 0.5 normal solutions is so small that they can be boiled for considerable periods of time without appreciable loss if the solution is not allowed to concentrate by evaporation. Since most chlorides are soluble and since hydrochloric acid is relatively inert toward oxidation or reduction, it is very extensively used as a standard acid.

Standard bases present more difficulties in storage, because they tend to attack glass containers and to absorb various gases, especially carbon dioxide. Barium hydroxide is sometimes used as a standard base but is sparingly soluble and forms insoluble salts; ammonium hydroxide solutions lose ammonia; potassium hydroxide has no distinct advantage over sodium hydroxide and is more expensive; therefore the latter is the more generally used reagent.

P. XV. The Preparation of Carbonate-Free Solutions of Sodium Hydroxide

Discussion. Sodium hydroxide cannot be used for the direct preparation of a standard solution because it cannot be obtained sufficiently pure and because it is too hygroscopic and too reactive with the carbon dioxide of the air. Carbonate is undesirable in standard alkali solutions because when titrated with acid using a strongly acidic indicator (for example, methyl orange) it is converted into carbonic acid, thus using two equivalents of the acid for each mole of carbonate present. When it is titrated with acid using a strongly basic indicator (for example, phenolphthalein), it is converted to hydrocarbonate (if the solution is cold) and thus uses only one equivalent of the acid; furthermore, this latter end-point is not obtained precisely except under very strictly controlled conditions. For these reasons it is an advantage to have standard alkali solutions which are relatively free of carbonate. It is very difficult to obtain sodium or potassium hydroxide which is free from carbonate, but, fortunately, sodium carbonate is relatively insoluble in 50 per cent sodium hydroxide solution, and by preparing such a solution and allowing it to stand until the sodium carbonate settles out (or filtering), a carbonate-free solution can then be prepared by dilution with water that is free of carbon dioxide.

Procedure XV: PREPARATION OF A CARBONATE-FREE SOLUTION OF SODIUM HYDROXIDE. Weigh out 16 g of sodium hydroxide sticks, dissolve them in 15 ml of water, transfer the solution to a 50-ml test tube (Note 1), stopper the mixture with a rubber stopper, and then allow it to stand in a vertical position until the precipitate settles (Notes 2, 3). Quickly pipet out 10 ml of the clear solution without stirring up the residue, and transfer it to a bottle which has been fitted with a two-hole rubber stopper carrying a siphon tube with a short rubber tube and pinch clamp at the bottom in one hole and a short inlet tube to which a soda-lime tube is attached in the other hole (Note 4). Immediately dilute the solution to a liter with water which has been just boiled and cooled (Note 5), and fit the stopper into place.

Notes:

1. This tube should be of resistance glass because of the rapidity with which ordinary "soft" glass would be attacked by the concentrated alkali. If resistance glass tubes are not available or if it is desired to keep this mixture for preparing future solutions, the inside of the test tube should be

first coated with paraffin; the alkaline solution should be cooled before being transferred to a paraffined container.

2. The settling of the sodium carbonate may require considerable time, usually several days. Therefore, if a centrifuge is available, the process can be expedited by centrifuging the mixture until the precipitate is thrown out. Otherwise the mixture can be filtered with the aid of suction through an asbestos or sintered-glass filter and collected directly in the container in which it is to be stored.

3. Since it requires some time for the sodium carbonate precipitate to settle and since there is considerable loss of sodium hydroxide in preparing the 50 per cent solution for only 1 liter of the diluted hydroxide, it is suggested that a stock supply of the concentrated solution be prepared in a paraffined container and kept available in the laboratory.

4. If the solution is to be kept for a considerable period, it is desirable that the inside surface of the bottle be protected by a layer of paraffin. To do this, clean and dry the bottle, warm it in an oven or in hot water, and pour into it sufficient melted paraffin to cover the inner surface. Roll the bottle until the sides are completely covered, tilt it until the bottom is uniformly covered, and allow it to cool in an upright position.

5. According to Kolthoff, *Biochem. A.*, **176**, 101 (1926), water in equilibrium with air of the usual carbon dioxide content is only 1.5×10^{-5} f. in carbon dioxide. This amount is negligible in alkali solution of the concentrations ordinarily used. However, distilled water is often found to be supersaturated to an amount 10 or 20 times greater than this equilibrium value; this excess is removed by boiling for a few minutes.

P. XVI. The Standardization of Sodium Hydroxide Solutions

Discussion. Alkali solutions can be precisely standardized against constant-boiling hydrochloric acid,[63] benzoic acid (C_6H_5COOH), or potassium hydrophthalate ($KHC_8H_4O_4$); commonly called potassium acid phthalate. Oxalic acid is sometimes used, but the hydrated compound ($H_2C_2O_4 \cdot 2H_2O$) is somewhat difficult to prepare with an exactly known water content, and the anhydrous acid is too hygroscopic for practical use. Constant-boiling hydrochloric acid is an excellent standard if it is available; however, for a single standardization its preparation is a lengthy process. Benzoic acid can be obtained from the Bureau of Standards, but the resublimed acid is so voluminous as to be somewhat inconvenient to weigh unless it is melted; also, the acid is so slightly soluble in water that it must be dissolved in alcohol for the titration. Potassium hydrophthalate, which is also supplied by the Bureau of Standards, has neither of the

[63] Hulett and Bonner, *J. Am. Chem. Soc.*, **31**, 390 (1909); Morey, *ibid.*, **34**, 1032 (1912); Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923); Shaw, *J. Ind. Eng. Chem.*, **18**, 1065. (1926).

difficulties mentioned in connection with benzoic acid and in addition has a high equivalent weight; it is therefore used here.

The ionization constant for the second hydrogen of phthalic acid is 3.1×10^{-6}, and it is calculated (assuming that the titration is made with 0.2 n. solutions and that therefore the final concentration of the salt is 0.1 f.) that the $[H^+]$ at the equivalence-point will be 5.6×10^{-10}. This value is obtained approximately by referring to Fig. 16 and tracing to the equivalence-point an imaginary curve for an acid whose constant is 3×10^{-6}. It is seen that this value lies within the transition range for phenolphthalein and that, furthermore, when the ratio of the equivalents of base to acid is 0.998, the indicator is largely in its acid form (the indicator constant, K_{In}, of phenolphthalein has the value 2×10^{-10}) and that when this ratio is 1.002, it is largely in its basic form; thus it is indicated that, using phenolphthalein as the indicator, phthalic acid can be titrated with sodium hydroxide (or any strong base) to an accuracy within 0.2 per cent.

It is obvious that methyl orange could not be used as the indicator for the above titration. However, for the titration of ammonium hydroxide ($K_B = 1.8 \times 10^{-5}$) with a strong acid it is seen that the titration curve would indicate that the $[H^+]$ at the end-point would be approximately 7×10^{-6} close to the transition range of methyl orange, and that when the ratio of acid to base was 0.998, the indicator would be very largely in the basic form, and that when the ratio was 1.002, it would be sufficiently converted to the acid form for a color change to be observed; therefore, an accuracy within 0.2 per cent could be attained. From these examples it is seen that with the aid of Fig. 16 the accuracy with which any acid can be titrated with a strong base, or with which any base can be titrated with a strong acid, can be predicted if the transition range of the indicator is known.

As either methyl orange or phenolphthalein can be used for the titration of strong acids with strong bases, and as weak acids can be titrated by the use of phenolphthalein and weak bases by the use of methyl orange, these two indicators can be used for nearly all of the neutralization titrations usually made. However, the indicators shown in Fig. 16 have certain specific advantages: Bromphenol blue is useful for the titration of carbonate or hydrocarbonate (HCO_3^-) to carbon dioxide; methyl orange for the titration of phosphoric acid to dihydrogen phosphate ($H_2PO_4^-$); methyl red for the titration of dilute solutions of strong acids and bases where methyl orange

would give an appreciable error; thymol blue for the titration of carbonate to hydrocarbonate; and thymolphthalein for titration of phosphoric acid or dihydrogen phosphate to monohydrogen phosphate ($HPO_4^{=}$).

Since the transition ranges of indicators are somewhat broad and, in many cases, not as sharply defined as would be desired for a precise titration, reference solutions are frequently necessary for obtaining the proper end-point. Such a reference solution should contain the same volume and the same amount of indicator as the titrated solution; in addition, it is desirable that it contain approximately the same amount of the salts or other products as are formed by the titration reaction. The titration is then carried out until the color in the titrated solution matches the color of the reference solution. Such a procedure is especially useful in the titration of polybasic acids to intermediate neutralization stages, since the *p*H change near the equivalence-point in such titrations is usually not sufficiently rapid to give very sharp end-points. As an example, if a titration of phosphoric acid to monohydrogen phosphate is to be made, an amount of monohydrogen phosphate (conveniently added as $Na_2HPO_4 \cdot 2H_2O$) equivalent to that to be formed in the titration should be dissolved in the same volume of water as would be present at the end-point, the same amount of indicator added, and this solution used as the indicator reference standard.

Procedure XVI: STANDARDIZATION OF A SODIUM HYDROXIDE SOLUTION AGAINST POTASSIUM HYDROPHTHALATE. Dry about 6 g of $KHC_8H_4O_4$ at 120°C. for 1 hour and allow the crystals to cool in a desiccator (Note 1). Precisely weigh out about 1.5 g of the phthalate and dissolve it in 50 ml of water in a 300-ml flask (Note 2). Add 3 drops of phenolphthalein indicator to the solution and titrate it with the 0.2 n. sodium hydroxide solution to be standardized (Note 3) until the first perceptible pink color is obtained (Note 4). Stopper the flask (Note 5). Add to a similar flask a volume of water equal to that of the titrated solution and the same amount of indicator solution, and carefully add the sodium hydroxide solution to it until a color matching that in the first flask is obtained (Note 6). Subtract the amount required for the blank from the first titration. Weigh and similarly titrate two more samples of the phthalate, and from the data thus obtained calculate the normality of the sodium hydroxide solution.

Notes:

1. $KHC_8H_4O_4$ is not hygroscopic. If properly prepared and dried, and thereafter protected from excessive moisture, the material should not contain over 0.05 per cent water; because of this, the preliminary drying may often be dispensed with. It has also been shown[64] that standard solutions of the hydrophthalate are stable over long periods of time; it is therefore possible to prepare such a solution and use it from time to time.

2. Carbon dioxide, if present in considerable amounts in this water, would cause an error in this standardization, because it would be converted to hydrocarbonate (HCO_3) at the phenolphthalein end-point, thus using an equivalent amount of the sodium hydroxide. The extent of this error is usually small; however, if desired, this possibility can be eliminated by first boiling the water in the flask, and then inserting a stopper carrying a soda-lime tube and cooling the water. (See Note 5, P. XV)

3. Alkaline solutions should not be allowed to stand in burets with glass stopcocks for any longer time than is absolutely necessary, and the buret should be rinsed as soon as the alkali is removed. Burets with tips connected by short pieces of rubber tubing (Mohr type) can be used for all work in which a high degree of precision is not required.

4. Care should be taken to use the same amount of indicator for each titration and for the blanks, since, especially with a one-color indicator, the *p*H range at which the color change is observed will be dependent upon the concentration of the indicator.

5. A solution which is alkaline to phenolphthalein will slowly absorb carbon dioxide from the air and become colorless.

6. In order to make a theoretically precise blank, the solution should contain an amount of sodium or potassium phthalate, $K_2C_8H_4O_4$, equivalent to the hydrophthalate taken for the titration. Experiments have shown that the correction as made will give results within the precision of the other measurements of the standardization.

P. XVII. The Preparation and Standardization of Hydrochloric Acid Solutions

Discussion. Standard solutions of hydrochloric acid can be obtained by preparing constant-boiling acid,[65] which is approximately 6 normal, and then diluting weighed amounts of this to the desired volume. More frequently, such solutions are prepared by diluting the concentrated acid of commerce to approximately the desired normality and then standardizing this solution against an appropriate primary standard, such as sodium carbonate or borax.[66] The former substance is more commonly available and easily prepared, and therefore it is used here. An optional procedure for the

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[64] Hoffman, *J. Research Natl. Bur. Standards*, **15**, 583 (1935).

[65] See references, p. 100.

[66] Kolthoff, *J. Am. Chem. Soc.*, **48**, 1447 (1926).

preparation of borax, $Na_2B_4O_7 \cdot 10H_2O$, and its use as a standard is given in Note 8 below.

Since sodium hydrocarbonate is more readily obtained pure than is the normal carbonate, it is prepared (or purchased) and converted into the latter. There have been many investigations and some contrary evidence as to the possibility of converting sodium hydrocarbonate to the anhydrous carbonate without obtaining some sodium oxide (or hydroxide) in the process.[67] However, there appears to be conclusive experimental proof that by heating pure sodium hydrocarbonate at 270° to 300°C. complete conversion to the anhydrous carbonate is effected and a product suitable for use as an acidimetric standard obtained.

Displacement Reactions. The titration of a carbonate with a strong acid is not, strictly speaking, a neutralization reaction, since the formation of water is not primarily involved. The reaction

$$Na_2CO_3 + 2HCl = H_2CO_3 + 2NaCl$$

is written ionically

$$CO_3^{=} + 2H^+ = H_2CO_3,$$

with the equilibrium expression being

$$\frac{[H_2CO_3]}{[CO_3^{=}][H^+]^2} = K_D,$$

where K_D is obviously the reciprocal of the total ionization constant of carbonic acid.[68] Such reactions are termed **displacement** reac-

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[67] Lunge, *Z. angew. Chem.*, **10**, 552 (1897); **17**, 231 (1904); **18**, 1520 (1905); Schmidt, *Z. anal. Chem.*, **70**, 321 (1927); Smith and Hardy, *J. Chem. Ed.*, **10**, 507 (1933); Waldbauer, McCann, and Tuleen, *J. Ind. Eng. Chem., Anal. Ed.*, **6**, 336 (1934); Smith and Croad, *ibid.*, **9**, 141 (1937).

[68] It should be pointed out that the above reaction proceeds in two steps as follows:

$$(1)\ CO_3^{=} + H^+ = HCO_3^-$$

and

$$(2)\ HCO_3^- + H^+ = H_2CO_3.$$

The end-point of the first reaction can be obtained by properly using phenolphthalein (or other indicators having approximately the same *p*H range). However, the *p*H change near the equivalence-point is so much less pronounced than it is for the second reaction that it should not be used for highly precise titrations. Simpson, *J. Ind. Eng. Chem.*, **16**, 709 (1924), has recommended a mixed indicator of 6 parts thymol blue and 1 part cresol red when it is desired to use this end-point for the analysis of carbonate-hydrocarbonate mixtures. The indicator changes from a violet-purple color in carbonate solution to a rose at the end-point and becomes orange-yellow with excess acid.

tions, since it was formerly considered that carbonic acid was displaced from its salt. It is obvious that the weaker the acid the greater the value of K_D, the constant for the displacement reaction, and the more complete the reaction. In considering the change in the $[H^+]$ of the solution with regard to determining the end-point of such titrations, it is to be observed (1) that the salt of a strong base and a weak acid will be alkaline by hydrolysis; (2) that during the titration the $[H^+]$ added will be used up as long as an appreciable concentration of the salt remains; (3) that at the equivalence-point one has essentially a solution of the weak acid; and (4) that as an excess of strong acid is added, the $[H^+]$ will rise very rapidly. Therefore, if one selects an indicator which has a transition range close to or slightly above that given by a dilute solution of the weak acid, a satisfactory titration can be made. For example, in considering the titration of sodium carbonate, it is to be observed that a solution saturated with carbon dioxide is 3.4×10^{-2} molal in H_2CO_3; and, as the ionization constant for the first hydrogen of carbonic acid is 3×10^{-7}, it can be calculated that the $[H^+]$ of the solution at the equivalence-point is approximately 10^{-4} molal. The transition range for methyl orange extends from about 4.5×10^{-5} to 10^{-3}; therefore methyl orange is perceptibly, though not completely, transformed to the acid form in such a solution, and though the further addition of acid causes a pronounced additional change toward the pink color, the end-point is not as sharp as would be desired. Because of this it is advisable to titrate with the acid to the first perceptible change, to heat the solution sufficiently to expel the carbon dioxide, then to cool it (since the methyl orange transition range is shifted in hot solutions), and to finish the titration with the cold solution. By this means a very satisfactory end-point is obtained.

The change in the $[H^+]$ during the titration of a salt can be predicted from the curves of Fig. 16 if one considers that upon hydrolysis the salt of a weak acid and a strong base produces hydroxyl ions and can therefore be considered as a weak base, thus:

$$A^- + HOH = HA + OH^-.$$

The equilibrium expression for this hydrolytic reaction is

$$\frac{[HA][OH^-]}{[A^-]} = K_H,$$

where K_H, called the hydrolysis constant, is obviously the reciprocal of the neutralization constant, thus:

$$K_H = \frac{K_w}{K_A}.$$

It is to be noted that the above equilibrium expression for a hydrolysis reaction has the same form as the ionization expression for a base in which the concentration of the un-ionized base is replaced by $[A^-]$ and that of the basic ion by [HA]. It follows that upon adding acid to such a solution the $[OH^-]$ and the $[H^+]$ will change, as does a solution of a base with an ionization constant of the same values as the hydrolysis constant of the salt. Therefore, to use Fig. 16 for displacement titrations, the hydrolysis constant is calculated, and the curve for a base with an ionization constant of that value is traced, or if titrating the salt of a weak base and a strong acid, the curve for the corresponding acid is followed. The use of Fig. 16 is thereby extended to displacement titrations.

Consider the application of this principle to the titration of borax, which is not complicated, as is the titration of carbonates, by the escape of carbon dioxide from the solution. Boric acid can be treated as a monobasic acid having a constant equal to 6.4×10^{-10}; therefore the hydrolysis constant is calculated as follows:

$$K_H = \frac{K_w}{K_A} = \frac{10^{-14}}{6.4 \times 10^{-10}} = 1.6 \times 10^{-5}.$$

Tracing a curve for a base whose constant is 1.6×10^{-5}, we see that at the equivalence-point the $[H^+]$ is approximately 8×10^{-6} and that methyl red (or methyl orange) would be a very satisfactory indicator for the titration. Such is the case, and if pure borax is available, it can be used accurately and conveniently as a standard for the acid. (See Note 8 below.)

The Use of Mixed Indicators. As will be seen by an inspection of the titration curves for the above displacement reaction, the change in the *p*H near the equivalence-point is much less pronounced than that obtained in titrating strong acids with strong bases; the same is also true of the titration of weak acids or bases. It is therefore desirable to employ indicators which have very narrow transition bands at some definite *p*H value. In order to obtain this, use has been made of a mixture of two indicators or of an indicator and an inert dye stuff. The use of such an indicator is of advantage in this procedure. (See Note 7 below.) For a discussion and extensive list of such indicators see Kolthoff and Furman, *Volumetric Analysis*, Vol. 2, pp. 62–66.

Procedure XVII: STANDARDIZATION OF AN HYDROCHLORIC ACID SOLUTION AGAINST ANHYDROUS SODIUM CARBONATE. Calculate the volume of the concentrated hydrochloric acid of commerce required to prepare 1 liter of 0.2 n. solution and measure it into a liter volumetric flask or cylinder. Dilute it to volume, transfer it to a ground-glass-stoppered bottle, mix it thoroughly, and allow it to cool to room temperature. Weigh approximately 5 to 6 g of $NaHCO_3$ (Note 1) into a clean platinum or nickel crucible (Note 2), support the crucible within a larger iron crucible by means of a triangle (Note 3), hang a thermometer so that the bulb is close to the crucible containing the $NaHCO_3$, and then heat the outer crucible so that a temperature of 270° to 300°C. is maintained for 30 minutes (Note 4). Stir the material occasionally with a clean platinum wire. Remove the crucible to a desiccator, allow it to cool, and weigh it. Repeat the heating—taking care that none of the material adheres to the wire (Note 5)—and weighing until the weight remains constant to within 0.5 mg. Transfer the sodium carbonate to a weighing bottle and keep it in a desiccator (Note 6).

Weigh out precisely 0.4 to 0.5 g of the prepared Na_2CO_3 (Note 6) into a 200-ml flask, dissolve it in 50 ml of water, add 2 drops of methyl orange indicator solution (Note 7), and titrate with the HCl solution, adding the acid slowly while inclining the flask, until the first perceptible change in color of the methyl orange (from a clear yellow toward pink) is obtained. Use the same volume of water and 2 drops of methyl orange in a similar flask as a reference solution. Heat the titrated solution to boiling for 2 to 3 minutes, frequently swirling it, cool it to room temperature by running tap water over the outside of the flask while swirling the contents, and again titrate to the first perceptible change of the indicator. Repeat this process with two more samples of the Na_2CO_3 and calculate the normality of the HCl.

Notes:

1. A special brand of $NaHCO_3$ for analytical purposes can be purchased and is usually sufficiently pure to be used directly. If this grade is not available, the $NaHCO_3$ can be prepared by saturating a solution with Na_2CO_3, filtering, and then saturating this solution with CO_2; pour off the solution,

wash the precipitate with a small amount of water, collect the crystals on a sintered-glass filter, and dry at 120°C.

2. A porcelain crucible or even a weighing bottle of resistance glass can be used as a container, but these are less effective, due to their smaller heat conductivity.

3. A sand bath may be used if the sand is clean and dry and the outside of the crucible carefully wiped clean before weighing.

4. Care should be taken not to exceed 300°C., since the decomposition of the Na_2CO_3 into Na_2O may become appreciable at higher temperatures.

5. After the carbonate has been once weighed, care should be taken to prevent any loss. Therefore, after stirring the material, the stirring wire should be carefully brushed with a small camel's-hair brush while held above the crucible. A small glass stirring rod may be used if care is taken to brush all particles from it.

6. Na_2CO_3 is noticeably hygroscopic, and therefore the bottle should be opened only when necessary and then closed as soon as possible.

7. The titration can be made more rapidly by adding 1 drop of phenolphthalein and rapidly titrating until the red color disappears; this is the end-point of the reaction

$$CO_3^{=} + H^+ = HCO_3^-.$$

The methyl orange can then be added and slightly less than the same amount of acid added without overrunning the end-point.

A mixed indicator, made by dissolving 0.1 g of methyl orange and 0.25 g of indigo carmine in 100 ml of water, gives a much sharper end-point, especially if working by artificial light. The indicator is greenish in alkaline solutions, and turns very sharply to gray at the end-point (pH = 4) and to violet with an excess of acid. If it is available, the use of this indicator is advised; 2 to 3 drops per 100 ml of solution are most satisfactory.

8. Borax, $Na_2B_4O_7 \cdot 10H_2O$, has the advantages over sodium carbonate of a higher equivalent weight and of not being hygroscopic, but has not been extensively used because of uncertainty in drying the hydrate without decomposition. It has been shown that pure borax can be obtained by simple recrystallization, that the product can be dried by washing with alcohol and ether, and that it can be stored in ground-glass-stoppered containers for a year without a change in composition of greater than 0.1 per cent.[69] The material can be prepared and the standardization carried out as follows:

Procedure: Preparation of the Borax. Dissolve 15 g of borax in 35 ml of water, filter out any residue, and cool to room temperature or below. Collect the crystals on a sintered-glass filter and wash with two 10-ml portions of cold water. Mix all the wash solutions thoroughly with the crystals with the aid of a stirring rod and then use suction to draw off the liquids. Wash with two 10-ml portions of 95 per cent alcohol and three 10-ml portions of ethyl ether. Spread the crystals on a watch glass and (1) allow them to stand in air (protected from dust and so forth) until they are free of ether

[69] Hurley, *J. Ind. Eng. Chem.*, Anal. Ed., **8**, 220 (1936); **9**, 237 (1937).

and have reached a constant weight (usually from 5 to 8 hours), or (2) place them in a vacuum desiccator and evacuate with the full force of an efficient water aspirator for 25 minutes, weigh, then again evacuate for 5-minute intervals until constant weight is obtained. Store the crystals in a ground-glass-stoppered container.

Standardization of the Acid Against the Borax. Weigh out precisely 1.3 to 1.5 g of the prepared borax, dissolve it in 50 ml of water, add 3 drops of methyl red indicator solution, and titrate with HCl until the color matches an equal volume of water to which has been added 3 drops of methyl red and 1 g of H_3BO_3 and 0.5 g of NaCl. Repeat the process with two more samples of the borax and calculate the normality of the HCl.

A considerable saving of time can be effected by the use of the vacuum desiccator. Experiments have shown that standardization values obtained from material prepared by its use agree within 0.1 per cent with those obtained by other methods. It is quite desirable that the comparison flask be used, or a slightly premature end-point may be taken.

The Applications of Neutralization and Displacement Methods

These methods, often collectively designated as *acidimetry* and *alkalimetry*, can be used for the estimation of acids and bases, the estimation of salts of weak acids or of weak bases, and the indirect determination of other substances which can be converted into, or stoichiometrically precipitated by, compounds of this type. Thus in this system of analysis, ammonium is estimated by being distilled as ammonia from an alkaline solution, collected in a known amount of acid, and the excess acid titrated (P. 96). Nitrate and nitrite are reduced to ammonia and similarly determined (P. 181). This same principle is employed in the well-known Kjeldahl method for the determination of the nitrogen in organic substances; in this method the organic nitrogen is converted into ammonium salt by being heated with concentrated sulfuric acid containing various added substances to aid in the decomposition of the organic material. The resulting solution is then made alkaline with sodium hydroxide, and the distillation and titration of the resulting ammonia is carried out as described in P. 96. Reference books on quantitative analysis should be consulted for the various modifications of the original Kjeldahl method, as well as for a more complete treatment of the determinations which can be made with the use of standard solutions of acids and bases.

Gravimetric Methods of Analysis

The Gravimetric Standardization of a Hydrochloric Acid Solution

Discussion. Although the chloride present in a hydrochloric acid solution can be very accurately determined gravimetrically by precipitating it as silver chloride and weighing the precipitate, in general it is preferable to standardize acid solutions volumetrically, rather than gravimetrically, if they are intended for use in acidimetric analyses. This is because the volumetric standardization (1) can be made quite accurately and by methods similar to those for which the solutions are being prepared, (2) can be carried out more quickly and easily, and (3) is based upon the acid concentration, whereas the gravimetric standardization is based upon the anion (in this case chloride) concentration.

The procedure for the gravimetric standardization is included here because (1) it can be carried out with exceptional accuracy; (2) it illustrates exceptionally well many of the principles and much of the technique involved in gravimetric analysis; and (3) the same principles and technique form the basis for a majority of the methods for the qualitative and quantitative separations of various elements or groups of elements. Because of this, the discussion of these principles and the description of the technique can be collected here and reference made to them when particular applications occur in the later procedures.

GENERAL PRINCIPLES OF GRAVIMETRIC METHODS

Discussion. It was pointed out in the discussion of volumetric methods that a given reaction had to meet certain requirements before it could be made the basis for a precise volumetric analysis. Similarly, certain factors have to be considered in the development of a gravimetric method. These may be classified into groups as they affect the following:

I. The solubility of the precipitate.

II. The physical characteristics and purity of the filtered precipitate.

III. The stability and composition of the weighted precipitate.

I. Factors Affecting the Solubility of the Precipitate

The factors affecting the amount of a given constituent which will remain in the filtrate when the precipitate is filtered may be classified as follows:

1. The common ion and activity effects (the solubility-product principle).
2. The formation of complex ions.
3. Hydrogen (and hydroxyl) ion effects.
4. Solvent effects.
5. Temperature effects.
6. Effect of time on the completeness of precipitation (supersaturation effects). These factors are discussed briefly below.

1. The common ion and activity effects (the solubility-product principle). It is a fundamental necessity for a gravimetric method that the precipitate be so insoluble (under the conditions of the precipitation) that the amount left in the saturated filtrate and in the wash solution be negligible in comparison with the other errors of the method (or, as is possible in certain cases, that a reliable correction can be made for the amount so lost). In some cases calculations can be made from solubility data as to whether the amount of the compound lost in the filtrate and wash solution will be within the accuracy that is desired, or can be reduced to the desired limits by the addition of a common ion; for making such calculations the solubility-product principle is employed. This principle has been discussed in P. VI, where it was applied in predicting the course of certain precipitation reactions, and reference should be made to that discussion. There it was pointed out that the solubility-product principle (and the mass-action law in general) is obeyed experimentally only when the activities of the substances are used instead of their concentrations, or if the latter are used, only under the following limitations: (1) With quite insoluble precipitates, (2) when the total ion concentration of the solution is low, and (3) with

TABLE III

THE SOLUBILITY OF SILVER CHLORIDE IN POTASSIUM CHLORIDE SOLUTIONS

KCl moles/liter	Ag moles/liter	$K_{S.P.}$
0.00670	1.7×10^{-5}	1.14×10^{-10}
0.00833	1.39×10^{-5}	1.16×10^{-10}
0.01114	1.07×10^{-5}	1.19×10^{-10}
0.01669	0.738×10^{-5}	1.23×10^{-10}
0.03349	0.388×10^{-5}	1.30×10^{-10}

salts of simple valence type. In Table III the experimental data of Jahn[1] have been used to show (1) the solubility of silver chloride in

[1] Jahn, *Z. physik. Chem.*, **33**, 454 (1900).

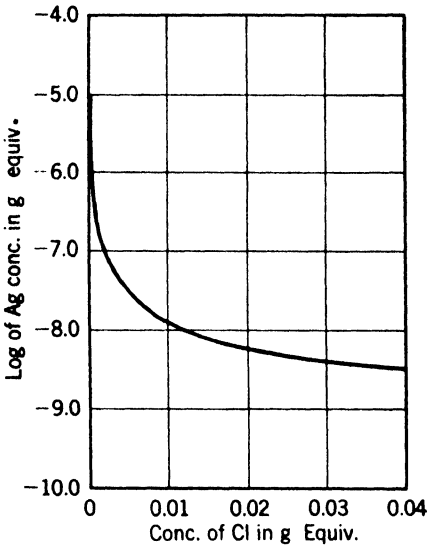

Fig. 17. The Solubility of Silver Chloride in Dilute Chloride Solutions.

dilute solutions of potassium chloride and (2) the constancy of the calculated solubility-product value when making the assumption that the potassium chloride is completely ionized and that the activities of the ions are equal to their formal concentrations. It is to be noted that the values for the solubility product agree reasonably closely in solutions which are below 0.01 formal in KCl. This agreement is to be compared with the values (shown in Fig. 9) for the solubility of silver sulfate, a more soluble salt and one containing a binegative ion, where—especially in the presence of an excess of sulfate ion—the solubility varies considerably more from the predicted value; in fact, the common ion causes very little decrease in the solubility of the salt. As previously stated, these deviations are due to the attractive forces existing between the ions in the solution, and these are responsible for the marked increase in the solubility of silver sulfate in solutions of salts not having a common ion.

2. The formation of complex ions. A still different effect from those mentioned above is shown in Figs. 17 and 18. In Fig. 17 is shown the decrease in the solubility of silver chloride caused by the common ion effect in low concentrations of chloride, and this should be contrasted with Fig. 18, where the data of Forbes[2] for the

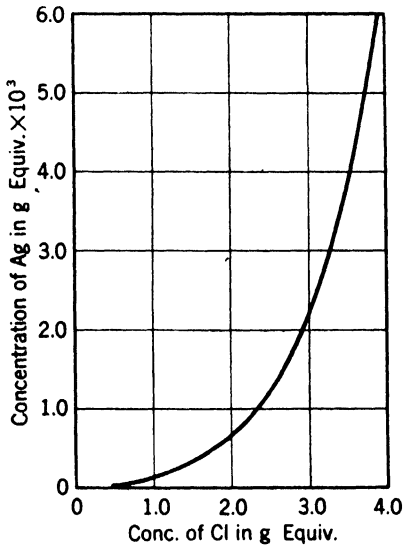

Fig. 18. The Solubility of Silver Chloride in Concentrated Chloride Solutions.

[2] Forbes, *J. Am. Chem. Soc.*, **33**, 1939 (1911).

solubility of silver chloride in concentrated solutions of potassium chloride are plotted. It can be shown that the remarkably rapid increase in the solubility of the silver chloride in the more concentrated solutions can be explained on the basis of the formation of complex ions (of the type $AgCl_2^-$, $AgCl_3^=$, and $AgCl_4^{\equiv}$), in which the positive silver ion is surrounded by the negative chloride ions.[3] It is thus seen that if these effects are ignored, calculations on the basis of the solubility-product principle would lead to erroneous and misleading predictions. Furthermore, the haphazard addition of a large excess of a precipitation reagent may defeat the purpose sought, since it is entirely possible that a large excess of even a common ion may cause an increase in the solubility of the precipitate. It is not to be inferred that the solubility-product principle does not apply to cases where complex formation exists, but merely that the additional equilibria involved in their formation must also be considered. It should also be noted that, as in the large majority of cases complex ions are formed as the result of adding an excess of a negative ion to a positive one, less pronounced effects will follow the addition of an excess of a positive ion as precipitant to a negative ion than the reverse. Thus, the solubility of silver chloride in 2 formal silver nitrate is only 5×10^{-5} formal, less than one tenth that in 2 formal chloride solution, although greater than it is in water. Other obvious applications of the tendency of certain elements to form complex ions are demonstrated in the solubility of silver chloride and of copper oxide in the presence of ammonia (because of the formation of the di-ammino silver ion, $Ag(NH_3)_2^+$, and the tetrammino copper ion, $Cu(NH_3)_4^{++}$).[4] Where the values of the dissociation constants of these compounds have been determined and are available, calculations can be made as to the effect of such compound formation on the solubility of a precipitate. Thus, as the value for the equilibrium-dissociation constant for the expression

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = K_{\text{Dissociation}} = 6.8 \times 10^{-8},$$

[3] On the basis of his calculations, Forbes did not find evidence of the ion $AgCl_2^-$ in these concentrated solutions, but concluded that $AgCl_3^=$ and $AgCl_4^{\equiv}$ were the species present; later work with less concentrated solutions, Forbes and Cole, *J. Am. Chem. Soc.*, **43**, 2497 (1929), and evidence from other sources have indicated that the simpler ion is also formed.

[4] These and other complex ions are discussed further in P. 11, in connection with their significance in the precipitation of the sulfides of the various elements from acid solutions, and in P. 64, where the complex compounds of cobalt are treated.

it can be predicted that silver chloride would be very soluble in a solution 0.5 f. in ammonia, but that silver iodide would be relatively insoluble and that a separation of iodide from chloride could be thus effected; this separation is an experimental fact.

3. Hydrogen (and hydroxyl) ion effects. The effects of hydrogen and hydroxyl ions on the solubility of a substance are treated in the general discussion of the preparation of the solution for the analysis and in P. 5. Examples of the various solubilities of the salts of a weak acid in various hydrogen ion concentrations are also given in P. 11, Table XI, where the solubilities of the sulfides in different solutions of acids and bases are shown. The adjustment of the hydrogen ion concentration is also of importance in gravimetric precipitations because it often effects the physical character of the precipitate (this effect is discussed later) and because it can be used to prevent the precipitation of undesired compounds. Thus if an attempt were made to precipitate silver chloride from a neutral solution, there would also precipitate any carbonate, phosphate, arsenate, or other anions of weak acids which form insoluble silver salts; the same would be true of the attempt to precipitate barium sulfate from a neutral solution.

When precipitating the hydroxides by addition of hydroxyl ion, each specific case has to be considered separately; thus a high concentration of hydroxyl ion is required for the complete precipitation of magnesium hydroxide, whereas with aluminum hydroxide, because of its amphoteric nature, an excess of hydroxyl ion has to be carefully avoided.

4. The effect of the solvent. In many cases the solubility of a salt can be reduced by altering the properties of the solvent or changing to a different medium. In general, inorganic salts, especially if they are highly ionized, are less soluble in organic solvents, such as alcohol and ether, than they are in water. Because of this effect, strontium chromate, which is appreciably soluble in water solutions, can be quantitatively precipitated from a solution containing a considerable proportion of alcohol. Likewise, the quantitative precipitation of potassium perchlorate has to be made from an alcoholic or other nonaqueous medium, and nickel chloride, which is very soluble in water, can be precipitated by passing hydrogen chloride gas into an ether solution.

5. Temperature effects. Where the precipitate is sufficiently insoluble and stable, and where other undesirable effects (such as the hydrolysis of certain salts or the oxidation of some of the con-

stituents present) are not encountered, there are definite advantages in carrying out the precipitation, filtering, and washing of precipitates at elevated temperatures, since, in general, the precipitates are more readily coagulated and brought into a filterable form. As an example, barium sulfate which has separated in such a finely dispersed condition as to pass through even a dense filter can be converted into a much coarser and more readily filtered form by keeping the solution near the boiling temperature for a short period. Solutions are more rapidly filtered when hot, mainly because their viscosity is much less; the specific viscosity of water is 0.637 at 15°C. and only 0.158 at 100°C. Experimentally it has been found that hot solutions will pass through a paper filter from five to ten times as fast as those at room temperature. Another advantage arises from the fact that the substances contaminating the precipitate are usually more soluble in hot solutions and are thus more readily extracted.

6. The effect of time on the completeness of precipitation. It is not generally realized that in many precipitation reactions there is a considerable lapse of time before equilibrium is reached. There may be two general causes for this. The first is the familiar phenomenon of supersaturation, which is most obvious with moderately soluble compounds and occurs even when the constituent ions of a salt are present in high concentrations. In the second case the substance may be extremely insoluble, and yet the rate of precipitation may be very slow because the constituent ions are present in such very minute concentrations. The slow precipitation of arsenic sulfide, As_2S_5, from acid solutions is a striking example of the latter case. This is undoubtedly due to the very low concentration of simple penta-positive arsenic ions in the solution and to a slow rate of formation of these ions from the other molecular species in which the arsenic exists.[5] Another example of this type of rate effect is involved in the precipitation of cobalt as potassium cobaltinitrite, $K_3Co(NO_2)_6$, where the precipitation has to be preceded by the oxidation of the cobaltous ion to the cobaltic state and by the formation of the complex cobaltinitrite ion.

Although no general rule can be given, it is quite important that a sufficient time elapse between adding the precipitant and beginning the filtration, not only for the precipitate to develop into a filterable form, but also for it to reach an equilibrium. Precipitation can be induced in supersaturated solutions by vigorous agitation, such as

[5] This precipitation is treated from the experimental point of view in the discussion of P. 11.

stirring or shaking; the expedient (often used in preparative work) of adding a crystal of the precipitate is usually not practical in analytical procedures. In cases of the second effect, precipitation can be hastened by providing a high concentration of the reactants, by increasing the temperature, and, in certain cases, by mechanical agitation.

II. (1) Factors Affecting the Physical Characteristics of the Precipitate

It would seem that the physical characteristics of a precipitate—that is, whether it is crystalline or amorphous, granular or gelatinous, whether it separates in a highly hydrous condition, and even its color—would be determined by its chemical composition. Thus it would seem that sulfides are of an amorphous nature, hydroxides gelatinous, and sulfates crystalline because of their chemical composition. However, owing in a large measure to the work of Von Weimarn,[6] it has been shown that these characteristics are influenced more by the conditions under which the precipitate forms than by its chemical composition.

Considering the mechanism of precipitation, it seems reasonable to expect that if a precipitate forms in a solution in which its normal solubility is only slightly exceeded, initially only a relatively few crystal nuclei will be formed, and that after these are present, the subsequent precipitation will consist mainly of an enlargement, or "growth," of these crystals. This subsequent growth of crystals is in accord with the experimental fact that the solubility of extremely small particles is appreciably greater than that of larger ones. This behavior is predicted from theoretical considerations and has been studied experimentally by various workers,[7] who have found solubility increases ranging from 15 to 80 per cent when studying small particles (ranging from 0.0001 to 0.0002 mm in diameter) of barium sulfate and of calcium sulfate monohydrate, $CaSO_4 \cdot H_2O$. Therefore a solution which is saturated with respect to the very small particles is obviously supersaturated with respect to larger ones, and as a result precipitation takes place on the larger ones, and the smaller ones tend to pass into solution.

If the initial precipitation takes place in a solution which is greatly supersaturated, then there will be formed a large number of crystal

[6] Von Weimarn, *Zur Lehre von den Zustanden der Materie* (1914).

[7] Ostwald, *Z. physik. Chem.*, **34**, 495 (1900); Hulett, *ibid.*, **37**, 385 (1901); **42**, 581 (1903); **47**, 357 (1904). Hulett and Allen, *J. Am. Chem. Soc.*, **24**, 667 (1902); Dundon and Mack, *ibid.*, **45**, 2479 (1923); Dundon, *ibid.*, **45**, 2658 (1923).

nuclei, and the precipitate will appear in a highly dispersed condition. With very insoluble precipitates ordinary methods of mixing the solutions will always result in a relatively high degree of supersaturation, and therefore the precipitate will appear as a large number of very small particles; in fact, they may be so small that they will remain colloidally dispersed. Furthermore, if a precipitate is extremely insoluble, the concentration of the saturated solution will be so small that the growth of large crystals at the expense of the more soluble smaller ones will be slow. According to Von Weimarn, this degree of supersaturation, which can be expressed as the ratio of the initial supersaturation of the substance (before precipitation begins) to its equilibrium solubility (or $[S - s]/[s]$, where S represents the initial concentration of the substance before precipitation begins and s the equilibrium solubility, each expressed in equivalents per liter), is a major factor in determining the physical characteristics of precipitates. From this principle the generalization is made that the physical characteristics of two precipitates will be largely the same, irrespective of their chemical nature, if they are produced under corresponding conditions, and the most important factor determining these conditions is the value of $[S - s]/[s]$. It follows that if the same substance is precipitated under conditions where $[S - s]/[s]$ has widely varying values, its physical characteristics will be quite different. As an example, barium sulfate, which normally appears as a finely divided but distinctly crystalline precipitate, can be made to separate in a colloidal or gelatinous form by causing it to precipitate from a highly supersaturated solution, or one where the value of $[S - s]/[s]$ is large. This can be accomplished in two ways: (1) by decreasing its solubility (for example, by the addition of alcohol to the aqueous solution), thus decreasing s, or (2) by mixing highly concentrated solutions, thus increasing S. As examples, it is found that the precipitate resulting from mixing equal volumes of 0.025 n. cobalt sulfate and 0.025 n. barium thiocyanate in 50 per cent alcohol has at first a distinctly colloidal appearance, and on coagulating might easily be mistaken for aluminum hydroxide, while the precipitate resulting from rapidly mixing equal volumes of 7 n. manganous sulfate and 7 n. barium thiocyanate is a viscous gel. Since colloidal solutions consist of finely dispersed particles (usually with diameters ranging from 10^{-4} to 10^{-6} mm), it would be expected that a high value of the ratio of $[S - s]/[s]$ would be favorable to their formation; this is true, as is shown by the fact that barium sulfate (a typically crystalline precipitate) can be produced as either a suspensoid or

even as a gel. On the other hand, by precipitating barium sulfate from a 4 n. hydrochloric acid solution, where s is considerably greater than it is in a neutral solution, the precipitation takes place quite slowly, and relatively large crystals can be obtained.[8]

Apparent exceptions to this rule can be noted in the fact that substances of approximately the same solubility precipitate in distinctly different physical form; barium sulfate and silver chloride furnish an example of this anomaly. These two substances have about the same solubility, yet normally appear as precipitates of a very different type—silver chloride as a curdy flocculated colloid and barium sulfate in a definitely crystalline form. The difference is explained by the fact that the solubility of barium sulfate increases much more rapidly as the particle size is decreased than does silver chloride, and therefore the initial supersaturation is much less with barium sulfate than with silver chloride.[9]

It is thus seen that larger and more readily filtrable particles can usually be obtained (1) if the initial supersaturation of the solution during the precipitation process is kept as small as possible and (2) if time is given for the extremely small particles first formed to increase in size. In addition to this "growth," which can be attributed to the increased solubility of the small particles, if a crystalline precipitate is caused to form very rapidly from relatively concentrated solutions, it is probable that many imperfections and strains will result in the process, and that if such a precipitate is allowed to age, a recrystallization and adjustment will take place. This process will usually result in a decrease in the total surface and gives a more filtrable precipitate. This process frequently is responsible for the changes taking place upon "digesting" (that is, maintaining the solution for a period of time at or near its boiling point) a very fine or colloidal precipitate in order to convert it into a form that can be filtered.[10]

Summing up the above with reference to most analytical precipitations where, in order to facilitate filtering and washing and to avoid colloidal solutions, it is desirable to obtain a coarsely granular or

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[8] A more detailed discussion of these effects is given by Washburn, *Principles of Physical Chemistry*, McGraw-Hill (1915), and by Smith, *Analytical Processes*, Longmans, Green (1929).

[9] Kolthoff, *J. Phys. Chem.*, **36**, 860 (1932). An extensive discussion of precipitation and coprecipitation phenomena is given in this article.

[10] For a discussion of this subject of the "ageing" of precipitates, see Kolthoff and Sandell, *Quantitative Analysis*, Macmillan, 1936, pp. 98–102.

crystalline precipitate, it is obviously advantageous (1) to mix the reagents very slowly and with effective stirring, (2) to use dilute solutions, (3) in many cases to *increase* the solubility of the precipitate, usually by the addition of an acid, or by working in hot solutions, and (4) to allow the precipitate to stand until the particle size is such that it will be retained by the filter.

II. (2) Factors Affecting the Composition and Purity of the Precipitate

Coprecipitation. It is a universally observed phenomenon that when a precipitate separates from a solution, it will carry out with it in varying amounts the soluble constituents of the solution; hereafter the term *coprecipitation* will be used to designate this phenomenon without implying any specific cause or mechanism. Coprecipitation effects are one of the most important factors involved in precipitation methods and have to be considered regardless of whether a separation or a gravimetric determination is desired. In general, coprecipitation is not the result of any one effect but may result from the operation of any one or more of the four following causes:

1. Adsorption.
2. Compound formation.
3. Solid-solution formation.
4. Mechanical inclusion.

Adsorption as a Cause of Coprecipitation. Adsorption may be broadly defined as the process which causes an increase in the concentration of a gas, liquid, or dissolved substance at an interface—that is, at the surface between two phases. In analytical chemistry there is special interest in the process whereby constituents of a solution are concentrated on the surfaces of precipitates. Charcoal is probably the best-known example of an effective adsorbing agent, and consequently is extensively used scientifically and industrially for collecting gases and for removing many substances from dilute solutions; an example of the latter is the commercial use of special charcoals for the recovery of iodine from oil-well brines.

The adsorption of acetic acid from aqueous solutions by charcoal was investigated quite early in the study of adsorption phenomena, and data showing the relation between the amount of adsorption taking place on a given amount of charcoal and the concentration of the acetic acid are shown in Table IV. If the adsorption process

TABLE IV

THE ADSORPTION OF ACETIC ACID FROM AQUEOUS SOLUTIONS BY CHARCOAL

Equilibrium concentration (c) of $HC_2H_3O_2$ moles/liter	Millimoles $HC_2H_3O_2$ per gram of charcoal (x/m)
0.0181	0.467
0.0309	0.624
0.0616	0.801
0.1259	1.11
0.2677	1.55
0.4711	2.04
0.8817	2.48
2.785	3.76

Freundlich, *Kapillarchemie*, 1909.

were of a chemical nature—due conceivably to the formation of insoluble compounds—it would be expected that definite saturation values would be found limiting the amount of material taken up by a given amount of adsorbing agent. If the process were of a physical nature, it would be expected to be more analogous to the distribution of a substance between two phases, and such a process should obey the distribution law. This law is formulated as follows:

$$\frac{C_2}{C_1} = K,$$

where C_1 and C_2 represent the concentrations of a common substance in two phases which are in equilibrium and where the substance exists in the same molecular form in each phase. Should the substance exist in different molecular aggregations in the two phases—for example, be polymerized in one phase—the equation would have the more general form

$$\frac{(C_2)^n}{(C_1)} = K,$$

where n is the number of molecules associated in the polymer, in agreement with the general mass-action law.

It has been experimentally found that adsorption is an equilibrium process and that it follows an empirical equation, called the adsorption isotherm, which has the following form:

$$\frac{x}{m} = Kc^{1/n},$$

where x represents the weight of material adsorbed by the weight m of adsorbing material, c represents the equilibrium concentration of the

adsorbed material, and K and n are constants. The constant K is highly dependent upon the specific conditions to which the equation is being applied, and n is always greater than 1, usually less than 5, and frequently approximately 2. It is seen that this equation bears a formal resemblance to the distribution law. In Fig. 19 is shown the curve obtained by plotting the data of Table IV. It is also evident that the equation may be written

$$\log \frac{x}{m} = \frac{\log c}{n} + \log K,$$

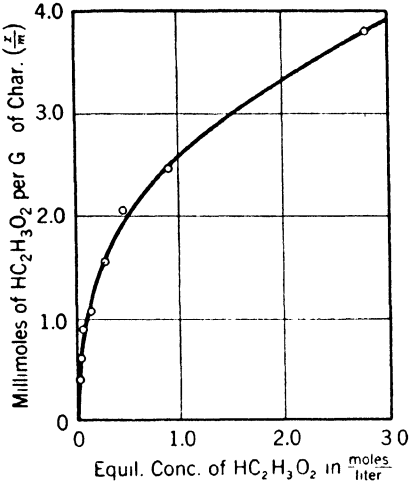

Fig. 19. The Adsorption of Acetic Acid from Aqueous Solutions by Charcoal.

and that a straight line should result from plotting the data logarithmically; this is also shown in Fig. 20. This graphical method is frequently used to determine whether a given process is due to adsorption, or to the presence of other effects which would cause a departure from the straight line.

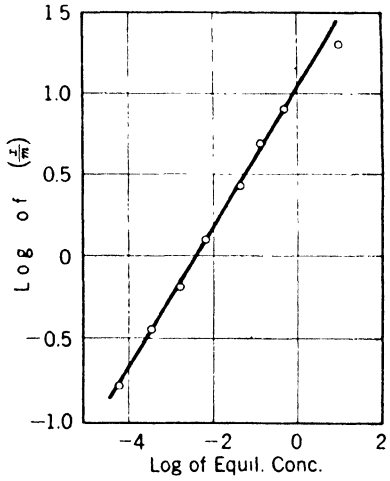

Fig. 20. The Adsorption of Acetic Acid from Aqueous Solutions by Charcoal (Logarithmic Plot).

Not only are molecular compounds adsorbed from solutions by solids, but it is also found that ions are similarly concentrated at the surface of precipitates; the charge associated with colloidal particles is in general due to this effect, and the presence of this charge contributes to the stability of the suspension.[11]

It is found that, as a general rule, precipitates tend to adsorb the ions of which they are composed.

[11] It should be pointed out that the solution does not acquire an electrostatic charge because of the adsorption of ions of a particular sign. This is prevented by the formation of a second loosely attached and more mobile layer of ions of opposite sign (thus producing the so-called electrical double layer). Even upon coagulation or filtration the double layer is carried with the precipitate, and the solution remains electrically neutral.

A colloidal suspension of silver chloride, bromide, or iodide which has been formed in the presence of an excess of the halide ion will be found to be negatively charged because of the adsorbed negative ions; in the presence of an excess of silver ions such a precipitate will be positively charged. The adsorption of silver nitrate by silver iodide has been extensively studied, and the results of one such study are shown in Fig. 21.

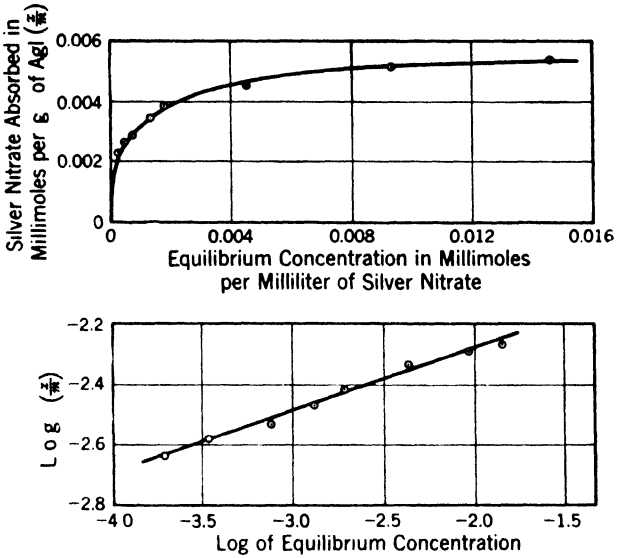

Fig. 21. The Adsorption of Silver Nitrate by Silver Iodide.

The silver halide first formed by the addition of silver nitrate to a solution containing halide ions is negatively charged and usually remains in suspension until quite near the equivalence-point; then as the concentration of the halide ion in the solution is reduced to a very small value, the adsorbed halide ions are withdrawn from the precipitate and coagulation takes place.[12] By adding a large excess of silver nitrate, the precipitate can be peptized, that is, again colloidally dispersed, and the particles will now have a positive charge.

[12] In many precipitation reactions this effect can be used to indicate when an approximately equivalent amount of the precipitant has been added and an unnecessary excess thus avoided. In certain cases the effect is so pronounced that the volumetric end-point can be taken with considerable precision by noting when this sudden coagulation or clearing of the solution takes place. Such a process is termed titrating to the "clear point." This effect has been studied for the titration of silver iodide by Lattermoser, Seifert, and Forstmann, *Kolloid Z.*, **36**, 230 (1925); also a volumetric determination of lead by titration with a molybdate solution to the clear point has been proposed by Sacher, *Kolloid Z.*, 276 (1926).

Such a suspension may be coagulated by the addition of negative ions to the solution; however, the coagulated precipitate will be found to have carried down with it some of the negative ions, and these may be an undesirable contamination for quantitative purposes. Since it is probable that all precipitates pass through the colloidal state to some extent in the mechanism of their formation, it is not surprising to find that marked adsorption may occur even with typically crystalline precipitates. Thus it has been found that the coprecipitation of potassium nitrate and of sodium chloride by a barium sulfate precipitate follows the adsorption equation.

The magnitude of the adsorption taking place in precipitation processes will vary from an amount not exceeding the usual quantitative errors to cases where even qualitative separations cannot be carried out. Adsorption phenomena are probably at least partly responsible for the coprecipitation effects shown in Tables XIX and XXI, where the limitations of the "ammonia precipitation" and the sodium hydroxide-peroxide process for separating the elements of the Ammonium Sulfide Group are shown. In many cases it is difficult to distinguish between adsorption and compound formation. Thus in the hydroxide separations just mentioned it is probable that the precipitates adsorb hydroxyl ion on their surfaces and that this results in the formation of the hydroxides of the soluble elements. A somewhat similar effect has been noted[13] in a study of the coprecipitation of zinc sulfide by copper sulfide, and has been attributed to the induced precipitation of zinc sulfide caused by the adsorption of hydrogen sulfide on the copper sulfide precipitate.

Space does not permit of an adequate treatment of even the most important of those adsorption and colloidal phenomena which are encountered in analytical precipitations and separations. For a more detailed treatment reference should be made to *Analytical Processes*, by T. B. Smith; *Elementary Quantititative Analysis*, by Willard and Furman; *Quantitative Inorganic Analysis*, by Kolthoff and Sandell; or to reference books and textbooks of colloidal and surface chemistry.

Compound Formation as a Cause of Coprecipitation. Compound formation was once thought to be a much more important cause of coprecipitation than is believed to be the case at present. As examples, the coprecipitation of zinc by chromium hydroxide in the ammonia precipitation was attributed to the formation of a zinc

[13] Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932); also see the discussion of P. 61.

chromite. This is unlikely because of the fact that in the hydroxide concentration provided in an ammonia precipitation there would hardly be a significant concentration of chromite formed; in fact, present evidence indicates that the solution of chromic hydroxide in more concentrated hydroxide solutions is due not to chromite formation but to the formation of a stable colloidal suspension in which there is a strong adsorption of hydroxyl ion. Such a suspension would tend to be coagulated by, and to carry down with it, a positive ion, such as zinc; in general, the greater the charge the more effective the coagulating action. Many cases formerly attributed to "double-salt" formation are now believed to be due to adsorption; the adsorption of cadmium salts by cadmium sulfide precipitate is such a case.[14]

Compound formation is a more probable cause of coprecipitation in cases where partially hydrolyzed products are formed, where complex compounds may exist, or where a preliminary adsorption process may be followed by compound formation. The attempted precipitation of bismuth hydroxide by ammonium hydroxide is likely to result in a mixture of hydroxide and basic salts in varying proportions depending upon the anions present, the hydroxyl ion concentration of the solution, the temperature, and other factors such as the method and rate of mixing the solutions. The coprecipitation of sulfate with a ferric hydroxide precipitate has been attributed to the formation of a basic ferric sulfate.

Solid Solutions (Mixed Crystals) as a Cause of Coprecipitation. It is possible to have a constituent uniformly distributed throughout a solid, and thus form what is known as a solid solution. For example, it was observed quite early[15] that if a solution of iodine in benzene was cooled until solid benzene separated, iodine would be uniformly distributed throughout the solid phase and *the concentration of the iodine in the solid phase was proportional to the concentration of the iodine in the liquid phase.*

The occurrence of isomorphism was also observed quite early. Isomorphous substances are those having so nearly the same crystal configuration that the constituents of one can be substituted in the crystal lattice of the other without causing an appreciable change in the crystal. Thus on evaporating a solution containing two isomorphous substances, homogeneous crystals of each substance will be obtained; however, each will be found to contain a certain proportion of the other substance. Since it seemed reasonable to assume that

[14] Weiser and Durham, *J. Phys. Chem.*, **32**, 1061 (1928).
[15] Van't Hoff, *Z. physik. Chem.*, **5**, 322 (1890).

isomorphous substances should have analogous molecular formulas, this rule was used by Mitscherlich as early as 1820 in deciding which multiple of the combining weight of an element should be its atomic weight. An experiment which strikingly shows mixed crystal formation can be performed by crystallizing potassium perchlorate from a solution containing even a very low concentration of permanganate ions. The crystals will remain pink even after washing (preferably with a saturated solution of potassium perchlorate) until the wash solution is colorless.

It has been found, however, that isomorphism is not necessary for solid-solution formation. The striking coprecipitation of nitrate by a barium sulfate precipitate, which previously had been attributed to compound formation (compounds of the type $Ba(NO_3)_2 \cdot BaSO_4$ having been postulated), has been recently studied[16] by means of X-ray diffraction experiments with results that indicate that solid solutions are formed.

Mechanical Inclusion (Occlusion) as a Cause of Coprecipitation. In many cases it has been made evident, especially from microscopic studies, that portions of the solution have been either entrapped by crystals or entrained in a mass of crystal capillaries and in this manner carried out with the precipitate. Such a process is properly termed occlusion, even though this term is sometimes used to designate coprecipitation in general. This effect can often be minimized by proper adjustment of conditions and method of precipitation and is probably the least serious of the causes of coprecipitation discussed. An example of it is found in the precipitation of potassium perchlorate, where it has been observed[17] that sodium perchlorate and perchloric acid are entrained by the precipitate.

General observations on coprecipitation effects. 1. *Coprecipitation effects often appear to be specific.* At the present time the fundamental principles of coprecipitation are too little understood and the conditions affecting it are too varied for general predictions to be made in regard to the occurrence or magnitude of the phenomenon; in many cases the effects appear to be controlled entirely by specific conditions. However, certain general tendencies have been noted and are discussed below. It should be mentioned that a considerable amount of intensive work is being carried out at the present time by various workers in regard to the mechanism of the formation of

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[16] Walden and Cohen, *J. Am. Chem. Soc.*, **57**, 2591 (1935).
[17] Smith and Ross, *J. Am. Chem. Soc.*, **47**, 774 (1925).

precipitates, their changes on ageing, the role of adsorption in coprecipitation, and other related topics; a much better general understanding of the subject should result from such investigations.

2. *The effect of the concentration of the coprecipitated substance.* Where coprecipitation results from adsorption alone, the effect of the concentration of the adsorbed substance can be predicted from the adsorption equation; regardless of the cause it is qualitatively apparent that the greater this concentration the greater the coprecipitation, other factors being constant.

3. *The effect of temperature on coprecipitation.* Since adsorption processes are exothermic, it is to be predicted that the higher the temperature the less the amount of adsorption taking place. On the other hand, where hydrolysis is involved in the coprecipitation process, raising the temperature is likely to increase coprecipitation. In certain cases where separations are being made which depend upon maintaining some substance in a supersaturated condition, raising the temperature appears to break up this supersaturated state and result in extensive coprecipitation. This effect is noted in the precipitation of zinc sulfide in the presence of cobalt (see discussion of P. 61).

4. *The effect of the solubility of the coprecipitated substance.* It has been observed that, where other conditions are constant, the amount of coprecipitation occurring increases as the conditions of the precipitation more nearly approach the saturation value of the coprecipitated substance. Thus in a determination of the sulfate in a solution which was approximately 0.04 n. in calcium chloride, a barium sulfate precipitate weighing approximately 1 g showed a loss in weight of 16 mg (replacement of barium by calcium), whereas under the same conditions with magnesium chloride present the error was 3 mg positive (coprecipitation of barium chloride).[18] In the separation of the bipositive elements manganese, cobalt, nickel, and zinc from the tripositive elements aluminum, iron, and chromium by a carefully controlled ammonia precipitation it was found that coprecipitation increased in the order named; zinc, the least soluble of the bipositive hydroxides, was the most extensively carried out with the tripositive hydroxides (see discussion of P. 51).

5. *Coprecipitation and complex-compound formation.* It is frequently observed that where a constituent of the precipitate tends to form a complex compound with some constituent of the solution, there will be coprecipitation of that compound. When sulfate is

[18] Blasdale, *Quantitative Analysis*, Van Nostrand, 1928, pp. 140 and 188.

precipitated as barium sulfate, ferric iron, which forms a complex compound of uncertain type with sulfate (or hydrosulfate), is much more extensively coprecipitated than aluminum (where any such complex is much less stable), or than ferrous iron.

6. *Coprecipitation varies with the methods and conditions of precipitation.* Since the physical characteristics of a precipitate, especially its surface, can be varied so extensively by the conditions of precipitation, it would be expected that such effects as adsorption would be similarly influenced. Also, as the concentration of the adsorbed ion is a factor in coprecipitation effects, it is possible to vary the effective concentration of such an ion during the formation of the precipitate (when coprecipitation is usually most pronounced) by the order of mixing the solutions. Thus in the precipitation of sulfate by addition of an excess of barium chloride, the coprecipitation of barium chloride will be less if it is added to the sulfate solution than if the mixing is made in the reverse order; however, if alkali-metal ions are present in the solution, more alkali sulfate will be coprecipitated when the barium chloride is added to the sulfate solution; because of this Popoff and Neumann[19] have recommended the reverse order of precipitation. The possible effects of the temperature at which the precipitation is made have been already mentioned above.

General methods for minimizing coprecipitation effects. Before leaving this topic, certain general methods for avoiding or minimizing coprecipitation effects are mentioned, even though some repetition is involved.

1. *Avoid introducing or remove substances known to cause coprecipitation.* As an example, in the determination of sulfur in a pyrite (FeS_2) material it is preferable to avoid a fusion process in the solution of the material because of the introduction of large amounts of sodium or potassium salts; if nitric acid is used in the solution process, it should be removed by repeated evaporation with hydrochloric acid; and the ferric iron should be either precipitated as ferric hydroxide or reduced to the ferrous form, which, as mentioned above, is relatively little coprecipitated.

2. *Keep the concentration of coprecipitated substances low.* This can be accomplished by avoiding large excesses of precipitants, or of acids and bases which have to be subsequently neutralized, and by making the precipitation from dilute solutions.

3. *Properly control the method and conditions of precipitation.*

[19] Popoff and Neumann, *J. Ind. Eng. Chem., Anal. Ed.*, **2**, 45 (1930).

Factors involved would be (1) the adjustment of the volume of the solution, (2) the order of mixing the reagents, (3) the temperature at which the precipitation is carried out, (4) the rate of addition of the precipitant, (5) the stirring of the solution, (6) the time allowed before filtering the precipitate, and (7) the selection of a suitable medium for the precipitation.

4. *Reprecipitation.* As a last resort, it is often necessary to dissolve the precipitate and to repeat the precipitation. Since in the second solution the concentration of the coprecipitated substance is relatively small, the coprecipitation is correspondingly decreased. It is obvious that a single reprecipitation is effective only when a small proportion of the absorbed substance is carried out in the first precipitation.

III. Factors Affecting the Composition and Stability of the Weighed Precipitate

In order to effect a gravimetric determination, it is necessary, after filtering and washing the precipitate, that it be (1) completely dried, (2) of definite composition, and (3) sufficiently stable to be precisely weighed.

Assuming that volatile contaminants are not present (usually as coprecipitated material), precipitates can be divided into two types, as follows:

(1) Those which are weighed in the same form as they were filtered.

(2) Those which have to be converted into a more stable and uniform compound before they can be weighed.

With precipitates of the first type it is necessary only to remove the superficial water (adsorbed or entrained) or other solvent medium. Examples of such precipitates are silver chloride, bromide, iodide, or thiocyanate, lead sulfate, barium sulfate, bismuth oxychloride, and nickel dimethylglyoxime. With such precipitates the drying can usually be accomplished by heating at a relatively low temperature, in some cases as low as 110°C. In certain cases where the water may be more firmly held, or where a high order of precision is desired —as in atomic-weight determinations—higher temperatures must be used; for example, in order to remove the last traces of moisture (usually less than 0.01 per cent) from a silver chloride precipitate, it must be heated until fused. If the precipitate has been collected on a paper filter, the necessity of completely burning the paper will often require a much higher temperature than is necessary to dry the precipitate within the usual analytical limits; for this reason, and because of the danger of reduction reactions occurring in the burn-

ing process, filtering crucibles are advantageously used for such precipitates.

The possibility of drying precipitates of this first type by treating them with some volatile solvent which has a great tendency to take up water, such as ethyl alcohol or a combination of alcohol and ether, and then removing this solvent by placing the crucible and precipitate in a desiccator and evacuating for a short time offers certain possibilities. A considerable saving of time is effected, since the whole process is carried out at room temperature and the crucible can be weighed without having to wait the 20 to 30 minutes necessary for it to cool to room temperature. Also, certain precipitates can be dried by this process which are unstable if dried by heat. Thus it has been found that magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$) can be dried in this manner.[20] More recently, the use of alcohol and ether followed by the aspiration of air through the precipitate or a brief treatment in a vacuum desiccator has been proposed by Dick[21] for the rapid drying of quite a number of precipitates. The accuracy of the method has been questioned[22] and confirmed by others.[23] Experiments[24] have indicated that when using sintered-glass filtering crucibles certain precipitates can be effectively dried by the process, but that the use of ether following the alcohol is not only unnecessary but in certain cases objectionable, since its rapid evaporation tends to cool the crucible until moisture condenses on it. Confirmatory determinations,[25] the results of which are shown in Table V, show that by sucking the wash water from the precipitate, washing it with first 95 per cent and then 99.5 per cent ethyl alcohol, aspirating the alcohol, and finally placing the crucible in a vacuum desiccator and evacuating it with an efficient water aspirator for 5 minutes (essentially the method used in Optional Procedure *D* given below) silver chloride, lead sulfate, and bismuthyl chloride precipitates can be so effectively dried that results agreeing surprisingly well with those resulting from conventional methods of drying can be obtained.

Use of the alcohol method with students for the gravimetric standardization of hydrochloric acid solutions has shown that, unless

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[20] Fales, *Inorganic Quantitative Analysis*, p. 222, Century, 1925; Worsham, Thesis, Columbia University, 1923.

[21] Dick, *Z. anal. Chem.*, **77**, 352-363 (1929); **78**, 414 (1929); **83**, 105 (1931).

[22] Moser and Von Zombory, *Z. anal. Chem.*, **81**, 95 (1930).

[23] Wassiljew and Sinkowskaja, *ibid.*, **89**, 262 (1932).

[24] Unpublished experiments by K. Watanabe and D. DeVault.

[25] Unpublished experiments by R. C. Custer.

TABLE V

A Comparison of the Use of Alcohol and of Heat for the Drying of Certain Precipitates

In carrying out these experiments, a definite volume of a solution of the element being determined was pipeted and the precipitation and washing of the precipitate carried out in the conventional manner. The crucibles, either sintered glass or Gooch-type asbestos, were prepared and dried by the alcohol method outlined above and then weighed. The crucible was then heated (at 150° to 200° when used for silver chloride and bismuthyl chloride precipitates and at 400° to 500° when used for the lead sulfate) and again weighed. The precipitate was then collected in the crucible, washed, treated by the alcohol method, and weighed. It was then heated to the temperature stated and again weighed. The weights obtained by the "alcohol method" for the empty crucible, for the crucible and precipitate, and for the precipitate are shown in Columns V, VI, and VII following the designation "alcohol" in Column IV; the weights obtained after drying by heat for the same crucible, for the crucible and precipitate, and for the precipitate are shown directly below and following the designation "heat" in Column IV.

I	II	III	IV	V	VI	VII
				Weight Found		
Exp. No.	Type Crucible	Precipitate	Drying Agent	Crucible	Crucible and Precipitate	Precipitate
1	Glass	AgCl	Alcohol	26.9606	27.2925	0.3319
			Heat	26.9606	27.2925	0.3319
2	Glass	AgCl	Alcohol	24.5138[a]	24.8440	0.3302
			Heat	24.5138	24.8440	0.3302
3	Asbestos	AgCl	Alcohol	16.2366	16.5678	0.3312
			Heat	16.2366	16.5677	0.3311
4	Asbestos	AgCl	Alcohol	15.1706	15.5017	0.3311
			Heat	15.1706	15.5017	0.3311
5	Glass	$PbSO_4$	Alcohol	26.9602	27.3263	0.3661
			Heat	26.9600	27.3257	0.3657
6	Glass	$PbSO_4$	Alcohol	24.5091	24.8752	0.3661
			Heat	24.5089	24.8747	0.3658
7	Asbestos	$PbSO_4$	Alcohol	16.3679	16.7329	0.3650
			Heat	16.3671	16.7324	0.3653
8	Asbestos	$PbSO_4$	Alcohol	15.2093	15.5749	0.3656
			Heat	15.2091	15.5746	0.3655
9	Glass	BiOCl	Alcohol	26.9605	27.2493	0.2888
			Heat	26.9599	27.2487	0.2888
10	Glass	BiOCl	Alcohol	24.5085	24.7958	0.2873
			Heat	24.5082	24.7951	0.2869
11	Asbestos	BiOCl	Alcohol	15.2893	15.5765	0.2872
			Heat	15.2889	15.5758	0.2869
12	Asbestos	BiOCl	Alcohol	14.7413	15.0290	0.2877
			Heat	14.7411	15.0287	0.2876

[a] On cleaning and weighing the crucible for subsequent determinations, a loss in weight of 0.0047 g was noted. It has been noted that an occasional glass crucible will show an erratic loss in weight from time to time, suggesting that the mat had not been perfectly sintered together.

a very thin mat of asbestos is used, complete drying is frequently not obtained unless the precipitate and crucible are repeatedly evacuated; therefore, the method may lose much of its rapidity unless used with a fabricated filtering crucible. Because of the quickness with which this method of drying certain precipitates can be carried out when used with sintered-glass crucibles, an optional procedure providing for its use is given below.

Precipitates of the second type can be divided into two different sub-groups. In drying those of the first sub-group a relatively high temperature is necessary because there has to be a complete elimination of what may be called water of constitution. This group includes the hydrous oxides (ferric and aluminum hydroxides, and silicic and "metastannic" acid are examples), which are of very uncertain composition and which have to be converted to the oxides before a stable compound of definite composition is obtained. The second sub-group of precipitates is composed of those which may be partly decomposed upon drying by heat, and therefore it is necessary to convert them into a compound of more uniform and stable composition before they can be weighed. Examples are magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$), which is converted by heat to magnesium pyrophosphate ($Mg_2P_2O_7$), and calcium oxalate ($CaC_2O_4 \cdot H_2O$), which is weighed as either the carbonate or the oxide.

The treatment of these precipitates will vary greatly; thus in order to convert calcium oxalate to calcium carbonate the temperature must be controlled between 475° and 525°C.,[26] or if the ignition is carried out in an atmosphere of carbon dioxide, the temperature can be raised to 700°C.[27] The complete dehydration of aluminum hydroxide or of silicic acid requires heating above 1000°C. for some time.

It should be emphasized that certain precipitates which are weighed in the same form as they separate are heated at higher temperatures because of the presence of coprecipitated compounds; thus barium sulfate, which can be dried at a relatively low temperature, is usually heated to approximately 900° in order to reduce the error caused by coprecipitated material. In Table VI are shown some of the precipitates most frequently used in gravimetric analysis, the form in which they are weighed, and the temperatures to which they are usually heated.

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[26] Willard and Boldyreff, *J. Am. Chem. Soc.*, **52**, 1888 (1930).
[27] Foote and Bradley, *J. Am. Chem. Soc.*, **48**, 676 (1926).

TABLE VI

PRECIPITATES FREQUENTLY USED IN GRAVIMETRIC ANALYSIS

Compound Precipitated	Compound Weighed	Temperature Used (°C.)	Remarks
$AgCl$	$AgCl$	130 to 150	Estimation of Ag or Cl.
$PbSO_4$	$PbSO_4$	500 to 600	Precipitate washed with dilute H_2SO_4.
$BiPO_4$	$BiPO_4$	200 to 300	Decomposes above 650°.
$BiOCl$	$BiOCl$	105 to 110	
CdS	$CdSO_4$	450 to 500	CdS treated with H_2SO_4
HgS	HgS	105 to 110	
Hg_2Cl_2	Hg_2Cl_2	105 to 110	
As_2S_3	As_2S_3	105 to 110	
$MgNH_4AsO_4 \cdot 6H_2O$	$Mg_2As_2O_7$	850 to 950	Estimation of As or Mg.
Sb_2S_3	Sb_2S_3	280 to 300	
$SnO_2(H_2O)_x$	SnO_2	1100 to 1200	
$Fe_2O_3(H_2O)_x$	Fe_2O_3	1000 to 1100	In oxidizing atmosphere.
$ZnNH_4PO_4 \cdot 6H_2O$	$ZnNH_4PO_4$	110 to 135	
	$Zn_2P_2O_7$	850 to 950	
ZnS	$ZnSO_4$	450 to 500	ZnS treated with H_2SO_4,
	ZnO	850 to 950	decomposes above 700°.
$NiC_8H_{14}N_4O_4$	$NiC_8H_{14}N_4O_4$	110 to 120	
CoS	$CoSO_4$	450 to 500	CoS treated with H_2SO_4.
MnS	$MnSO_4$	450 to 500	May decompose above 550°.
$MnNH_4PO_4 \cdot H_2O$	$Mn_2P_2O_7$	850 to 950	
$Al_2O_3(H_2O)_x$	Al_2O_3	1050 to 1200	
$BaSO_4$	$BaSO_4$	350 to 900	For Ba or S.
$SrSO_4$	$SrSO_4$	450 to 500	
$CaC_2O_4 \cdot H_2O$	$CaCO_3$	475 to 525	
	CaO	1200	
$MgNH_4PO_4 \cdot 6H_2O$	$Mg_2P_2O_7$	1000 to 1100	For Mg or P.
$KClO_4$	$KClO_4$	350	
$NaCl$	$NaCl$	600	
$SiO_2(H_2O)_x$	SiO_2	1200	

THE OPERATIONS OF GRAVIMETRIC ANALYSIS

The Filtering of Precipitates

The operation of filtering has for its object the separation of the precipitate from the solution in which it has been formed. This is accomplished by passing the solution through some porous medium which will be capable of passing the solvent and the constituents which are in true solution, but which will retain even very finely divided precipitates—down to those having diameters of approximately 1 to 2μ (1μ, called *one micron*, is 0.001 millimeter). With particles of less than 0.2 to 0.5μ colloidal properties become evident,

and although it is possible to devise filtering media which will retain even colloidal suspensions, special apparatus is required, and the rate of filtration is so slow that it is not practical for analytical purposes to try to retain particles of less than approximately 1μ. Certain restrictions are imposed upon the material used for a filtering medium. (1) It must be relatively inert to the various solvents and solutions to be filtered. This implies that it must not be weakened or disintegrated during the filtering process, and that it must not introduce any contamination into the solutions passed through it. (2) It must not retain, either by adsorption or by absorption the soluble constituents of the solution. (3) For quantitative purposes (where the precipitate is to be subsequently weighed) it must either remain constant in its weight or be capable of complete removal—for example, by being burnt or volatilized. The various media most commonly used in analytical processes are discussed below.

Filtering media. The filtering media which are most extensively used in analytical work are paper, asbestos, glass, quartz, porcelain, and platinum. The relative advantages of these different agents are discussed below.

Paper filters. The medium used almost exclusively for qualitative work and still used most frequently for quantitative purposes is pure cellulose paper. Paper filters have several disadvantages: (1) They are not inert, being attacked by concentrated solutions of both alkalies and acids, and by powerful oxidizing agents; (2) they are lacking in mechanical strength, are not readily adapted to vacuum filtration, and often disintegrate, introducing fibers into otherwise clear solutions; (3) they have the property of adsorbing constituents from the solutions passed through them; and (4) they cannot be dried to a constant weight for precise quantitative work. Their chief advantages lie in their cheapness, availability, and superior filtering efficiency, especially in the filtration of gelatinous precipitates. This advantage over other filtering media is in part due to the larger surface exposed and a larger ratio of pore space to total surface. Paper filters are obtainable in various degrees of porosity, those of more open texture being suited for the rapid filtration of easily retained precipitates and the more dense ones being adapted for finer precipitates; the finer filters will retain particles of approximately 2μ in diameter, and the coarser ones will retain particles of about 6μ in diameter.

When used for gravimetric work, paper filters have a serious disadvantage in that they cannot be dried to constant weight and

therefore have to be ignited or burnt before the precipitate can be weighed. This process is often unsatisfactory for the following reasons: (1) It may require a higher temperature than is necessary to dry the precipitate and one at which the precipitate may be unstable. (2) Many precipitates (for example, the silver halides and barium sulfate) are appreciably reduced during the burning of the paper and have to be subsequently treated to correct this reduction. Where this reduction is serious, it is necessary to remove most of the precipitate from the paper and burn it separately, a process which invites mechanical loss. (3) There always remains after burning the paper a nonvolatile residue, or ash.

Quantitative (ashless) paper filters. In order to reduce this error, paper filters which are intended for quantitative work are washed in the process of manufacture with hydrochloric and hydrofluoric acids to remove as completely as possible the nonvolatile inorganic salts and the silicon compounds. This process increases the cost of these filters but reduces the weight of the ash to a very low value. The average weight of this ash in various types of filters is shown in Table VII.

TABLE VII

THE WEIGHT OF THE ASH OF VARIOUS TYPES OF FILTERS

Diameter of Filter (cm)	Qualitative (mg)	Quantitative (mg)
7	0.2 to 0.9	0.02 to 0.05
9	0.4 to 1.3	0.03 to 0.08
11	0.6 to 3.3	0.05 to 0.11

It is seen that the ash of the quantitative filters has been reduced to such a small value that it can be precisely corrected for or even neglected in most routine work. Because of the development of several types of satisfactory filtering crucibles, the use of filter papers is no longer recommended for precipitates which can be dried at low temperatures (100° to 500°C.) or which have to be separated from the filter before the paper is burned.

Asbestos filters. For quantitative work asbestos is almost universally used in porcelain crucibles with perforated bottoms (so-called Gooch crucibles), although the form originated by Gooch[28] was of platinum (see Fig. 22). When used for qualitative work,

[28] Gooch, *Proc. Amer. Acad.*, **13**, 342 (1878).

asbestos filters can be made upon circular bevel-edged perforated porcelain plates or upon a wad of glass wool supported in an ordinary funnel (see Fig. 23). Asbestos is a calcium-magnesium silicate, and that used for quantitative purposes should be of a white, silky, long-fibered variety, free from magnetite and iron. It has been found that even the asbestos purchased and designated specifically "for quantitative analysis" should be acid-treated and washed before being used. Asbestos can be safely heated to moderately high temperatures and, when used for gravimetric work, Gooch crucibles (and other filtering crucibles) have the great advantage over paper that they can be dried to constant weight, and the disadvantages connected with the burning of a paper filter are eliminated. Asbestos filters are intended for use with suction. With coarse crystalline precipitates and with a thin properly made mat, they afford a more rapid filtration than paper, although asbestos (and other filtering media such as glass and porcelain) is not as satisfactory as paper for gelatinous precipitates, since these tend to clog the relatively small filtering surface. Asbestos is not so satisfactory for precipitates which have to be heated to very high temperatures, since some specimens tend to lose weight, and the asbestos insulates the precipitate from the heat of the burner; the perforated porcelain crucibles are also subject to cracking at high temperatures unless used with extreme care. Asbestos filters (and filtering crucibles in general) should be heated to a constant weight at the temperature subsequently to be used for drying the precipitate. They possess the disadvantage that they require more time in their preparation than a paper filter; also, some asbestos tends to absorb water so rapidly as to cause difficulty in weighing.

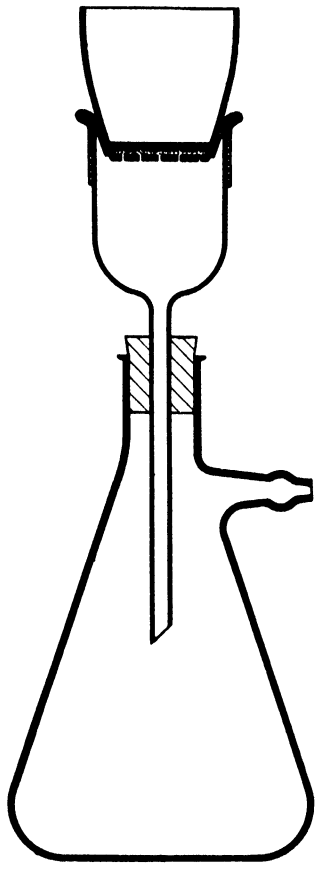

Fig. 22. Asbestos Filter in Gooch Crucible with Holder for Quantitative Work.

Filtering crucibles. Filtering crucibles of various materials are

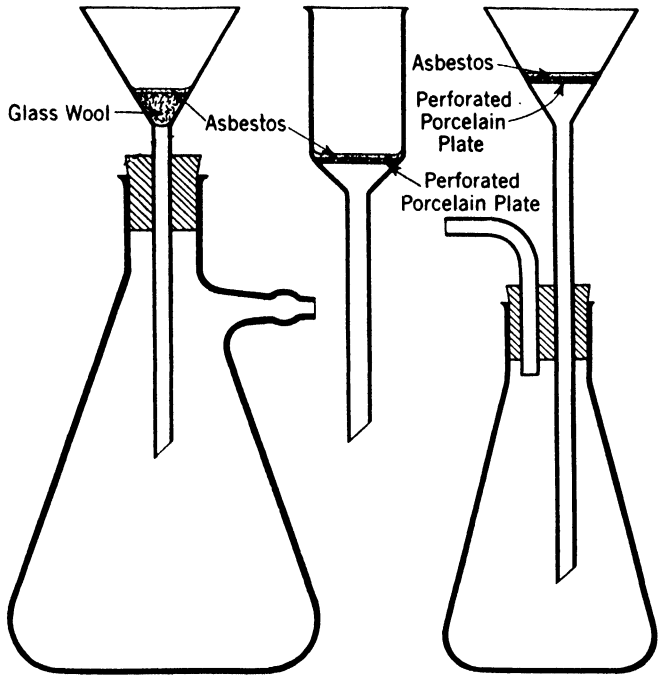

Fig. 23. Asbestos Filters for Qualitative Work. Suction Flasks.

now offered which have a filtering element of the same material fabricated in place as an integral part of the crucible; among the materials so used are glass, quartz, porcelain, and platinum. Such crucibles possess the advantage over paper (as does the Gooch-type asbestos filter) that they can be dried to constant weight. They possess the advantages over the asbestos filter that they are ready for immediate use, that the filtering elements can be obtained with various pore sizes, that they are more quickly brought to a constant weight, and that they are less hygroscopic thereafter. They possess the disadvantage that special methods are necessary in order to clean the precipitate from them. The characteristics of these crucibles are discussed briefly below.

Sintered-glass crucibles.[29] The filtering element in the bottom of these crucibles is composed of glass particles which have been powdered and graded as to size, and then sintered together (in place) to form a filtering crucible of the desired porosity (see Fig. 24). They possess the advantage of being transparent, of quickly coming to constant weight, and of being easy to clean. With care in heating

[29] At the present time these crucibles seem to be made only of Jena glass by Schott and Gen. of Jena.

and cooling, they can be used up to 600°C. They can be used with strong acids (except hydrofluoric) and with moderately concentrated bases. A tendency of some of these crucibles to lose weight after being heated much above 150°C. has been noted; otherwise they are excellent.

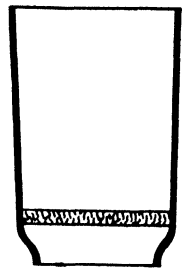

Fig. 24. Sintered-Glass Filtering Crucible.

Sintered-quartz crucibles. These crucibles are similar to the glass crucibles but are constructed of clear quartz and possess the advantage that they can be used for temperatures up to 1200°C. They are expensive.

Porous porcelain crucibles. These crucibles are similar to sintered-glass crucibles, but are constructed of porcelain and have a porous porcelain filtering element in the bottom. They can be obtained in any desired porosity, and can be heated up to 1000° to 1200°C.

Platinum filtering crucibles (Munroe type). These crucibles, proposed by both Munroe[30] and Neubauer,[31] are similar in design to a Gooch crucible except that they are constructed of platinum and the filtering element is a porous layer of platinum; this is prepared by building up a layer of ammonium chloroplatinate of the desired thickness and then igniting. These crucibles have many advantages. They can be made to retain fine precipitates, yet filter rapidly; they quickly attain constant weight and can be heated to high temperatures, and because of their superior heat conductivity, precipitates in them are not insulated as they are by asbestos mats. They are usually formed with a cap which fits over the bottom and protects the precipitate from possible action of gases from burners. They are expensive, however, and the mats have to be frequently renewed, especially when used at high temperatures. They are recommended for use in highly precise work. The following references are valuable for details of the preparation, use, and cleaning of these crucibles:

Snelling, *Chem. News*, **99**, 229 (1909); *J. Am. Chem. Soc.*, **31**, 456 (1909); Swett, *ibid.*, **31**, 928 (1909).

The Washing of Precipitates

In washing a precipitate, the first consideration is the selection of the most effective washing medium. It is not often that this will be pure water. In making this selection, the following factors have

[30] Munroe, *J. Anal. App. Chem.*, **2**, 241 (1888); *Chem. News*, **38**, 101 (1888).
[31] Neubauer, *Z. anal. Chem.*, **39**, 501 (1900).

to be considered: (1) the solubility of the precipitate, (2) the stability of the precipitate, (3) the nature of the material to be washed out, (4) the tendency of the precipitate to become colloidal, and (5) the effect of the wash solution or its constituents on the drying and heating of the precipitate.

If the precipitate is appreciably soluble, it will be necessary to reduce its solubility in the wash medium. This is often accomplished by (1) the addition of a common ion; (2) the use of some special solution, an example being the washing of an magnesium ammonium arsenate precipitate (P. 88) with dilute ammonium hydroxide; (3) the addition of organic liquids (frequently alcohol); and (4) the use of cold wash solutions (especially where the solubility of the salt has a high temperature coefficient).

Certain precipitates may undergo changes if washed with water; thus bismuth phosphate may be partly converted into a basic salt. Other precipitates, certain sulfides for example, may be partly oxidized unless the wash solution is freed of oxygen, or an inhibiting substance (such as hydrogen sulfide) is present.

It is essential that the nature of the ions and compounds in the filtrate be considered in selecting the wash medium. This is especially important in separations, for, if the precipitation has taken place in a strongly acid solution and the precipitate were washed with water, some of the constituents of the filtrate may be partly precipitated. Thus, arsenic can be separated from antimony by precipitation as sulfide from a 9 f. hydrochloric acid solution, but if the solution adhering to the precipitate were diluted by addition of wash water, precipitation of antimony sulfide would be likely to result.

The method of washing will be determined by the nature of the precipitate and the method of filtering. The advantages of decantation apply to the washing as well as the filtering process; settling the precipitate by centrifuging will often facilitate a decantation process. The type of filter used and the nature of the precipitate will indicate whether suction can be used to advantage.

In washing a precipitate, it is usually desirable, because of solubility effects and to prevent unduly diluting the filtrate, to use the smallest possible volume of wash solution. For these reasons it is usually more effective to wash with repeated small portions of wash solution than with a smaller number of larger portions. This can be shown by an application of the expression

$$C_n = \left(\frac{V_r}{V + V_r}\right)^n C_0,$$

where C_0 is the original concentration of any material in the solution left with a precipitate, C_n the concentration after n washings, V the volume of wash solution added, and V_r the volume of solution left after each washing. Thus if a precipitate weighing 0.2 g has left with it and the filter 0.5 ml of solution and 0.1 g of contaminating material, and is washed with 20 ml of water, added in one case in 10-ml portions and the other in 5-ml portions, it is seen that in the first case there will be left 2.3×10^{-4} g of material and in the second only 6.8×10^{-6} g, these corresponding to an error of 0.1 per cent and 0.004 per cent respectively.

These calculations indicate that precipitates can be washed with relatively small volumes of water; however, the assumption has been made *that the foreign material has been merely held in the solution remaining on the precipitate and filter and that it has been uniformly distributed through each portion of wash water.* In many cases, especially when dealing with bulky precipitates, it may be difficult to get the wash water into effective contact with all portions of the mass, and, more important yet, *the foreign material is likely to be adsorbed on the precipitate.* Because of this latter effect, calculations such as the above are likely to be extremely misleading, and *the only safe way to determine when a precipitate has been washed is by making suitable tests on the wash solution.*

Procedure XVIII: THE GRAVIMETRIC STANDARDIZATION OF A HYDROCHLORIC ACID SOLUTION. In the procedures below the hydrochloric acid solution is standardized by precipitating and weighing the chloride as silver chloride. The discussion of the general principles and operations of gravimetric analysis just preceding should be read and understood before carrying out these procedures.

The procedures below provide for the use of various filtering media and for the optional use of alcohol as a drying agent when using a sintered-glass or other fabricated filtering crucible.

Precipitation of the silver chloride. Pipet a 25-ml portion of the solution to be standardized into a 400-ml beaker (Notes 1, 2) and add approximately 150 ml of water. Add dropwise the calculated volume of a 0.2 n. $AgNO_3$ solution (Note 3), stirring the mixture vigorously (do not spatter or splash it) during the addition, and then add 5 ml in excess (Notes 4, 5, 6). Do not carry out this precipitation or the subsequent operations in sunlight or very intense artificial illumination. Heat the mixture to approximately 60°C. and stir

it frequently until the precipitate settles rapidly, leaving a clear solution (Note 7). Keep the beaker covered when not stirring the solution.

Filtering and washing the precipitate. Optional method A. Using a Gooch-type filtering crucible (a perforated porcelain crucible with asbestos filtering mat). *Preparation of the crucible.* Select a crucible of the proper size (for this precipitate one of about 20 to 30 ml capacity), clean it thoroughly, and fit it into a filter crucible holder (be sure that the rubber does not extend beyond the bottom of the crucible so that the filtrate comes in contact with it). Fit the stem of the crucible holder or of the funnel in a one-hole rubber stopper and support it in a suction filter flask of the type shown in Fig.22 (Note 8). Shake up a water suspension of acid-washed chloride-free asbestos (Note 9) and pour it through the crucible (with the suction turned off) until a uniform mat of asbestos of about 1 to 2 mm thickness is obtained(Note 10.) Place a perforated porcelain plate on the mat and, applying very gentle suction, pour into the crucible just enough of the asbestos suspension to fill around the edges and the perforations of this plate (Note 11). Wash the mat until the water passing through is free of asbestos fibers. (Carefully guide the first portion of water onto the plate with a stirring rod so that the mat is not disturbed, and thereafter do not allow one portion to run out entirely, thus exposing the mat, before adding the next.) Place the crucible in a small beaker, cover it with a glass and place it in an oven at 110° to 120°C. for 1 hour (Note 12). Place the crucible in a desiccator (see Note 2, P. V), allow it to cool for 20 to 30 minutes, and weigh it. Again heat the crucible for 20 minutes, cool, and weigh. Repeat this process until the weight remains constant within 0.2 mg (Note 13).

Filtering and washing the precipitate. Insert the crucible in the holder and, applying a very slight suction (Note 11), decant the clear solution through the filter (Note 14). Carefully guide the first portion of the solution onto the plate with a stirring rod, and thereafter do not allow the crucible to become empty (Note 15). Note carefully if any asbestos fibers appear in the first portions of the filtrate; in this case it must be refiltered (Notes 16, 17). Prepare a wash solution by adding 5 ml of 6 n. HNO_3 to 500 ml of

water and put this in a small wash bottle. (Label this "special wash bottle.") Wash the precipitate by decantation with three 25-ml portions of this wash solution, transfer it to the crucible (Note 18), and wash with the dilute acid until 2 to 3 ml of the washings give no precipitate upon the addition of a single drop of HCl (Note 19). Finally, wash with 5 ml of water, added dropwise.

Drying the precipitate. Place the crucible in a covered beaker and heat it at 120°C. for 1 hour (Note 20). Cool the crucible for 30 minutes in a desiccator and weigh. Repeat the heating and weighing until the weight is constant to 0.2 mg. Calculate the normality of the hydrochloric acid solution.

Notes:

1. The concentration of the HCl will determine the volume to be taken. If less than 25 ml are pipeted, the precision of that measurement is not sufficient for a standardization; it is also desirable that the weight of the silver chloride precipitate be not less than 0.3 g (to reduce the weighing error) and not larger than 1 g (to avoid difficulty in the filtering and washing of the precipitate). Duplicate (for very precise work, triplicate) determinations should be made.

2. The above procedure can be applied to the determination of the chloride in soluble salts. In that case weigh out an amount of the sample which contains from 0.15 to 0.25 g of chloride, and dissolve this in 150 ml of water to which has been added 0.25 ml of 6 n. HNO_3. If bases or the salts of weak acids are present, the solution should be first neutralized and the excess of acid indicated above added.

3. The calculated volume of the $AgNO_3$ may be measured in a graduate and added from a dropper, or it may be added from a graduated pipet or buret. In order to avoid splashing, the solution should be delivered very close to the surface of the solution or flowed down the side of the beaker.

4. Stirring rods used for this purpose should have their ends fire-polished and should not be rubbed against the walls of the vessel; otherwise small particles of glass may be chipped off or the inside of the vessel scratched; precipitates form in such cracks and are difficult to remove.

5. Except when standardizing a solution whose concentration is already closely known, the amount of silver nitrate to be added cannot be previously calculated. In such cases the equivalent amount can be determined by noting when no more precipitation takes place upon adding a portion of the reagent. This is done by adding the $AgNO_3$ in successively smaller portions as the rate of precipitation is seen to be decreasing, until finally the effect of a few drops is noted. As the equivalence-point is approached, the mixture must be shaken vigorously after each addition of $AgNO_3$ and the precipitate allowed to settle so that the effect of the next portion can be observed in the supernatant liquid. Usually the precipitate will remain

colloidally dispersed until near the equivalence-point, when a distinct coagulation will be observed. See P. 22 and P. 27 for discussions of the application of this method of determining the "end-point" to the quantitative estimations of silver and of chloride. After the equivalent amount of silver nitrate required has been noted, the 5-ml excess is added.

6. Vigorous shaking is very effective in coagulating a silver chloride precipitate. For this reason a conical flask with a ground-glass stopper can be used advantageously in this procedure, as the stopper can be inserted after each addition of reagent and the flask shaken vigorously. If, before removing the stopper, a few drops of water are poured around it, this water will be drawn into the flask as the stopper is withdrawn and will effectively wash down any precipitate adhering to the stopper or the neck of the flask.

Do not heat these flasks or allow them to cool with the stopper in place; it is not advisable, nor should it be necessary, to use vaseline or other lubricants on the ground-glass joint.

7. It is a general rule that a test should be made to ascertain if sufficient of the precipitating reagent has been used by adding a small additional amount to the clear supernatant liquid, or to the first portion of the filtrate coming through the filter, and then, after allowing sufficient time, to note if any additional precipitate forms.

8. Suction flasks are conical flasks made with a side-neck and with thick walls to withstand the external pressure when a vacuum is produced. It is unsafe to heat solutions in them.

When a water aspirator is used for suction, the possibility of contamination of the filtrate by tap water being sucked back into the filter flask should be prevented. This is done by fitting a conical flask with a two-hole stopper carrying an inlet and outlet tube and then connecting the inlet tube to the filter flask and the outlet tube to the aspirator; such an arrangement also safeguards against solution in the filter flask overflowing into a vacuum system.

9. It has been found that even the asbestos purchased and designated specifically for "quantitative analysis" should be further acid-washed and treated before being used (see the Appendix). When asbestos is used for a chloride or silver determination, the analyst should assure himself that it is chloride-free.

10. The thickness of mat to be used will vary with the type of precipitate to be retained. With a silver chloride precipitate that has been properly coagulated, a thin, moderately fast filtering mat may be used. When looking at the light through such a mat, the perforations of the crucible should be dimly visible; by such an inspection imperfections in the mat may often be detected. If the holes are not discernible, or if, after applying the top plate with its film of asbestos, water runs through the filter slowly with full suction applied, the mat had better be remade. The thinner the mat (which will retain the precipitate) the more rapid the filtration and washing of the precipitate, and the more quickly the crucible can be dried and brought to constant weight.

11. This plate (the so-called Witte plate) and the additional asbestos serve to prevent the disruption of the mat, and not as an aid to filtering. If care is taken when pouring solutions upon the mat, the plate may be dis-

pensed with and more rapid filtering obtained. When adding a solution to the empty crucible, a slight suction should always be applied, and the solution should be guided with a stirring rod held against the plate, or, if the plate is not used, with the stirring rod held just above the mat. Too strong suction should be avoided, since it may break the mat and in many cases will so pack the precipitate against the mat as to clog it and slow the rate of flow.

12. After being cleaned, and especially when hot, crucibles should not be placed directly on the floor or shelves of ovens, or on desk tops and such surfaces; materials thus picked up may contaminate the analysis or change the weight of the crucible. For the same reason, crucibles should be handled with a clean pair of crucible tongs and as little as possible with the hands.

The beaker containing the crucible should be covered to prevent particles of dust, rust, and so forth, from falling into the crucible. More rapid drying will be obtained if the cover glass is supported by a glass triangle, or on three small lengths of glass rod which have been bent into the shape, ∩, and hung over the side of the beaker.

To prevent confusion when running duplicate analyses, crucibles should be marked before being used, either by filing notches on the edges or, preferably, by means of a "china-marking" pencil. The pigment of these has an inorganic base, usually iron, and, if the crucible is lightly marked and then heated, this residue fuses into the surface. The beaker itself should be marked on the roughened place provided for that purpose. (See Note 6, P. V.)

13. As a general rule when a crucible is being prepared, it should be treated with the same wash solution and heated to the same temperature as is to be subsequently used with the precipitate.

14. As a general rule, precipitates should be coagulated and then allowed to settle before beginning the filtration. Then as much as possible of the clear solution should be decanted through the filter, care being taken not to stir up the precipitate. In this manner it is frequently possible not only to filter a mixture completely, but also to wash the precipitate without removing it from the precipitating vessel. This is termed *filtering by decantation* and should be practiced whenever the nature of the precipitate permits, since it is a more rapid and efficient process. This is due to the fact that, since the precipitate usually partly clogs the filter, making the filtration much slower, it can be much more thoroughly treated with the wash solution in the beaker than on the filter.

After adding a portion of wash solution and thoroughly mixing it with the precipitate, it is an advantage to allow the vessel to stand in an inclined position. The precipitate then tends to settle compactly into the space at the juncture of the bottom and side of the vessel and is less likely to be stirred up when the vessel is further tilted to pour out the clear solution.

15. Whenever a solution is poured from one vessel to another or to a filter, the liquid should be guided by means of a stirring rod placed against the lip of the vessel. This not only prevents splashing of the solution on the filter or in the receiving vessel, but prevents the solution from running down the under side of the lip of the vessel from which it is poured. With some vessels the lip is so constructed that this may take place even with the use

of a stirring rod; in such cases rub the under side of the lip with the thinnest possible film of vaseline or other grease.

16. Having successfully filtered a precipitate from the solution in which it was formed, it is usually an advisable precaution to remove this solution from the receiving flask before beginning the washing process. Many precipitates that filter perfectly from their original solution tend to become colloidal (or, as it is termed, to "peptize") and pass through the filter when treated with a wash solution; should this occur, or should a break subsequently occur in the filter, much less solution will have to be refiltered.

17. The original filtrate and the first portion of wash water should be treated with a slight excess of hydrochloric acid, the precipitate allowed to settle, the solution decanted away, and the residue transferred to the "silver residue" container. After this procedure is finished, the weighed silver chloride precipitates should also be added to the same container for later recovery.

18. When transferring a precipitate from a vessel, extreme care should be taken that none is lost by spattering. Suspend the precipitate in a small amount of the wash solution and slowly drain it from the beaker into the crucible, using the stirring rod to guide it to the bottom of the crucible. While holding the inclined beaker with the stirring rod held against the lip in one hand, direct a gentle stream of the wash solution (contained in a small wash bottle) against the bottom and sides of the beaker until all of the precipitate has been washed out. If the precipitate sticks to the sides of the beaker (and as a general precaution), gently rub the entire inner surface of the beaker with a "policeman," a stirring rod capped at one end with a short piece of soft gum rubber tubing specially made for the purpose by being sealed at one end. ("Policemen" should not be used as stirring rods, since they are attacked by some solutions, may disintegrate, or may be hard to clean if left in the solution when the precipitation takes place.)

If difficulty is experienced in removing the precipitate from the sides of the vessel (or the "policemen"), it may be dissolved by adding about 10 drops of ammonia to 2 to 3 ml of water and flowing this solution over the surfaces to be cleaned. This solution should then be made just acid with HNO_3, a drop of the silver nitrate solution added, the solution diluted to about 10 ml, and the precipitate coagulated by shaking or heating and then collected on the filter and washed with the remainder of the precipitate.

19. It is impossible to calculate or state how much wash water will be required for a given precipitate, since the physical nature of the same compound will vary enormously with the conditions of precipitation, as well as with the nature of the other ions present in the solution. Therefore, it should be an invariable rule to continue the washing until some substance known to be present in appreciable amounts in the original filtrate, and for which a sensitive test can be made, is shown to be absent from the wash solution.

When washing a precipitate, the original solution and each successive portion of wash water should be allowed to drain from the filter before the next portion is added. It has been shown in the discussion that the amount of wash solution required will be determined largely by the volume of solution left each time with the precipitate and filter, and also that it is more effective to wash with several small portions than with one large portion of the same total volume. However, a precipitate should never be allowed

to dry or cake and crack before and during the washing; when using an asbestos filter, it is also desirable that sufficient solution be left in the crucible to protect the mat when another portion is added.

20. If an oven or electric furnace is available in which the temperature can be controlled between 150° and 200°C., the precipitate can be first dried for 20 minutes at 110°C. and then for the same length of time at the higher temperature. The precipitate should be gradually heated at first, or it tends to "cake" and enclose the water, so that a fusion is necessary thereafter to complete its expulsion. If the precipitate is heated to this higher temperature the crucible should be similarly treated before the initial weighing.

Optional method B. Using a sintered-glass, porous porcelain, or platinum-sponge filtering crucible. Since the filtering element has been fabricated in place, these crucibles are ready for use as soon as they are cleaned (Note 1). The precipitation of the silver chloride, the preliminary heating of the crucible, the filtration, the washing, and the final heating of the crucible and precipitate are carried out as directed above.

Note:

1. Sintered-glass and porcelain crucibles may be cleaned by the use of any acid cleaning solution except HF; prolonged treatment with concentrated alkalis is not advisable, although ammonia and cyanide solutions can be used. The proper solution to use will be determined by the substances it is desired to remove from the crucible. The solvents mentioned below are applicable.

Platinum ware should not be treated with an acid solution containing an oxidizing agent and a chloride, bromide, or iodide; even ferric chloride will attack platinum. Swett, *J. Am. Chem. Soc.*, **31,** 932 (1909), has made an extended study of the various solvents which may be used with platinum crucibles and which are most effective in dissolving the precipitates commonly used in gravimetric analysis. Those most generally effective include (1) sulfuric acid with either nitric acid or with ammonium chloride added, (2) nitric acid, (3) hydrochloric acid with ammonium chloride or oxalic acid added, (4) sodium hydroxide, (5) sodium sulfide, (6) ammonium hydroxide, and (7) sodium cyanide. The original article should be consulted for a list of about 40 solvents with the precipitates for which each is most effective.

Optional method C. Using a paper filter. Carry out the precipitation as directed in Method *A*. Select a quantitative filter of the proper size and porosity (Note 1), fit it to a funnel, and then filter and wash the precipitate by decantation as directed in Method *A* above. Cover the funnel (Note 2), place it in a drying oven (at 100° to 110°C.), and leave until dry.

Clean and mark a porcelain crucible, place it on a clean triangle (Note 3), warm it gently at first, and then heat it for 10 minutes (Note 4). Do not cause the crucible to glow. Allow the crucible to cool somewhat, place it in a desiccator for 20 minutes, and weigh. Repeat the heating, cooling, and weighing until the weight is constant to 0.2 mg.

Remove the filter paper from the funnel (Note 5) and transfer most of the precipitate to a clock glass (or smaller piece of glazed paper) placed in the center of a piece of black glazed paper, about 10 inches square (Note 6). Cover the clock glass containing the precipitate with a larger clock glass. Fold the filter paper, turning in the edges, and roll it up so that the portion containing the precipitate is at one end of the roll. Wind spirally around the other end a piece of platinum wire about 4 inches long, one end of which has been sealed into a glass rod (Note 7). Place the crucible on the glazed paper, hold the roll of filter paper vertically over the crucible with the end containing the precipitate uppermost, and ignite it at the top with a very small oxidizing flame. As the roll burns down, use the flame to burn completely any particles of charred paper which remain. Collect the ash in the crucible. Brush any ash from the wire or from the paper into the crucible with a small camel's-hair brush or feather. Place the crucible on a triangle, inclining it with the bottom against one side of the triangle, and heat it with a small flame until any particles of carbon are burned. Do not overheat the crucible (Note 8). Let the crucible cool and moisten the residue with 2 drops of 16 n. HNO_3, then with 1 drop of 6 n. HCl. Evaporate the acids by playing a small flame around the upper walls of the crucible. Care must be taken not to hurry the process, or spattering will result. Cool the crucible sufficiently to place it on the glazed paper, and very carefully transfer the main portion of the precipitate to it from the watch glass. Add to the precipitate 2 drops of 16 n. HNO_3 and 1 drop of 6 n. HCl and again evaporate the acids. Heat the crucible, slowly raising the temperature, until the precipitate just begins to fuse around the edges. Let the crucible cool somewhat, place it in a desiccator for 20 minutes, and weigh. Again heat to incipient fusion, cool, and weigh, repeating the process until the weight is constant to 0.2 mg.

Notes:

1. Quantitative filters are made from paper which has been treated with hydrochloric and hydrofluoric acids until the nonvolatile materials (principally compounds of iron, calcium, and silicon) are reduced to a very small value. The average weight of the nonvolatile residue, or ash, in various types of filters is shown in Table VII above, and is usually indicated on the package.

It is also possible to obtain paper filters, both qualitative and quantitative, of varying degrees of retentiveness and rate of filtration. If the precipitate is very finely divided or colloidal, the more retentive, although less rapid, filtering type must be used; with curdy or gelatinous precipitates the more rapid filtering type may be used.

The size of the filter to be used should be determined largely by the size of the precipitate (or residue) which is to be collected and not by the volume of the solution to be filtered. The sizes most commonly used are 7, 9 and 11 cm in diameter. In general, the precipitate should not fill the filter over one-third full in order that the washing can be carried out effectively and safely. The funnel used should be of such size that the paper never comes closer than 0.5 to 1.0 cm to the top; papers that are too large should be cut to size after being folded. The paper should be folded so as to fit the funnel closely (it is usually necessary to fold the paper on a slight bias and to use the larger half), and, before beginning the filtration, it should be tested by filling it with water. The stem should fill with water and hold this column of water, which, by the suction it produces, greatly increases the rate of filtration. Air leakage frequently occurs down the folded edge of the outside half of the paper; this can be minimized by tearing off the upper corner of this fold. A filter and funnel thus fitted are shown in Fig. 25. The beveled tip of the funnel should always be made to touch the inside of the receiving vessel.

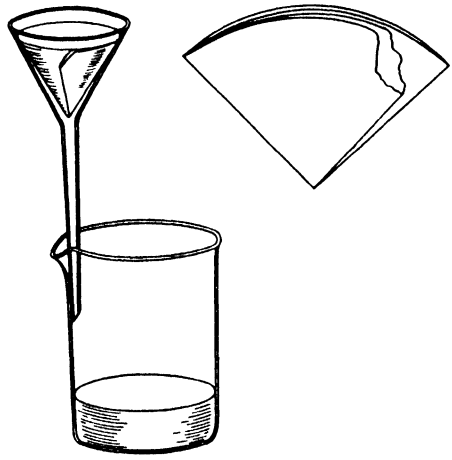

Fig. 25. Paper Filter and Funnel.

When the above precautions are observed, the use of suction with paper filters is usually unnecessary, unless the precipitate is large and of a bulky nature. When suction is used, the lower portion of the filter must be supported by a smaller filter of hardened paper, a perforated platinum cone, or a small circular piece of cloth; the latter aid may be purchased or cut from surgical gauze or other similar cloth. Only a moderate suction can be used, and care must be taken in applying it in order to avoid breaking the filter. Precipitates which are so colloidal in nature as to pass through the filter can often be retained by adding paper pulp to the mixture before beginning the filtration. This may be purchased in the form of readily

disintegrating tablets, or may be made by tearing a quantitative paper into small bits and violently shaking it with water in a test tube. A silver chloride precipitate which has been properly coagulated should be retained by a medium or rapid filtering paper and should not require the use of either paper pulp or suction filtration.

2. The funnel can be covered by a watch glass or by moistening the outer edge of a filter paper and crimping it over the edge of the funnel.

3. Triangles for high-temperature ignitions are preferably made of fused silica, of clay tubes on heavy metal wire, or of platinum. Triangles of nichrome alloy are satisfactory for medium temperatures but are not recommended for high-temperature ignitions, especially with platinum crucibles. Triangles should be kept scrupulously clean, since any material is likely to fuse to the crucible.

4. For general purposes, care should be taken that the burner be adjusted so that an oxidizing (nonluminous) flame is produced. A luminous yellow flame causes carbon deposition on vessels and crucibles, does not produce as high temperature, and is very injurious to platinum ware.

A properly adjusted Bunsen burner can produce a temperature of from 900° to 1050°C. in a covered platinum crucible; a Tirrill burner, 1050° to 1150°C.; a Meker burner, 1150° to 1250°C.; and a blast burner, 1100° to 1300°C. The temperature attained in a porcelain crucible will be from 200° to 300° less (Hillebrand and Lundell, *Quantitative Inorganic Analysis*, p. 99).

In judging temperatures, it can be remembered that at approximately 500°C. a perceptible red glow is produced; this becomes bright red at around 1000°C. and an intense white glow at 1500°C.

5. In removing a filter from a funnel, the paper may be raised by inserting a clean spatula between it and the funnel and then folded forward so that only the outside of the filter is handled. An alternative method is to tear a small piece of paper from a quantitative filter and use this against the inside of the filter when lifting it; this paper is then burned with the filter. In case any precipitate has been spattered or has "crept" onto the funnel above the filter, it can be first wiped up with this paper.

6. Most of the precipitate can be removed by inverting the filter and gently rubbing the insides together; this should not be done so vigorously as to cause particles of the paper to be rubbed off. This operation and the subsequent burning of the filter should be carried out in a place which is absolutely free of air currents.

7. The wire should be wrapped about that part of the filter where there is no precipitate; otherwise this may fuse or be reduced during the ignition and adhere to the platinum.

8. Since silver chloride fuses at 455°C. and becomes appreciably volatile at higher temperatures, the crucible should not be heated above the faintest red glow.

Optional method D. Using a filtering crucible and drying the precipitate with alcohol. The precipitation of the silver chloride, the filtration, and the washing of the precipitate are carried out as above in *A*. The filtering crucibles are

cleaned, washed with water, and then treated as directed below (Note 1).

Treat the clean crucible with 10 ml of boiling water and by means of an efficient aspirator draw a rapid stream of air through it for 2 to 3 minutes. Remove the crucible from its support and dry the outside of it (and the part of the filter support which is in contact with it) with a clean lintless cloth. Replace it and before applying suction, wash down the inside, and soak the mat with a 4-ml portion of 95 per cent C_2H_5OH. Suck off this alcohol with the aspirator and then similarly treat the crucible with two 3-ml portions of 95 per cent C_2H_5OH and with two 3-ml portions of 99.5 per cent C_2H_5OH. Again draw air through the crucible for 3 to 5 minutes. Remove the crucible, wipe the outside with the lintless cloth, place it in a vacuum desiccator connected to an efficient water aspirator, evacuate the desiccator, and maintain the vacuum for 5 minutes. Remove the crucible and weigh it. Repeat the evacuation in the desiccator until the weight is constant to 0.2 mg.

Collect the precipitate on the crucible and wash it as directed in the procedures above. After washing the precipitate, treat the crucible and precipitate as directed in the preceding paragraph (Note 2).

Notes:

1. Experiments have shown that asbestos filters are difficult to dry in a short time by this method; therefore their use is not recommended.

2. Silver chloride precipitates frequently coagulate, so that water may be held in the precipitate and not be extracted by the alcohol. Therefore, such precipitates should be broken up with a stirring rod as the alcohol is applied; any precipitate adhering to the rod should be washed off with alcohol.

Part II

THE SYSTEM OF ANALYSIS FOR THE BASIC CONSTITUENTS

TABULAR OUTLINE I

Preparation of the Sample, Preliminary Observations, and Preparation of the Solution

P. 1. Obtaining and Preparing the Sample.
P. 2. Treatment of Solutions and Suspensions.
P. 3. Preliminary Observations and Tests.
I. Observation of Physical Characteristics.
II. Detection of Organic Substances and of Water.
III. Solubility Tests (Detection of Oxidizing Agents).
P. 4. Elimination of Organic Substances.

Preparation of the Solution.

P. 5. *Weigh a 1-g sample* (0.5 g of a metallic substance).
Treat with water, then 6 n. HNO_3. (If completely dissolved, treat by P. 11.)
If not dissolved:
Treat with 16 n. HNO_3. Evaporate. (*Heat with $HCHO_2$ if oxidizing agents are present.*)

Solution: *If sample dissolves, treat by P. 11.*	Residue: AgCl, AgBr, AgI, $BaSO_4$, $SrSO_4$, $PbSO_4$, HgS, Al_2O_3, Cr_2O_3, Fe_2O_3, $Cr_2(SO_4)_3$, SnS_2, $Sn_3(PO_4)_2$, SnO_2, Sb_2O_3, SiO_2, silicates, silicides, SiC, C, Si; also most of many cyanides. $Ag_2(CN)_2$, $Ni(CN)_2$, complex cyanides, $Fe_4(Fe(CN)_6)_3$, and of $CaSO_4$, CaF_2, $BiPO_4$, $BiAsO_4$, and so forth (see Note 12, P. 5).

P. 6. *Treat with 6 n. HCl.*
If not dissolved:
Treat with 12 n. HCl and 16 n. HNO_3.

Solution: *Treat by P. 11.*	Residue: AgCl, AgBr, AgI, $BaSO_4$, $SrSO_4$, $PbSO_4$, Al_2O_3, Cr_2O_3, $Cr_2(SO_4)_3$, SnS_2, SnO_2, SiO_2, silicates, silicides, SiC, C, Si, $Ag_2(CN)_2$; also most of any $CaSO_4$, CaF_2 (see Note 3, P. 6).

P. 7. *Fume with $HClO_4$ (or H_2SO_4), adding HNO_3.*
Cool, add HF (bubbles; presence of silica).
Add more HF, fume (*or evaporate to dryness*).

Solution: *Treat by P. 11.*	Residue: $BaSO_4$, $SrSO_4$, $PbSO_4$, Al_2O_3, SnO_2, a few silicates, C (graphite), SiC (carborundum) (see Note 9, P. 7).

P. 8. *Fuse with Na_2CO_3. Boil with water.*

Solution: *Acidify with HCl. Treat by P. 6.*	Residue: Carbonates and hydroxides. *Treat with HCl. Treat by P. 6.*

The Preparation of the Sample, Preliminary Observations, and Preparation of the Solution for the Analysis

P. 1. Preparation of the Sample

Discussion. *Methods of sampling.* The importance which attaches to the method of securing the sample of the original material is often not sufficiently realized by an inexperienced analyst. In order to appreciate the difficulties involved in this process, especially when the material is a nonhomogeneous solid, the following facts should be considered: First, the weight of the sample used for an analysis usually does not exceed 1 g; second, if the analysis is to be of value, this small amount of material must have a composition which is the same, within the accuracy of the analysis, as that of the entire mass of the material being analyzed; third, the mass of the original material—it may be a carload or a shipload or a mineral deposit of considerable size—is usually very large relative to the size of the sample; and fourth, this material may be quite heterogeneous, as, for example, an ore deposit composed of widely differing minerals. It must, therefore, be strongly emphasized that the analyst is not justified in undertaking an analysis unless he has himself sampled the material or has adequate information as to the method by which the sample has been secured.

The methods used in securing samples will vary with the physical nature of the material. A more detailed discussion of the procedure used for securing samples of non-metallic heterogeneous solid substances will be given, as it is probable that material which can be included under this classification will be analyzed most frequently. Alloys and metallic substances cannot be assumed to be perfectly homogeneous and, as they are often non-friable, have to be sampled by special methods. Solutions, if well shaken, are homogeneous, and sampling is therefore usually simplified. The analysis of gases requires special apparatus and technique and will not be treated in this book.

The principles involved in securing a sample of a non-homogeneous solid are simple. The operations, which may be laborious and time-consuming, consist in taking a representative portion of the original material, reducing it to a smaller particle size, and then taking a representative portion of this finer material, this process being

repeated until a sample of the proper size for laboratory use is obtained. It is fundamental that each portion be representative of the entire mass from which it is taken; in other words, its average composition must be, within the limits of the errors of the proposed analysis, the average composition of the original material. It follows that the size of the first portion taken will be determined by two factors, the nature of the original material and the accuracy of the analysis; the more heterogeneous the material and the more accurate the analysis the larger the first portion will have to be. It also follows that the smaller the particle size to which each portion is reduced—the finer it is crushed or ground—the smaller the fraction of it which then can be taken. In general, each portion should be of such size that the largest particle of that portion, no matter what its composition, could be removed or added without changing the average composition of the portion by more than the errors of the subsequent analysis.

The directions given in the following procedures must of necessity be of a very general nature. More detailed treatments of the sampling of various types of materials will be found in the following texts and reference works:

The sampling of non-metallic materials:

Fales, *Inorganic Quantitative Analysis*, Century, 1925.

Mellor, *A Treatise on Quantitative Inorganic Analysis*, Griffin and Co., 1913.

The sampling of metallic materials:

Lord and DeMorest, *Metallurgical Analysis*, 5th Ed., McGraw-Hill, 1924.

Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*, Wiley, 1932.

The treatment of samples in the laboratory, with especial reference to minerals:

Hillebrand, *Analysis of Silicate and Carbonate Rocks*, Bulletin 700, U. S. Geological Survey, 1924.

Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929.

Procedure 1: PREPARATION OF THE SAMPLE. In the following procedure the method is varied according to whether the material to be sampled is (I) *a non-metallic solid*, (II) *a metallic solid*, or (III) *a solution or suspension.*

(I) *The material is a non-metallic solid:* Take uniformly throughout the body of the material from 20 to 50 portions

of such size that from $\frac{1}{50}$ to $\frac{1}{200}$ of the total mass is withdrawn (Notes 1, 2).

Reduce the material to a finer state of aggregation (Note 3), pile it into a cone-shaped mound, flatten out this mound into a disk, divide the disk into quarters, and reject the two opposite quarters (Note 4). Repeat this quartering process until the proper amount of material (determined by the particle size) remains (Note 2). Again crush, grind, or powder this portion and quarter it, repeating this process until a bulk sample of from 1 to 5 lbs. is obtained.

Again reduce the material to a smaller particle size, spread it uniformly over a clean piece of glazed paper, oilcloth, or rubber sheeting (about 20 in. square), pull one corner over until it touches the opposite corner, and then repeat this with each successive corner until the material is thoroughly mixed. Pull each corner over in such a manner that the material rolls over and over and does not merely slide together. The material may now be "coned" or mounded and quartered by means of a spatula (Note 11). These operations are repeated until a portion of 50 to 100 g is obtained.

Grind this portion in a hardened steel or agate mortar and again quarter; repeat this process until a portion of 5 to 10 g is reduced to a very fine powder (Note 5). Transfer this laboratory sample to a clean, dry, ground-glass-stoppered bottle. Treat this material as directed in P. 3.

(II) *The material is a metallic solid:* Clean the surface (Note 6), and, by means of drilling, chipping, or cutting, take portions uniformly from the material (Note 7). Crush, grind, or cut these portions into a finely divided condition (Note 8), spread the material out evenly on an oilcloth or glazed paper, divide it into a suitable number of small squares, and take sufficient material from each of these to give a laboratory sample of 5 to 10 g. Treat this material as directed in Section II of P. 5.

(III) *The material is a solution or suspension:* Take, in a clean glass bottle, that volume of the solution or suspension which is thought to contain from 5 to 10 g of solid material (Notes 9, 10). Close the bottle with a ground-glass (or if it is not attacked by the solution, a new cork) stopper. Shake the bottle vigorously before withdrawing a portion for an analysis. Treat this material as directed in P. 2.

Notes:

1. The method of taking these portions will vary with the substance. With gross materials, such as cement clinker or ore bodies, shovelfuls of the material may be withdrawn from uniformly spaced locations. An endeavor should be made to secure coarse and fine particles in the same proportion as they occur in the material. Sampling may be done advantageously when material is being moved—for instance, unloaded from a car or being carried on a conveyor—as portions can then be taken at definite intervals.

2. The ratio of sample withdrawn to the total mass of material is determined by the accuracy desired in the analysis and by the homogeneity and physical state of the substance. Thus this ratio would be much larger in sampling a material such as coal or uncrushed ore than it would be in sampling a well-ground and mixed material such as cement. It is necessary to make the portion of such size that the loss of the largest particle, whatever its composition, will not change the average composition by more than the accuracy desired in the analysis.

3. This can be done with a hammer or other suitable instrument, or, if available, a power crusher or pulverizer can be used. It is of course necessary that no instrument or containers be used in crushing, grinding, or powdering the substance which will introduce an appreciable amount of foreign material into the sample. If iron or steel apparatus (crushers, grinders, mortars, and so forth) have been used on non-magnetic materials, it is common practice to remove particles of iron thus introduced into the sample by spreading the material on a clean piece of paper in a very thin layer and moving a strong magnet slowly over the entire sample. The magnet must not touch the sample, or particles of iron will be brushed off, but it must be held as closely as possible. The sample should be then rolled and the process repeated.

The size to which the particles must be crushed is determined by the weight of the portion; thus with a portion of 1000 lbs. the particle size should not exceed 1 in. in diameter, with 50 lbs. the particles should not exceed about 0.4 in., and with ½ lb. the particles should pass a No. 10 sieve (the openings of this size sieve are squares with sides approximately 0.079 in.).

It is often desirable to reserve a portion of the original untreated material for an examination of its physical characteristics by Part I of P. 3.

4. This process, known as "quartering," is very generally used in the taking of samples.

5. An agate mortar and pestle is commonly used for the final grinding. Care should be taken not to pound the material in such a mortar but to use a rotary grinding motion of the pestle. Mortars made of hardened steel are also satisfactory for this operation. Power grinders must be used with caution, as they introduce extraneous material.

6. The surface of the material should be cleaned of all rust, dirt, sulfide, or any other acquired coating. This surface layer may be removed with a wire brush, an emery wheel, or a file. Grease and organic matter usually may be removed by washing with ether.

7. Alloys, castings, and other fabricated materials are often not homogeneous, and therefore samples must be taken from all sections. This can

be done by drilling through or cutting sections from the object at uniform distances. A lathe often can be used to advantage in taking cuttings. Molten metals can be most effectively sampled when they are being poured, by withdrawing small portions at regular intervals. Sections can be taken from sheet metals by means of shears.

8. Brittle metals may be crushed in a hardened steel mortar; softer material may be milled, cut, or filed (with a *clean* file) into finer particles. This is desirable in order to obtain a representative sample and because the more finely divided the material the greater the surface and the more rapid the rate at which it will be attacked by solvents.

9. The volume of solution taken for an analysis will be determined by the amount of inorganic solid material present. This may amount to as much as several gallons in the case of potable waters or only a few milliliters with concentrated commercial preparations. In most cases the approximate concentration of the solution can be estimated from preliminary information, or by evaporating a small portion and noting the amount of residue.

10. Most solutions, unless they contain suspended matter, can be assumed to be homogeneous. Samples of drinking water from wells or reservoirs can be taken by submerging the bottle (after washing it with the water) and allowing it to fill under the surface; if taken from a stream, portions should be taken at various places across the line of flow; if taken from a pipe line, the water should be allowed to run for some time in order to clear the line of accumulated material. Commercial preparations vary so greatly that no general procedure can be used, and the analyst must suit the method to the specific case, being sure to take representative samples in the case of suspensions and emulsions, to avoid loss in handling volatile solutions, and to guard against change or contamination after taking the sample.

11. This "rolling" process secures thorough mixing of the sample and prevents the loss or segregation of particles of a given size. This is important where it is desired to take a small sample from a large amount of material by the "spotting" process, that is, by removing numerous small uniformly spaced portions from the mass of the material.

P. 2. Treatment of Solutions or Suspensions

Discussion. If the material is a solution (with no suspended material), it is necessary to determine the total concentration of solid matter present so that such a volume may later be taken for the analysis as will give about 1 g of solid inorganic constituents. This determination is made by evaporating a small volume of the solution on a water bath and weighing the residue. The residue is also used to determine if any non-volatile organic material is present, and for carrying out the preliminary test of P. 3. Before the solution is evaporated, it is neutralized in order to avoid possible loss of volatile constituents such as certain acids, or $AsCl_3$ from a hydrochloric acid solution.

If the material contains suspended matter in significant amount, it may be desirable to filter out the suspended material and to analyze it and the solution separately; by this means information both as to the composition of the solution and of the suspended material is obtained. Otherwise, depending upon the information desired from the analysis, the suspended material may be filtered out and rejected, or it may be disregarded and the suspension treated as though it were a clear solution.

Procedure 2. TREATMENT OF SOLUTIONS OR SUSPENSIONS. If the material is a clear aqueous solution (Note 1), pipet 10 ml of it into a weighed porcelain crucible, and test it with litmus paper. If it is acid, make it just alkaline with NH_4OH, evaporate it to dryness on a steam bath, cool the crucible in a desiccator, and weigh it. Treat the residue (Note 2) by P. 3.

If the material is a suspension, either (a) treat the suspension by the paragraph above as though it were a clear solution, or (b) filter out the suspended material and treat the residue by P. 3 and the solution by the paragraph above.

Notes:

1. Inorganic material may sometimes be dissolved in a volatile organic solvent such as ether, alcohol, or benzene. Such solutions may be treated in a similar manner in order to determine the total solids present. Such a solvent may often be identified by distilling it off and noting its boiling point, odor, and other physical characteristics.

2. If an insufficient amount of solid material is obtained, a larger volume of the solution will have to be evaporated.

The residue is treated by P. 3 in order to detect organic material and to note if any residue remains after the heating, since the solution may have contained only an acid or an ammonium salt.

P. 3. Preliminary Observations and Tests

Discussion. Valuable information as to the composition and physical characteristics of an unknown substance often can be obtained by means of an examination made with the aid of a magnifying lens or, preferably, a low-power microscope. It is usually possible to determine whether the material is a homogeneous substance or a mixture and whether it is crystalline or amorphous or composed of particles of each type, and the color and crystalline

nature of individual crystals can be noted, so that often an identification can be made.[1]

Organic compounds may often interfere with the course of an analysis by separating in a voluminous form, thus making filtrations and such operations difficult; by causing the precipitation of otherwise soluble cations; or by forming un-ionized or complex compounds with certain cations and preventing their precipitation. Thus oxalate may cause the precipitation of certain alkaline earth elements and at the same time prevent the precipitation of aluminum or chromium with the Ammonium Sulfide Group. For these reasons organic material must be tested for before beginning an analysis and, if present, must be removed or destroyed. Organic matter is tested for here by heating a small portion of the solid material in a test tube made of resistance glass, or, if a more certain indication is desired, by heating with concentrated sulfuric acid and noting if charring occurs. Indications of other constituents may be also obtained in both of these processes.

When the material is heated in the tube, any water which may be present is driven off and may be detected by causing it to condense in the upper, and cooler, portions of the tube. By noting the amount of condensate, a rough guess as to the amount of water present can be made; if an approximate estimation is desired, a supplementary procedure for determining the "loss on ignition" is provided in Note 5. This information is often of value, as it enables one to sum up all the constituents present in the material. Further information can be obtained by determining the water lost by drying at 110°C.

It is often advantageous to obtain some information as to the solubility of the material in different solvents before beginning the systematic preparation of the solution. Therefore, preliminary tests on small samples are made in order to ascertain the solvent effect of water, of nitric acid, and of hydrochloric acid. Information as to the presence of silver and of large amounts of sulfides may also be obtained; this information is useful in reaching a decision as to whether to treat the sample first with nitric or hydrochloric acid. The relative advantages of these acids for this purpose are mentioned in the discussion of P. 5, last paragraph.

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[1] A microchemical technique has been developed whereby, even when the amount of the material is very small, quite complete analyses can be performed. References: Chamot and Mason, *Handbook of Chemical Microscopy*, Wiley, 1930; Emich, *Microchemical Laboratory Manual*, Wiley, 1932.

Because the presence of considerable quantities of oxidizing agents would cause the formation of sulfur and sulfate in the hydrogen sulfide precipitation, it is desirable that these be reduced prior to that treatment. Accordingly, an incidental test for the presence of oxidizing agents is made, and, if they are found present, formic acid is used to insure their reduction during the preparation of the solution. This test depends upon the oxidation of chloride in a hydrochloric acid solution to chlorine, which can be detected by its color, smell, or the use of starch-iodide paper. Unfortunately, the precipitation of sulfur in the hydrogen sulfide precipitation is not entirely eliminated. Certain less powerful oxidizing agents, ferric salts, for example, do not give the chlorine test and may not be completely reduced by the formic acid, and yet oxidize hydrogen sulfide to sulfur.

Procedure 3: I. PRELIMINARY OBSERVATIONS. Note closely the physical characteristics of the material, such as color, approximate density, odor, and feeling when rubbed between the fingers. Examine a small portion of it with the aid of a magnifying lens or low-power microscope. Observe whether it is homogeneous, and whether it is crystalline or amorphous or a mixture of both types of substances. If a mixture, try to identify the individual constituents by their color and form (Note 1).

II. SOLUBILITY TESTS (DETECTION OF SILVER AND OF CERTAIN OXIDIZING AGENTS). Transfer approximately 0.1 g of the finely divided material to a test tube (25 ml or larger), add to it 10 ml of water, shake the mixture vigorously, and note the result. Heat the mixture to boiling and note any changes. Test the solution with litmus (Note 6). If a residue remains, add 5 ml of HNO_3 and note if any reaction occurs (Note 7); again heat the solution, keeping it almost boiling as long as the material appears to be dissolving (Note 8). If the material is completely dissolved, treat the solution by the second sentence of the next paragraph.

If complete solution was not obtained, treat another 0.1-g portion with 5 ml of 16 n. HNO_3, warming the mixture as long as a reaction appears to be taking place (Notes 9, 10). Add 10 ml of water (Note 11) and just 0.1 ml of 3 n. NH_4Cl, and then heat the mixture almost to boiling. (White precipitate, presence of silver. Note 12.)

Treat another 0.1-g portion with 5 ml of 12 n. HCl; gently

warm the mixture as long as the material appears to be dissolving. (Chlorine gas in the tube, presence of oxidizing constituents. Notes 13, 14.) If complete solution is not obtained, add to the mixture 1 ml of 16 n. HNO_3 and again warm it (Note 15).

III. DETECTION OF ORGANIC SUBSTANCES AND WATER. Transfer 0.1 to 0.2 g of the material to the closed end of a test tube, 10 to 15 cm long and about 1 cm in diameter, made of resistance glass (Pyrex or Jena). Clamp the tube in a nearly horizontal position, wrap a moist strip of paper or cloth near the upper, open end, and heat the lower, closed end of the tube, very gently at first and then finally with the full heat of the burner (Note 2). Note any changes taking place in the material, any deposit forming on the inside of the tube, or any gas issuing from the tube. (Charring of the material, accompanied by a tarry deposit, or smoking, accompanied by a "burnt" odor, presence of organic substances. Notes 3, 4. Aqueous deposit, presence of water, Note 5.)

If it is desired to estimate the water present, treat a portion of the material as directed in Note 5 below.

If organic substances have been found present, proceed as directed in P. 4.

If the material does not contain organic substances, proceed as directed in P. 5.

Notes:

1. Although in the large majority of cases the analyst can, and should, obtain some previous information as to the nature of the material, occasionally he has to deal with a completely "unknown" sample. In such cases the preliminary examination may furnish information which will materially assist in the subsequent analysis. Often by the color of individual crystals or by the smell of the substance, especially if it is warmed, predictions can be made as to the constituents present. It may be advantageous to make these observations on representative specimens of the original material which have not been crushed or ground. It is to be emphasized, however, that these are only predictions, and cannot be relied upon until fully substantiated by the analysis.

2. When an unknown substance is heated, the tube should be kept in such a position that personal injury will not result should an explosion occur. Caution should be taken in smelling any gases given off.

3. A black residue resulting from heating the material does not conclusively prove the presence of organic substances, as certain salts, such as the nitrates and carbonates of copper, cobalt, and nickel, may be decom-

posed to give black oxides. The characteristic charring and the formation of a tarry deposit which accompanies the heating of organic material are much more conclusive.

From the amount of material taken and the residue remaining, an estimate of the amount of organic matter present can be made. If desired, this can be more accurately determined by transferring a larger portion of the material to a weighed porcelain crucible, again weighing the crucible, then gently heating it over a burner until the organic matter is completely charred without flaming, and finally heating with the full heat of the burner until all the carbon is burned off. Upon allowing the crucible to cool and weighing it, the weight of the inorganic constituents is obtained. It is to be realized, however, that water and certain other inorganic constituents, such as CO_2 and mercury compounds, may be also driven off by this treatment.

A more distinctive and sensitive test for organic substances can be made by carefully adding 0.1 to 0.2 g of the substance to 5 ml of 36 n. H_2SO_4 and then heating the mixture. Under these conditions, most organic substances, even in small quantities, darken the solution; thus 1 mg of tobacco or starch and 2 mg of tartaric acid were easily detected by this test.

Considerable information regarding the acidic constituents present may also be obtained by heating the substance with sulfuric acid, especially if the material is treated with 2 to 4 ml of 6 n. H_2SO_4, warmed, any reaction noted, 5 ml of 36 n. H_2SO_4 slowly added, and the mixture heated. Upon being warmed with the dilute acid, many sulfides will evolve H_2S; carbonates will give CO_2; cyanides will give HCN, detected by its odor; sulfites will give SO_2; thiosulfates will give SO_2 and free sulfur; acetates will smell of acetic acid; nitrites will give a brown gas, NO_2; and chlorine, bromine, or iodine will result from the presence of these halogens together with oxidizing agents. Upon heating the concentrated acid, SO_2 will be given off if reducing agents—such as organic matter, iodides, metals, or sulfur—are present; volatile acids such as HCl and HNO_3 will be expelled. Oxalates will not be decomposed by the dilute acid, but will give CO and CO_2 upon being heated in the concentrated acid.

4. Although this so-called "closed-tube" test is used primarily to detect organic substances and water, much supplementary information may also be obtained. Thus, if the material is completely volatilized, non-volatile substances cannot be present, and the material is composed wholly of such substances as ammonium salts, mercury compounds, or organic substances. If a deposit other than water or the characteristic tarry, gummy material caused by organic substances is obtained on the sides of the test tube, it should be carefully examined. A white, more or less crystalline deposit indicates the possible presence of the following: ammonium salts; the chlorides of mercury; when anhydrous, the chlorides of tin, arsenic, aluminum, iron, and antimony; arsenic trioxide; phosphorus oxides; and many organic compounds which may sublime without charring. A gray deposit may be caused by mercury compounds, and examination of this deposit with a lens may show the presence of droplets of free mercury; metallic arsenic gives a black deposit, which in a mixture will appear gray. A yellow deposit indicates arsenic sulfide, sulfur due to sulfide, or elementary sulfur.

Gases that may also be evolved may aid in identifying the presence of certain acidic constituents. Carbon dioxide, from a carbonate, oxalate, or other organic substance, is indicated if a turbidity is produced upon suspending a drop of $Ba(OH)_2$ solution in a small loop of platinum wire and inserting this in the tube. Sulfur dioxide, detected by its smell, indicates sulfites, thiosulfates, or sulfides. Oxygen, detected by inserting a glowing splinter in the tube and noting if it flames, indicates a nitrate, chlorate, peroxide, or higher oxide such as PbO_2. Hydrogen sulfide may sometimes be detected when a moist sulfide is heated. A brown gas indicates NO_2 from a nitrate or nitrite. A violet vapor indicates iodine, which can also be recognized by a mirror-like or crystalline sublimate and by its smell. Bromine or chlorine may be expelled from certain salts.

5. Adsorbed water, or the so-called hygroscopic moisture, will almost always be found present in small amounts in materials which are exposed to the air; this water will usually be less than 1 per cent of the total and can be fairly completely expelled by drying the material at 110°C. for an hour. Water may also be held mechanically enclosed within crystals, causing them to decrepitate when heated; in certain cases water is held by capillary forces in minerals having, as do certain of the zeolites, a porous structure.

Water present owing to the causes just discussed is sometimes classified as non-essential water to distinguish it from water which is assumed to be present in some systematic molecular or crystal structure and which bears some definite stoichiometric relation to the other constituents of the molecule in which it is present. This essential water may be also divided into two classes: water of crystallization and water of constitution. Water of crystallization can usually be expelled below 200°C. Water of constitution is usually expelled only at higher temperatures and is accompanied by a distinct change in the chemical nature of the molecule; acidic substances such as $Ba(H_2PO_4)_2$ or $KH_2Al_3(SiO_4)_3$ and basic compounds such as $Mg(OH)_2$ or $Fe(OH)_2C_2H_3O_2$ contain water of constitution.

A determination of the "loss on ignition" and an approximate estimation of the hygroscopic and total water present can be made as follows:

> Heat a porcelain crucible over a Meker-type burner, cool, and weigh. Weigh 0.5 to 1 g of the material into the crucible and heat in an oven at 110°C. for 1 hr. Cool and weigh. Again heat the crucible over the burner, raising the temperature slowly, for 20 to 40 min. Cool and weigh. Repeat the heating and weighing until constant weight is obtained.

The hygroscopic water will be obtained from the loss in weight on heating at 110°C.; however, hydrated salts may lose much of their water at this temperature. As the material may contain other volatile constituents (such as organic matter, carbonates, and mercury compounds) or constituents (such as sulfides) which may be changed by being heated in the air to the temperature given by a Meker burner, the results of this procedure should be interpreted only after the complete analysis has been made. The above procedure is sometimes used for making an approximate determination of the carbonate in limestones.

6. If the material appears to have partly dissolved, another 10-ml portion of water should be added and the effect noted: a moderately soluble substance may be thus completely dissolved. An examination of the water-insoluble residue will sometimes show that one of the constituents of the original material has been extracted or all but one insoluble constituent have been dissolved. The test with litmus will show whether the solution is alkaline—indicating soluble hydroxides ($NaOH$, $Ca(OH)_2$, and so forth) or salts formed from slightly ionized (weak) acids and highly ionized (strong) bases (Na_2CO_3, Na_3PO_4, and so forth)—or acidic—indicating acids (P_2O_5, $H_2C_2O_4$), acid salts ($NaHSO_4$), or salts formed from weak bases and strong acids ($FeCl_3$, $Bi(NO_3)_3$, and so forth).

Indicator test papers can now be purchased[2] which give more quantitative information than does litmus in that they show a continuous change in color as the hydrogen ion concentration of the solution is varied over a wide range (from *p*H 2 to *p*H 10), and by their use the *p*H of a solution may be determined to within 1 to 2 *p*H units. If such papers are available, they can be used to advantage for determining the approximate *p*H of this solution. These papers should be dipped in the solution being tested and immediately withdrawn, as their coloring material readily passes into the solution, and future color indications of the constituents of the solution may be thereby obscured.

7. Carbonates or sulfides will be indicated by effervescence, the latter being detected by the smell of H_2S; sulfites will give SO_2, which can also be detected by smell; nitrites will be decomposed, and brown fumes of NO_2 will form in the test tube; and cyanides will produce the characteristic odor of HCN (DANGER).

8. A residue that is insoluble in water but soluble in dilute HNO_3 indicates the presence of water-insoluble salts of weak acids, the more common ones being sulfides, carbonates, sulfites, phosphates, arsenates, borates, and chromates (see Table VIII and Note 12, P. 5). A precipitate forming on adding the acid suggests the presence of a soluble silicate, or of antimony or tin dissolved in an alkaline solution.

An insoluble residue indicates the presence of insoluble salts of strong acids, of certain very insoluble salts of weak acids, such as mercuric sulfide, or of native or high-temperature products. Substances of the latter classes, even if soluble when newly precipitated, are often converted by heat or time into very resistant forms which dissolve with extreme slowness. Examples of these substances are the silicates, aluminum and iron oxides, and oxides and sulfides of stannic tin.

9. Upon treating the material with concentrated HNO_3, the appearance of brown fumes will indicate the presence of reducing material. Thus, most metallic substances present will be dissolved and most metallic ions in a lower oxidation state will be oxidized, mercurous, arsenious, antimonous, stannous, cuprous, and ferrous salts all being converted into a higher oxidation state. Many acidic ions will also be changed. Thus sulfide will form

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[2] "Alkacid," Fisher Scientific Co., 711–723 Forbes St., Pittsburgh, and "Hydrion," R. P. Cargille, 118 Liberty St., New York. "Nitrazine" is useful for a more restricted range (see Note 1, P. 161).

sulfur and sulfate, sulfite will give sulfate, nitrite will give NO_2, and chloride, bromide, and iodide will all be oxidized to the free halogen.

10. If the material has been insoluble in dilute HNO_3 but has dissolved in the concentrated acid, the presence of difficultly soluble sulfides is strongly suggested; thus silver sulfide would be rapidly dissolved by this treatment. A white residue, apparently precipitated by the HNO_3, indicates the presence of silicates or of antimony or tin. The nitrates of lead, barium, and strontium are only moderately soluble in concentrated HNO_3; however, these precipitates are crystalline and dissolve when the solution is diluted. If a large amount of free sulfur is formed, it is desirable that the material be first treated with HCl when a solution is being prepared for the analysis. This treatment will in most cases cause the sulfide to be expelled as H_2S, and avoid the formation of the large amounts of sulfate which result from treating a sulfide with concentrated HNO_3.

11. If there is a residue which remains suspended in the solution and which would prevent the analyst from noting the formation of a precipitate, the mixture should be filtered before adding the NH_4Cl.

12. The formation of a precipitate upon adding only 0.1 ml of NH_4Cl indicates the presence of silver or of a large quantity of lead. If the precipitate remains upon heating the solution, the presence of silver is proved; the small amount of lead chloride which would be formed by only 0.1 ml of the NH_4Cl would dissolve. Mercurous mercury, if originally present, would have been oxidized by the treatment with hot HNO_3. If silver is present, the solution resulting from treating the original material with HNO_3 (P. 5) should be filtered and treated separately by P. 11. This avoids precipitating all of the silver as chloride upon adding HCl in P. 6 and the difficult treatment necessary to redissolve this precipitate. Only 0.1 ml of NH_4Cl is added, as this will cause 0.1 mg of silver to give a detectable precipitate in the hot solution even in the presence of 500 mg of lead.

13. The more powerful oxidizing agents, such as permanganates, chlorates, bromates, iodates, or chromates, which are also usually soluble, will give chlorine without the solution being warmed. Nitrates and insoluble oxidizing compounds, such as lead dioxide or lead chromate, may require warming. Nitrites would cause a brown gas, NO_2, in the tube, but this is darker colored and will be more quickly expelled than the chlorine. The presence of chlorine in the tube may be shown by its yellow color and characteristic odor. Chlorine in small amounts may be detected by inserting in the tube a strip of filter paper which has been moistened with a solution containing potassium iodide and starch; the immediate formation of a brown or dark color shows the presence of chlorine. However, any other oxidizing gas in the tube will cause the same reaction, and the smell of Cl_2 is so sensitive a test that it is usually sufficient.

14. The dissolving in the HCl, without evolution of Cl_2, of material insoluble in nitric acid indicates the presence of slowly dissolving oxides, notably those of iron, chromium, and aluminum. Concentrated HCl is a more effective solvent than HNO_3 for such substances, owing to the formation of stable complex ions.

15. Certain substances, such as HgS, will dissolve in the mixed acids, owing to the combination of a powerful oxidizing action and the above-men-

tioned tendency toward complex formation. Thus the sulfide ion will be removed by oxidation to sulfur or sulfate and the mercuric ion will combine with the chloride ion to form the very slightly ionized complex ion $HgCl_4^-$ (see the discussion of P. 6).

P. 4. The Elimination of Organic Material

Discussion. Organic material can be destroyed in a "dry way" by heating to a high temperature in air and thus volatilizing or burning it off. Such a procedure is not used except in special cases, as it involves the possible loss by volatilization of certain of the inorganic constituents. Thus all mercury compounds would be lost; the chlorides of many of the other metals are volatile at higher temperatures; and upon being heated with carbon many of the basic constituents are reduced to the metal, which may be volatile. Furthermore, upon being heated to a high temperature, many metallic compounds are decomposed into oxides which are very slowly dissolved upon treatment with acid; thus the ignited oxides of aluminum, chromium, iron, and tin are not appreciably attacked by even prolonged treatment with concentrated acids. Organic material is more commonly destroyed in a "wet way" by heating with concentrated sulfuric and nitric acids. Although an effective treatment, this introduces sulfate into the analysis and causes the precipitation of lead, barium, strontium, and calcium as the slightly soluble sulfates; also, after fuming with sulfuric acid, chromium is converted into the compound $Cr_4H_2(SO_4)_7$, which dissolves with extreme slowness. Because of these facts, perchloric acid is used in place of sulfuric in this procedure.

The Properties of Fuming Perchloric Acid. Heretofore, perchloric acid has not been used extensively in analytical processes for two reasons. First, the cost has been prohibitive, and, second, there apparently has been a general apprehension as to the possibility of explosions. The cost of the acid is now more reasonable, and extensive experience has shown that, if properly handled, perchloric acid can be used relatively safely. Aqueous perchloric acid is an extremely stable reagent when dilute, reduction being impossible except by a few very powerful reducing agents such as chromous and titanous salts, and even these react slowly. When the acid is heated to fuming, it becomes a powerful oxidizing agent, converting chromic and manganous ions to chromate and manganese dioxide, respectively. If the acid is heated to fuming with organic substances, especially alcohols, or with certain reducing agents,

such as antimonous salts, violent and dangerous explosions will occur. However, it has been shown by Noyes and Bray[3] that, if nitric acid is added to such mixtures, they can be fumed, or even evaporated to dryness, and in no case was it possible to cause the mixture to explode.[4] Furthermore, it has been shown by Noyes and Bray that the mixture of nitric and perchloric acid oxidizes organic substances more rapidly and with less charring than does sulfuric acid. The only insoluble perchlorate which may precipitate is the potassium salt; this, however, is readily soluble in hot water.

Many types of organic material, such as fatty acids, oils, greases, and so forth, can be eliminated by extracting them with ether (in which most inorganic substances are insoluble) and then collecting the residue on a filter paper or separating the ether by means of a separating funnel. Information as to the nature of the material being analyzed, or a trial with a small portion, will indicate the most effective treatment.

In addition to organic material there are certain acidic constituents which may interfere with the course of the systematic basic analysis. The effect of phosphate in precipitating the alkaline earth elements with the Ammonium Sulfide Group is discussed in P. 54, and a method for eliminating phosphate is provided there (arsenate would behave similarly but is removed by the hydrogen sulfide precipitation). Although oxalate is an organic anion, it may decompose without charring sufficiently to give a positive test for organic material, and it would tend to prevent the precipitation of aluminum and chromium hydroxides (because of the formation of complex ions) with the Ammonium Sulfide Group and to cause the precipitation of alkaline earth oxalates with that group. Fluoride may cause the partial or complete precipitation of alkaline earth fluorides with the Ammonium Sulfide Group, although these fluorides are usually so resistant to solvents that in preparing the solution the sample would have to be treated with fuming perchloric acid (P. 7), which would volatilize the hydrofluoric acid. Ferrocyanide and ferricyanide are troublesome, as they form slightly soluble precipitates with many of the cations and as they are partially decomposed in hot acid solutions with the formation of blue precipitates. Because

[3] Noyes and Bray, *Qualitative Analysis for the Rare Elements*, Macmillan, 1927.

[4] Recent reports of explosions with nitric and perchloric acid mixtures, *J. Ind. Eng. Chem., News Ed.*, **15**, 214, 332 (1937), indicate that care should be taken to carry out the operations in the procedure below so that, should an explosion occur, personal injury will not result.

of these effects it is desirable that the analysis for the acidic constituents be made before carrying out the basic system of analysis. If these interfering anions are found present, they can be removed or decomposed by the treatment with nitric and perchloric acid of the procedure below. In addition, certain anions (such as nitrite, sulfite, thiosulfate, and certain of the oxy-halogens) which would cause the formation of sulfur in the hydrogen sulfide precipitation (P. 11) are decomposed by fuming perchloric acid.

Procedure 4: THE ELIMINATION OF ORGANIC MATERIAL. If organic matter has been found present (P. 3), and if the original material is a non-metallic solid, weigh and transfer to a casserole that quantity of the material which, from the information obtained in P. 3, is estimated to contain about 1 g of inorganic residue (Note 3, P. 5). Treat as directed in the second paragraph below.

If organic matter has been found present and if the original material is a solution or suspension, measure out into a casserole that volume of the solution which is estimated to contain 1 g of solid inorganic material (Note 3, P. 5). If the solution is acid, make it neutral with NH_4OH, and evaporate it just to dryness.

Add slowly 10 to 20 ml of 16 n. HNO_3 and cautiously warm the mixture; cool it (by immersing the bottom of the casserole in cold water) if the reaction becomes too vigorous (Note 1). Heat the mixture until no more action seems to be taking place, add slowly 5 ml of 9 n. $HClO_4$, place the casserole on a steam bath, and heat it, adding more HNO_3 as this evaporates, as long as brown fumes are given off. Finally, evaporate the mixture until dense white fumes are evolved (*Caution:* Note 2). If the solution is dark colored, due to charred material, add 2 ml more HNO_3 and again fume, repeating this process until the solution is clear (Note 3).

If there is no residue (Note 4), dilute the solution to 50 ml and treat it by P. 11 (Note 5).

If there is an insoluble residue, treat the mixture by P. 6.

Notes:

1. When organic substances are treated with concentrated nitric acid, the reaction, although it starts slowly, may become so rapid as to cause loss by spattering. For this reason the acid should be added first in small por-

tions and the mixture heated slowly, so that, if the reaction becomes too vigorous, it can be controlled by cooling the casserole.

2. The possibility of obtaining an explosion when the procedure is carried out as directed is extremely small; however, since perchloric acid explosions are so violent as to be quite dangerous, it is advised that the casserole be placed on a ring stand and allowed to evaporate behind a screen in a hood or other place such that, should an explosion occur, no one will be injured.

If perchloric acid is not available, or if it is desired to avoid its use, an equal volume of 18 n. sulfuric acid may be substituted. The disadvantages of this acid are pointed out in the discussion above.

3. If much manganese is present, a dark precipitate of MnO_2 may form on vigorously fuming the acid. This is readily recognized and can be dissolved by adding a few drops of formic acid and again heating the mixture.

4. Salts, especially $KClO_4$, may crystallize in the fuming acid. Therefore, if a crystalline residue is obtained, it is admissible to dilute the mixture before deciding whether or not there is an insoluble residue.

5. If the mixture has been fumed for a considerable period, so much of the acid may have been lost that proper conditions for the H_2S precipitation in P. 11 may not be obtained. In this case, the solution should be made just neutral to litmus with NH_4OH, and 5 ml of 6 n. HNO_3 should then be added.

THE PREPARATION OF THE SOLUTION FOR THE ANALYSIS

General Discussion of the Solution of Solid Substances

Two general methods are available by which solid substances may be brought into a soluble form: first, by treatment in the "wet way" with solutions of various solvents such as nitric or hydrochloric acid alone, mixed acids such as nitric and hydrochloric or sulfuric and hydrofluoric together, or an alkaline solvent like sodium hydroxide; and second, by treatment in the "dry way," which usually consists in fusing the material with some flux such as sodium carbonate or potassium hydrosulfate. Each of these methods has its merits. The treatment with acids is favored in qualitative work because no basic ions are introduced into the analysis, and also because fusion processes may cause the volatilization of certain constituents, may require more specialized technique and more elaborate apparatus, and are usually more time-consuming. However, there are a large number of insoluble salts of strong acids and many native and high-temperature products which are completely decomposed only by a fusion process. When adequate information as to the qualitative composition of the material is available, it is usually possible to select at once the proper method of attack; however, for qualitative work it seems desirable to use a systematic

TABLE VIII

The Preparation of the Solution

(Solvents, Types of Solvent Action, and Substances Dissolved)

Procedure	Solvents Used	Type of Solvent Action	Type of Substances Dissolved (Examples)
P.5	(a) H_2O	Solution (ionization, solvation)	Water-soluble compounds
	(b) HNO_3 (dilute)	I. Hydrogen ion effects 1. Neutralization 2. Displacement 3. Oxidation ($2H^+ + 2E^- = H_2$)	I 1. Hydroxides, basic oxides, basic salts 2. Salts of weak acids 3. Certain metals (Zn, Al)
		II. Oxidation ($NO_3^- + 4H^+ + 3E^- = NO + 2H_2O$)	II. Certain vigorous reducing agents (ferrous and stannous salts)
	(c) HNO_3 (conc. hot)	I, II. Oxidation ($NO_3^- + 2H^+ + E^- = NO_2 + H_2O$)	Reducing compounds (sulfides, alloys, metals, etc.)
P.6	(a) HCl (conc.)	I, III. Reduction ($2Cl^- = Cl_2 + 2E^-$)	Oxidizing compounds—higher oxides (MnO_2), oxidizing salts ($PbCrO_4$)
		IV. Complex ion formation	Compounds of cations forming complex ions ($HgCl_4^=$, $SnCl_6^=$)
	(b) HCl (excess) and HNO_3 (conc.)	I, II, III, IV	Those above; also noble metals (Pt, Au) requiring both oxidation and complex formation
P.7	(a) $HClO_4$, fuming (or H_2SO_4)	I, II (only when fuming) V. Displacement by volatilization (of lower boiling acids)	Salts of volatile acids (sulfides, halides, fluorides, etc.)
	(b) $HClO_4$ and HF (excess)	IV	Primarily silicates (formation of H_2SiF_6 and SiF_4)
P.8	(a) Na_2CO_3 (solution)	VI. Metathesis (carbonate and hydroxide) VII. Hydroxyl ion effect 1. Neutralization 2. Displacement 3. Oxidation	Compounds of cations forming insoluble carbonates and hydroxides 1. Acidic oxides 2. Salts of weak bases 3. Certain reactive metals (Al, Zn)
	(b) Na_2CO_3 (fusion)	VI, VII VIII. High temperature	As above, more rapid and extensive
	(c) Na_2CO_3 and $NaNO_3$ (fusion)	VI, VII, VIII, and II	As above; also compounds of elements forming acids in their higher oxidation states (Cr, Mn)

treatment of the material, first with single acids, then with mixtures, and finally, only when it is absolutely necessary, with a fusion process.

The successive reagents used in bringing materials into a soluble form are outlined in Table VIII. There is also indicated the type of solvent action exerted by each reagent or combination of reagents and, furthermore, the type of compounds usually brought into solution by these reagents. A more detailed discussion of the reactions of the solvents and the specific compounds dissolved by each will be found in the subsequent procedures.[5]

P. 5. Treatment of the Sample with Nitric Acid

Discussion. The first step in the systematic treatment to prepare a solution for the analysis of a material is to treat it with water alone. A compound may dissolve in a pure solvent, such as alcohol or water, as undissociated molecules, as does sugar or glycerin, or it may pass into the solvent partly or completely as ions, as does acetic acid or sodium chloride. In general, the greater the ionizing tendency of the liquid (measured largely by its dielectric constant) the more effective it is as a solvent for most inorganic compounds. The solution process may also be accompanied by solvation (in the case of water as the solvent, hydration); this involves the formation of some type of a compound between the molecules or ions of the solute and the molecules of the solvent. Thus it is known that in many cases the positive metallic ions form stable compounds with water molecules, an example being the hydrated copper ion, $Cu(H_2O)_4^{++}$. It is now generally believed that hydrogen ions exist largely in solution as $H^+(H_2O)$, usually written H_3O^+ and called the "hydronium ion." Ionization and solvation are probably the most important factors determining the solvent properties of a pure liquid.

The amount of a compound which will pass into a given solvent is increased by the addition to the solvent of any substance which will react with the molecules or ions of the solute already present. As the concentration of these ions or molecules is decreased by this reaction, more of the solute must pass into the solvent in order to maintain the saturation equilibrium. Therefore, after the treatment with water the preparation of the solution consists in the addition of reagents which, because of various types of reactions with the solute ions or molecules, increase the amount of the solid passing into the solvent.

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[5] For a general discussion of methods of preparing a solution of various materials, see Fales, *Inorganic Quantitative Analysis*; for methods especially adapted to silicate and carbonate rocks, see Hillebrand, *Analysis of Silicate and Carbonate Rocks*, or Hillebrand and Lundell, *Applied Inorganic Analysis*.

The Solvent Action of Nitric Acid. The first of the reagents so added is nitric acid. As was shown in Table VIII, two general types of solvent action are obtained by the use of this acid. The first of these includes what may be termed the hydrogen ion effects and would be obtained by the use of any strong acid. These effects are the result of the tendency of hydrogen ions to enter into three different types of reactions, namely: (1) neutralization, (2) displacement, and (3) oxidation. The first of these hydrogen ion effects results from the fundamental neutralization reaction when water is the solvent medium:

$$H^+ + OH^- = H_2O.$$

Because of this, those substances, such as the hydroxides, basic oxides, and basic salts, which ionize in aqueous solution to produce hydroxyl ions are dissolved by strong acids. In certain cases these substances may have been converted—usually by high temperatures—into forms which dissolve so slowly that they are considered as being practically insoluble; examples are ignited aluminum and stannic oxides.

The second hydrogen ion effect, displacement, is a result of the type reaction

$$H^+ + A^- = HA,$$

where A^- represents the anion of a weak acid. This accounts for the general increase in the solubility of the salts of weak acids in the presence of other acids. The term *displacement* arises from considering that the weaker acid is displaced from its salt. The action of hydrogen ion as an oxidizing agent, in consequence of the electronic reaction

$$2H^+ + 2E^- = H_2,$$

is of most importance as a solvent effect in the solution of certain reducing metals, such as zinc or aluminum. Neutralization, displacement, and electronic reactions have been discussed from the mass-action point of view in the section dealing with the preparation and standardization of solutions.

The second general solvent effect obtained from the use of nitric acid is due to its strong oxidizing tendency. This tendency makes it especially effective in dissolving metals, alloys, and sulfides. Sulfide ion is oxidized to elementary sulfur or to sulfate, depending upon conditions, such as the concentration and temperature of the acid. The course of the reaction and the products resulting from the

reduction of nitric acid are determined largely by the concentration of the solution and the potential of the reducing agent. The two principal reduction reactions with their potentials are as follows:

$$1.\ H_2O + NO_2 = NO_3^- + 2H^+ + E^-; \qquad -0.79\ v.$$
$$2.\ 2H_2O + NO = NO_3^- + 4H^+ + 3E^-; \qquad -0.94\ v.$$

In dilute solutions, except with very powerful reducing agents, nitric oxide is the product; in concentrated solutions nitrogen dioxide is the invariable product. The latter is true because, even though the direct product of the reaction is nitric oxide, it is oxidized by concentrated nitric acid, the equilibrium constant for the reaction

$$NO + 2NO_3^- + 2H^+ = 3NO_2 + H_2O$$

being 5×10^{-9}. With dilute solutions of nitric acid and very powerful reducing agents, such as zinc, the reduction product may be ammonia, as follows:

$$3H_2O + NH_4^+ = NO_3^- + 10H^+ + 8E^-; \qquad -0.77\ v.$$

It is to be emphasized that the rates with which the above reactions take place are often so extremely slow that predictions made from the potential values would be misleading. Thus cold solutions 1 n. in nitric acid can be saturated with hydrogen sulfide without appreciable reduction taking place; the reaction becomes rapid only when the acid concentration is greater than 2 n. and the solution is hot. The specific behavior of many of the more common substances upon treatment with nitric acid is mentioned in Note 12 of this procedure.

Either nitric or hydrochloric acid could have been used first in this systematic treatment of an unknown solid, and each has its merits and disadvantages. Thus hydrochloric acid furnishes a non-oxidizing solvent which is more generally effective in bringing metallic oxides into solution than is nitric acid. Owing to its reducing character, it dissolves insoluble oxidizing substances, such as manganese dioxide and lead chromate, and it reduces oxidizing agents such as permanganates and chlorates, thus minimizing the formation of sulfur during the precipitation of the Hydrogen Sulfide Group. Against these desirable features of the use of hydrochloric acid are to be considered the danger of loss of certain elements, especially arsenic in the tripositive state, and the formation of insoluble silver chloride, which makes necessary, whenever silver is present, a long and troublesome treatment before complete solution of the substance is obtained. The initial use of nitric acid avoids the possibility of loss of arsenic by volatilization of the trichloride,

causes solution of most silver compounds, and is more generally effective in attacking alloys. Its objectionable oxidizing action, especially that of converting sulfides to sulfate, is largely avoided by using first a cold dilute solution so that most of the hydrogen sulfide formed may be expelled without oxidation. Also, it has been found possible to provide for the reduction of most oxidizing substances by using a simple treatment with formic acid. For these reasons, a treatment with nitric acid is provided for first in this system, although its use is governed to a large extent by the information gained in the preliminary tests in P. 3.

Procedure 5: TREATMENT OF THE SAMPLE WITH NITRIC ACID. (I) *Non-Metallic Solids.* If the original material is a non-metallic solid, weigh out a sample of approximately 1 g and transfer it to a 200-ml flask (Notes 1, 2, 3).

Add to the sample 20 ml of water and, if the substance does not dissolve completely, heat the mixture almost to boiling (Note 4). Test the solution with litmus paper, make it just acid with HNO_3 (or first just basic with NH_4OH, if it is already acid) and then add just 5 ml more HNO_3 (Note 5). (If a clear solution is obtained, treat it by P. 11.)

If the substance has not dissolved, cover the flask with a watch glass and slowly heat the mixture almost to boiling; hold the temperature at that point, without evaporating any of the acid, as long as the substance seems to be dissolving (Notes 6, 7). (If the substance has dissolved, treat the solution by P. 11.)

If the substance has not dissolved, remove the watch glass, evaporate the mixture to 2 to 3 ml, add to it 5 ml of 16 n. HNO_3, and then evaporate it almost to dryness (Note 8), using a steam bath to remove the last 1 to 2 ml of the liquid.

If, in P. 3, the presence of oxidizing substances was not detected, omit the remainder of this paragraph. If oxidizing agents were found present, add to the residue 5 ml of water 1 ml at a time, warming after each addition, and 1 to 15 ml of a 90 per cent solution of $HCHO_2$, formic acid (Note 9). Heat the mixture just to boiling as long as any reaction seems to be taking place, and then evaporate the mixture almost to dryness as directed above. Add 5 ml of HNO_3 and again evaporate almost to dryness.

If the original substance has not been converted into a soluble form (Notes 11, 12), treat the residue by P. 6 (Note 10).

If the original substance has apparently dissolved, add to the residue just 5 ml of HNO_3 and then 10 to 30 ml of water (Note 13). If the residue dissolves slowly, cover the flask and heat the mixture to 80° to 90°C. If a clear solution is obtained, treat it by P. 11 (Note 14); if not, treat the mixture by P. 6

(II) *Metallic Solids.* If the original material is a metallic solid, weigh out a sample of approximately 0.5 g and transfer it to a 200-ml flask (Notes 1, 2, 3)

Add to the substance 10 ml of HNO_3, cover the flask with a watch glass, slowly heat the mixture just to boiling, and gently boil it as long as the substance seems to be dissolving. If there seems to be a slowly dissolving residue, add 5 ml of 16 n. HNO_3 to the mixture and again boil it.

If the substance has not been converted into a soluble form (Notes 11, 12, 14), treat the mixture by P. 6 (Note 10).

If the substance has apparently dissolved, evaporate the solution just to dryness, using a steam bath to remove the last 1 to 2 ml of liquid.

Treat the residue by the last paragraph of Part I of this procedure.

(III) *Solutions.* If the original material is a solution or suspension, measure out into a flask that volume of the solution which is estimated to contain 1 g of solid material (Note 15), make it neutral with NH_4OH or HNO_3, evaporate (or dilute) it to 50 ml, add just 5 ml of HNO_3, and treat it by P. 11 (Note 16).

Notes:

1. The sample should have been subjected to the preliminary observations and tests of P. 3, and the decision as to whether it should be treated first with HNO_3, by this procedure, or directly with HCl, by P. 6, should be based upon any previous knowledge of the substance and upon the information gained in the tests of P. 3 (see the last paragraph of the discussion above and also Note 10, P. 3).

If, in P. 3, the sample has appeared to be insoluble in the HCl, HNO_3, and the mixed acids, time will be saved by omitting both P. 5 and P. 6 and proceeding directly to P. 7.

2. The sample should have been prepared by P. 1 and should have been reduced to a very fine powder. It is recommended that the sample be kept

in a closed glass "weighing bottle" and that the sample be weighed by difference. That is, the weight of the bottle and material is found, a portion of the substance thought to be slightly less than 1 g is tapped directly into the flask, and the bottle is then closed and approximately weighed. From the weight thus found, the additional amount to be taken to give a sample of approximately 1 g can be estimated, this amount added to that in the flask, and the weighing bottle then weighed to the precision desired.

3. The precision with which the sample should be weighed or measured is determined by the accuracy desired in the analysis. Thus, a 1-g sample weighed to within 1 mg will justify results to $\pm$ 0.1 per cent, which, except in special cases, is greater than the precision which can be attained by the separations and estimations of this system of analysis.

4. It is sometimes desired to determine separately the portion of the substance which is "water soluble." In this case, after treating the substance a sufficient length of time to be sure that the soluble constituents are extracted, the mixture should be filtered, decanting as much as possible, the residue washed, the acidity of the filtrate adjusted as directed in the next sentence of the procedure, and this solution then analyzed separately.

5. A careful adjustment of the acidity is necessary at this point, as the subsequent separation of the Hydrogen Sulfide Group from the other elements is highly dependent upon attaining a certain acid concentration—namely, 0.3 n.—when the solution is later treated with H_2S.

If the test papers mentioned in Note 6, P. 3, are available, they can be used to advantage in this procedure, as, by neutralizing this solution to a *p*H of approximately 3, the extensive precipitation of easily hydrolyzable constituents, such as bismuth and ferric salts, may be prevented and a more precise adjustment of the acidity for the hydrogen sulfide precipitation may be obtained.

6. The mixture is warmed slowly in order that, insofar as possible, any sulfides present may dissolve and the hydrogen sulfide formed may be expelled without oxidation. Oxidation of the hydrogen sulfide would result in the formation of sulfur and sulfate, the latter causing precipitation of any barium or strontium, or, if present in considerable amounts, of lead and calcium.

7. If there is a crystalline residue which seems more soluble in the hot solution, or which seems to require only a larger volume of solution in order to dissolve completely, the mixture should be diluted to 50 ml and, if a clear solution is obtained, treated by P. 11.

8. When evaporating a solution almost to dryness, only sufficient liquid should be left to keep the residue wet. This operation is used when drying the residue might cause it to be converted into an insoluble or slowly dissolving form, or cause loss due to spattering or volatility of some of the constituents. The use of a steam bath to remove the last few milliliters of solution eliminates spattering and the danger of overheating portions of the residue. This operation can be carried out over a flame if the vessel is kept in constant motion and if all parts of the residue are continuously kept wet; however, the danger of loss by spattering has to be carefully guarded against.

9. The volume of $HCHO_2$ to be added can be judged by the amount of

oxidizing substances found in P. 3. Reduction of a permanganate is indicated by the disappearance of pink color; reduction of a chromate is indicated by the formation of a clear green solution with disappearance of the yellowish color. The $HCHO_2$ is oxidized to carbon dioxide and water.

10. If an unchanged residue of the original sample is apparent in considerable amount, this residue should be treated directly by P. 6, unless the presence of silver has been indicated in P. 3. In that case the residue should be treated by the next paragraph of this procedure. The formic acid may produce a dark precipitate, owing to the precipitation of metallic mercury or silver; this residue should dissolve when it is treated with the 5 ml of 16 n. HNO_3 and the mixture is again evaporated almost to dryness.

11. If there is doubt as to whether or not the substance has dissolved, or if there is a considerable crystalline residue which may dissolve when treated with acid or when the solution is diluted, the residue should be treated by the next paragraph of the procedure.

12. Of the more common substances which would remain undissolved by treatment with concentrated HNO_3, there may be listed the following groups: (1) AgCl, AgBr, AgI, $BaSO_4$, $SrSO_4$, $PbSO_4$; (2) HgS; (3) Al_2O_3, Fe_2O_3, CrO_3, $Cr_2(SO_4)_3$, SnS, $Sn_3(PO_4)_4$; (4) MnO_2, PbO_2, SnO_2, Sb_2O_3, SiO_2; (5) many silicates; (6) silicides of such metals as iron, manganese, and chromium, SiC (carborundum), C (graphite), Si, and many resistant alloys. Substances dissolving to only a slight extent would include $CaSO_4$, CaF_2, $PbCrO_4$, $BaCrO_4$, $BiPO_4$, $BiAsO_4$, and many cyanides and complex cyanides. It is seen that these compounds include several classes of substances, and their insolubility is explained by various causes. Thus the first group is composed of insoluble salts of strong acids, and it would not be expected that they would greatly increase in solubility in acid solutions. It would be expected that HgS would dissolve in an acid solution, because HgS is a salt of a weak acid and, moreover, sulfide is oxidized by concentrated HNO_3; however, HgS is so extremely insoluble that it is only very slowly attacked. The group including Al_2O_3, $Cr_2(SO_4)_3$, SnS, and $Sn_3(PO_4)_4$ exhibits a rather common phenomenon, being composed of substances which, when first precipitated, are quite soluble but which when heated or found native are not appreciably attacked by acids even on prolonged treatment. Chromic sulfate behaves in this manner, even a short fuming with sulfuric acid converting it into a very resistant compound having the unusual formula $Cr_4H_2(SO_4)_7$.[6] MnO_2, PbO_2, and, more typically, SnO_2, Sb_2O_3, and SiO_2 are acidic oxides which are insoluble in non-reducing or non-complex-forming acids. Many silicates are not appreciably attacked by acids other than HF, and those which are decomposed give a precipitate of hydrous silicic acid. Finally, there is a large group of substances, such as certain silicides, carbides, elementary substances (graphite, silicon), and alloys, which are very resistant to nitric acid. In some cases this may be due partly to the formation of protective coatings.

By the treatment with formic acid most of any insoluble oxidizing com-

[6] Caley, *J. Am. Chem. Soc.*, **55**, 3947 (1933), has shown that this and many other resistant compounds such as SnO_2, $PbSO_4$, and the alkaline earth element sulfates are readily decomposed by hot concentrated hydriodic acid.

pounds, such as MnO_2, PbO_2, or $PbCrO_4$, are reduced and consequently dissolve in the HNO_3 next added.

13. The larger volume of water should be added if there is considerable crystalline residue which seems to be dissolving with the addition of more water. If, however, the residue dissolves completely in the acid and a precipitate forms upon adding water, the mixture should be treated, without filtering, by P. 11. Such a precipitate is caused by the hydrolysis of compounds of antimony, tin, or bismuth; as these precipitates are metathesized into sulfides in P. 11, it is not necessary to redissolve them.

14. If only a small residue is left, it is usually advisable to filter the solution through an ashless filter paper, decanting as much as is possible in order to retain the residue in the flask, to wash the residue and paper by decantation with 5 ml of hot water, and to treat the filtrate and washings by P. 11 and the residue by P. 6. Also, if silver has been detected in P. 3 or is thought to be present, it is better to treat the solution obtained at this place (which will usually contain all of the silver) by P. 11, thus avoiding the formation of difficultly soluble AgCl in the next procedure.

If the substance is an alloy containing antimony or tin, these two elements will be rendered insoluble by the evaporation with HNO_3 and will remain as a white residue. Often, especially in the case of alloys, it is advisable to filter out this precipitate and thus separate these elements at this point. Furthermore, as antimony is often known to be absent, the residue will consist only of hydrated SnO_2 and can be either ignited and weighed or dissolved in HCl and treated directly by P. 49 to determine the amount present.

15. If the material is a suspension, either (a) treat the suspension as though it were a clear solution, or (b) filter out the suspended material and treat this residue by Part I and the solution by Part III of this procedure. If it is desired to know the weight of suspended matter in a given volume of solution, a known volume of the original solution should be filtered, and the precipitate dried and weighed.

16. If a precipitate forms on neutralizing the solution and does not redissolve on adding HNO_3, it should be filtered out and treated by Part I of P. 5. From an alkaline solution such a precipitate would result from sulfides held in solution by an excess of an alkaline sulfide, from silver halides dissolved in a cyanide or ammonia solution, from amphoteric hydroxides (antimony or tin) dissolved in an excess of a hydroxide, or from soluble silicates which on acidification precipitate silicic acid. If it is known that the precipitate is caused by elements of the Hydrogen Sulfide Group—for example, by the hydrolysis of antimony or bismuth salts, or by silver halides held in an alkaline solvent—the precipitate need not be filtered out, as it will be metathesized to sulfide by the H_2S treatment in P. 11.

P. 6. Treatment of the Sample with (1) Hydrochloric Acid, and (2) Hydrochloric and Nitric Acids

Discussion. In this procedure the systematic treatment of the sample is continued by the use of hydrochloric acid and, where it is necessary, a mixture of nitric and hydrochloric acids.

The Solvent Action of Hydrochloric Acid. By the use of a concentrated hydrochloric acid solution three general solvent effects are obtained. The first of these is the hydrogen ion effect, which is obtained by the use of any strong acid. The second is obtained because of the tendency of chloride ion to reduce certain higher oxides (for example, MnO_2 and PbO_2) and also the anions of certain oxygen acids, especially the insoluble chromates. The third general effect is due to the tendency of chloride ion to form soluble complex compounds with most of the elements of the Hydrogen Sulfide and Ammonium Sulfide Groups. These complex compounds and their influence on the solubility of the sulfides of the Hydrogen Sulfide Group elements are discussed in P. 11.

The Solvent Action of a Mixture of Nitric and Hydrochloric Acids. A mixture of nitric and hydrochloric acids, the so-called "aqua regia" solution, is a tremendously effective solvent, as it combines in one solution the solvent effects of both nitric and hydrochloric acids. Thus there is obtained the oxidizing effect of nitric acid with the complex-forming tendency of hydrochloric acid. The particular effectiveness of this mixture in dissolving the so-called noble metals (gold and the platinum group elements) is due to the strong tendency of these metals to form very stable chloride complexes ($AuCl_4^-$ and $PtCl_6^=$ are examples), and not to the existence of an exceptionally high oxidizing potential—frequently attributed to the presence of nitrosyl chloride (NOCl) and other products of the reaction between the nitrate and chloride ions.

After this treatment, the mixture is evaporated almost to dryness in order to render more insoluble any silicic acid which may have been formed. Care has to be taken not to boil the hydrochloric acid solution before addition of the nitric acid (or other oxidizing agent), as arsenious chloride is quite volatile; on evaporating 25 ml of 6 n. HCl containing 250 mg of arsenic (as arsenious chloride) to 5 ml, 97 per cent of the arsenic was lost.

Procedure 6: TREATMENT OF THE SAMPLE WITH (1) HYDROCHLORIC ACID, AND (2) HYDROCHLORIC AND NITRIC ACIDS. If the sample has been treated by P. 5, treat the mixture or the residue obtained in that procedure, in the same 200-ml flask (Note 1), as directed in the third paragraph of this procedure.

If the sample has not been treated by P. 5, weigh out a sample of approximately 1 g (Notes 2, 3, P. 5) if it is a nonmetallic solid or 0.5 g if it is a metallic solid, transfer it to a 200-ml flask, and treat it as directed in the next paragraph.

Add to the residue (or sample) 10 ml of 6 n. HCl, cover the flask with a watch glass, and heat the mixture to 80° to 90°C. (do not boil it!) as long as the substance seems to be dissolving. If the substance has dissolved, add to the solution 10 to 30 ml of water (Note 2; also Notes 11, 13, P. 5) and just 4 ml of NH_4OH and treat it by P. 11.

If the substance does not seem to be dissolving, or is only slowly dissolving, evaporate the mixture to 3 to 5 ml (Note 3), add to it 10 to 20 ml of 12 n. HCl and 5 ml of 16 n. HNO_3, cover the flask with a watch glass, and again heat the mixture just to boiling as long as the substance seems to be dissolving (Note 4). Finally evaporate the mixture almost to dryness (Note 3), add to the residue just 5 ml of 6 n. HCl, warm the mixture with the flask covered until all the soluble salts seem dissolved, and then add to the mixture 10 to 20 ml of water (Note 13, P. 5). Filter the solution through a quantitative (ashless) paper filter (see p. 134) and wash the residue with two 2-ml portions of 1 n. HCl and then with five 2-ml portions of hot water, collecting these washings with the filtrate. Treat the filtrate by P. 11. Treat the residue by P. 7.

Notes:

1. If the insoluble residue obtained in P. 5 has been filtered, it should have been retained in the original flask insofar as was possible by filtering and washing by decantation. The residue carried onto the filter can be combined with that in the flask in the following manner: Open the filter and carefully tear away that portion of it to which no residue has adhered. Lay the filter against the side of a funnel (the funnel just used, or, for this and similar operations, a larger one with the stem cut off short is more convenient; a funnel with a capillary stem cannot be used). Wash the residue from the paper into the flask, using the 10 ml of HCl next to be added and applying it in a fine stream by means of a dropper. Finally, the paper can be similarly washed with hot water. Usually such a small fraction of the residue will adhere to the paper that it can be neglected and the paper can be discarded. If an appreciable amount of the residue remains on the paper, or if a very accurate analysis is desired, the paper should be folded into a compact roll, and a stout platinum wire, which has one end sealed into a glass rod, wrapped in a spiral around it. The paper is then held above a crucible (which is preferably placed in the center of a square of black glazed paper), and the filter is gradually heated with a small oxidizing flame from a gas burner until it has completely burned. Any ash remaining on the wire can then be brushed into the flask with a small camel's-hair brush, and any ash which has dropped into the crucible or onto the paper can be similarly added to the flask. If unburned portions of the filter paper drop into

the crucible, they can be ignited by heating the crucible. The black oxides of certain metals should not be mistaken for charred paper. After cooling, the residue is transferred to the flask.

2. Certain moderately soluble chlorides, such as $PbCl_2$ and $HgCl_2$, may precipitate and not be dissolved completely with this volume of water; in such cases, the mixture, or a portion of it, may be further diluted and the effect noted.

3. The hydrochloric acid solution has not been boiled before this in order to avoid possible loss of arsenic, or, to a much smaller extent, mercury, antimony, or tin. Especially if arsenic is thought to be present, the evapora-

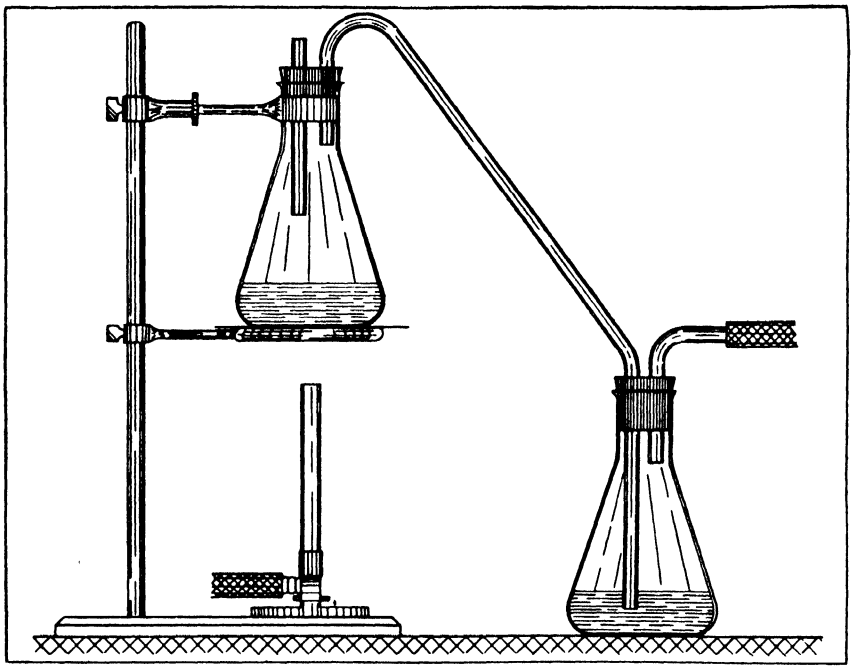

Fig. 26. Apparatus to Prevent the Loss of Volatile Chlorides.

tion should be carried out in such a way that the volatile chlorides of these elements can be condensed and recovered. This can be accomplished by transferring the mixture to a distilling flask and distilling it to the volume indicated, at the same time collecting the distillate in 50 ml of cool water. The operation can be more rapidly and effectively performed as follows: Place in the flask a two-hole rubber stopper carrying in one hole a glass inlet tube which extends about two thirds of the distance to the solution (see Fig. 26). In the other hole insert a tube which is bent in the form of a U so that it can be extended through a hole in a similar stopper in another 200-ml flask. The second flask should contain 50 ml of water, and the tube should be made to extend just under the surface of this water. In the second hole of the stopper of this flask insert a short glass tube and connect this by means of rubber tubing to a water aspirator, which is adjusted so that a

rapid stream of air is drawn through the two flasks. By boiling the mixture in the first flask and cooling the second flask with a bath of cold water, rapid evaporation is obtained and any volatile chlorides are quite completely condensed in the second flask. The condensed solution, after being used also for the second evaporation in this procedure, is made neutral to litmus with NH_4OH, 5 ml of 6 n. HCl are added to it, and, disregarding any precipitate, it is treated by P. 11. Any precipitate obtained there is combined with any precipitate obtained by P. 13 or is treated separately by P. 41 to P. 49. The filtrate is discarded.

4. If there is a residue which seems to be slowly dissolving, more of the two acids should be added and the boiling continued. Of the insoluble substances mentioned in Note 12, P. 5, those which would probably dissolve would include HgS, Fe_2O_3, $Sn_3(PO_4)_2$, Sb_2O_3, most cyanides and complex cyanides, $BiPO_4$, and $BiAsO_4$. The solution of HgS is due to the stability of the $HgCl_4^-$ ion which is formed, combined with the oxidation of the sulfide by the mixture. Oxides and salts of the metals of the Hydrogen Sulfide Group and the Ammonium Sulfide Group are in general more soluble in HCl than in HNO_3, because of the tendency of these elements to form complex compounds in HCl solutions. Any oxidizing substances, such as MnO_2 or $PbCrO_4$, not reduced by the formic acid would be reduced and dissolved by the concentrated HCl. The slowly dissolving substances, such as ignited or native Al_2O_3 or SnS_2, would be only slightly attacked by the mixed acids.

P. 7. (1) Treatment of the Sample with Perchloric Acid; (2) Detection and Estimation of Silica by the Use of Hydrofluoric Acid

Discussion. By heating the residue from the "aqua regia" treatment with nitric and perchloric acids until the latter fumes, several effects are obtained. First a powerful oxidizing action is obtained. This is due at first entirely to the oxidizing effect of the nitric acid in the dehydrating medium furnished by the mixed acids; perchloric acid does not exhibit its powerful oxidizing tendency until it becomes quite concentrated and hot. Then it may oxidize manganous ion to manganese dioxide or chromium to chromic acid (see discussion of P. 4).

The Solvent Action of Fuming Perchloric (or Sulfuric) Acid. Next, upon fuming the perchloric acid, many insoluble salts of volatile acids are dissolved, the acids being volatilized from the solution at the high temperature of the fuming acid (280°C.). Thus, such salts as calcium fluoride, silver bromide, and silver iodide are dissolved. The solvent action on the last two is made more effective because of oxidation of iodide and bromide by the fuming acid; some of the iodide is even converted to iodate. Silver chloride is more slowly dissolved, however, as suggested in Note 2, if the chlo-

ride is metathesized into bromide by addition of hydrobromic acid; this can then be dissolved by further fuming with the perchloric acid. Sulfuric acid is even more effective, because of its higher boiling point, in dissolving the insoluble salts of volatile acids; thus silver chloride is readily dissolved by fuming sulfuric acid.

The Precipitation of Silicic Acid by Fuming Perchloric Acid Finally, the fuming perchloric acid has the effect of partially dehydrating and quantitatively precipitating silicic acid. This effect is obtained because (1) silicic acid is a very slightly ionized acid, and therefore most silicates are decomposed by treatment with a strong acid: (2) silicic acid is an insoluble acid, although when first precipitated it tends to form colloidal solutions, which are not coagulated except by partially dehydrating the silicic acid; (3) fuming perchloric acid is a good dehydrating medium and is thus effective in causing the precipitation of colloidal silicic acid; and (4) perchloric acid does not form any soluble complex acids with silicic acid, as does hydrofluoric acid.

Silicic acid is more commonly dehydrated and made insoluble by evaporating a hydrochloric acid solution to dryness, heating the residue for some time, digesting with hot dilute hydrochloric acid until the soluble constituents are dissolved, and then filtering out the silicic acid. Disadvantages of this process are (1) the time required for the evaporation and drying, (2) the fact that the precipitate usually retains an appreciable amount of the soluble basic constituents of the solution, and (3) the fact that the process has to be repeated with the filtrate in order to precipitate the silica quantitatively. The amount of silica remaining in the first filtrate depends upon the quantity and nature of the other constituents present, and various other factors such as the temperature and the time for which the residue is dried; often as much as several per cent of the total will pass into the first filtrate.

The dehydration and precipitation of silicic acid by fuming perchloric acid has been the subject of several investigations;[7] these have shown that practically complete precipitation can be obtained and that the precipitate is cleaner than that obtained by the evaporation process. Because of these facts and the quickness of the method, it is used here.

Fuming sulfuric acid will also dehydrate and precipitate silicic

[7] Willard and Cake, *J. Am. Chem. Soc.*, **42**, 2208 (1920); Gibson, *Rock Products*, **35**, 70 (1930); Meier and Fleishman, *Z. anorg. Chem.*, **88**, 84 (1932); Fish and Taylor, *J. Chem. Ed.*, **10**, 246 (1933).

acid; this process, while frequently used in the analysis of ferrous alloys, is not practical for qualitative systems because of the precipitation of insoluble sulfates.

In the large majority of cases, the residue remaining after this treatment will consist entirely of silicic acid, which is estimated by heating it to a temperature sufficiently high (1000° to 1200°C.) to convert it to anhydrous silicon dioxide and then weighing it. Most other basic constituents remaining in the residue are converted into oxides at this temperature and are weighed as such. In order to eliminate the silica, the ignited residue is treated with hydrofluoric acid in the presence of concentrated perchloric acid. The hydrofluoric acid reacts with silica (or silicates) as follows:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

If an excess of the acid is added, the complex fluosilicic acid is formed, thus:

$$SiF_4 + 2HF = H_2SiF_6.$$

However, upon fuming the solution, this reaction is reversed as the volatile silicon tetrafluoride and hydrogen fluoride are expelled. Therefore, by this operation the complete elimination of silicon is accomplished. Often, after this process, no significant residue remains and further treatment is obviated. If any residue remains, the perchloric acid is evaporated, and the residue is heated as before and again weighed; the weight of this residue is subtracted from the first weight to give the true weight of the silica present. The residue, if appreciable, is treated with hydrochloric (or nitric) acid, and the solution so obtained is analyzed for the basic constituents. Only rarely will there be any residue after the treatment with these acids; in case there is, it should be fused with Na_2CO_3 as directed in the next procedure. Reference should be made to Hillebrand, *Analysis of Silicate and Carbonate Rocks*, Bulletin 700, U. S. Geological Survey, 1924, or to Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929, for an extensive discussion of the methods for determining silica.

If it is not desired to estimate the amount of silica present, the dehydration and precipitation of the silica and the ignition and weighing of the silica and the residue remaining after the hydrofluoric acid treatment can be dispensed with. The silica is volatilized by adding the hydrofluoric acid to the fumed perchloric acid solution, and the fluorides and excess hydrofluoric acid are volatilized by again fuming the perchloric acid solution.

Modified procedures are given below for the case (*A*) where it is desired only to detect and remove the silica and (*B*) where an estimation of the amount present is wanted. In Note 11 below is given a procedure whereby the estimation of the silica in silicates which are decomposed by acids can be made directly without going through the previous procedures of this system.

Procedure 7: (1) TREATMENT OF THE SAMPLE WITH PERCHLORIC ACID; (2) DETECTION AND ESTIMATION OF SILICA. Transfer the residue from P. 6 to a 200-ml round-bottom flask (Note 1, P. 6), add to it 5 ml of 9 n. $HClO_4$ (Note 1) and 1 ml of 16 n. HNO_3, and heat the mixture until dense white fumes are evolved. If there is a residue which seems to be slowly dissolving, add cautiously 1 ml more of 16 n. HNO_3, insert a test-tube condenser in the neck of the flask, and boil the mixture as long as the residue appears to be dissolving (Note 2); then again evaporate the mixture to fuming (Note 3). If the substance has dissolved, add to it 10 to 20 ml of water and treat it by P. 11.

(*A*) *Procedure for Use when Only the Detection and Elimination of Silica Is Desired.*

Transfer the mixture to a platinum crucible, using as little water as possible, again evaporate it just to fuming, and allow it to cool (Note 4). Place the crucible under a hood, add to it 5 or 6 drops of 48 per cent HF (*Caution:* Notes 5, 6), and then warm it to 70° to 80°C. (Formation of bubbles, presence of silica.) If silica is present, add 5 ml more HF and keep the mixture just boiling (or evaporate it on a steam bath) as long as the residue seems to be dissolving. If the residue seems to be slowly dissolving, add repeatedly 1-ml portions of HF and of 16 n. HNO_3 after the previous portion has almost entirely evaporated or the $HClO_4$ begins to fume. Finally, evaporate the mixture almost to dryness (Note 7) and treat it by the last paragraph of this procedure.

(*B*) *Procedure for Use when an Estimation of the Silica Is Desired.*

Cover the flask with a watch glass and keep the mixture just fuming for 10 min., adding more $HClO_4$ if the mixture tends to solidify. Cautiously add 50 ml of water, heat the mixture almost to boiling for 2 to 3 min., and filter the hot solution through a quantitative paper. Wash the residue

with 10 to 20 ml of hot 0.12 n. HNO_3, collecting the washings with the filtrate (treat the filtrate by P. 11). Wash the precipitate and the entire filter with hot water until it is free of acid (Note 10).

Remove the filter from the funnel (see Note 5, P. XVIII *C*), fold it, and transfer it to a platinum crucible which has been previously heated and weighed. Heat with the low flame of an ordinary burner until the paper is dry, and then slowly increase the heat until the paper has completely charred and the carbon has burned without any flaming. Cover the crucible and slowly raise it to the highest temperature obtainable with a Meker or similar burner for 10 min., taking care that the platinum is exposed to an oxidizing flame only (Note 1, P. 8). Cool the crucible in a desiccator and weigh it. Repeat the heating and weighing of the crucible until its weight is constant to 0.2 mg. Add to the residue 2 ml of 9 n. $HClO_4$. Place the crucible under a hood, slowly add to it 5 or 6 drops of 48 per cent HF (*Caution:* Notes 5, 6), and warm it to 70° to 80°C. (Formation of bubbles, presence of silica.) If silica is present, add 3 ml more HF and evaporate the mixture almost to dryness, add 0.3 g of solid oxalic acid ($H_2C_2O_4 \cdot 2H_2O$), evaporate to dryness, and heat the crucible with a burner as before for 5 min. (Note 12). Allow it to cool and again weigh it. From the loss in weight calculate the amount of silica which was present. If there is any residue, place the crucible under a hood, add to it 1 to 2 ml of 9 n. $HClO_4$, evaporate the mixture almost to dryness, and treat it by the next paragraph.

Transfer the residue to a 200-ml flask with the aid of as little water as possible, add to it 5 ml of 6 n. HCl (Note 8), cover the flask with a watch glass, and heat the mixture just to boiling as long as the residue seems to be dissolving. Add to the mixture 10 to 20 ml of water, filter the hot solution through an ashless filter, and wash it with five 2-ml portions of hot water. Treat the filtrate by P. 11. Treat the residue by P. 8 (Note 9).

Notes:

1. If $HClO_4$ is not available, H_2SO_4 may be substituted for it. In that case, 10 ml of 6 n. H_2SO_4 should be used. No danger is involved in using perchloric acid at this point, as all organic material has been removed and

any reducing material has been oxidized by the treatments with concentrated nitric acid.

2. If much silver is present (as AgCl), it will dissolve only incompletely even on prolonged treatment. If the preliminary treatment in P. 3 has indicated the presence of silver, or if a characteristic residue of AgCl is seen to be present, it can be decomposed as follows:

> Add to the flask 1 to 3 ml of 9 n. HBr, heat the mixture, add 1 ml of 16 n. HNO_3, and again fume the $HClO_4$ (using a test-tube condenser to prevent undue evaporation) until the residue is dissolved. Replenish the HNO_3 as it is distilled. By this treatment, even 500 mg of silver can be brought into solution (see Note 9).

A test-tube condenser (see Fig. 27) is made by selecting a test tube which fits loosely in the neck of the flask and closing it with a two-hole rubber stopper. One hole of the stopper carries a glass tube which extends to the bottom of the test tube and is connected by rubber tubing to a water supply; the other hole carries a shorter glass tube with a piece of rubber tubing leading to a drain. Cold water is run in through the longer tube and out the shorter, the test tube being inserted in the flask so that it extends slightly below the neck.

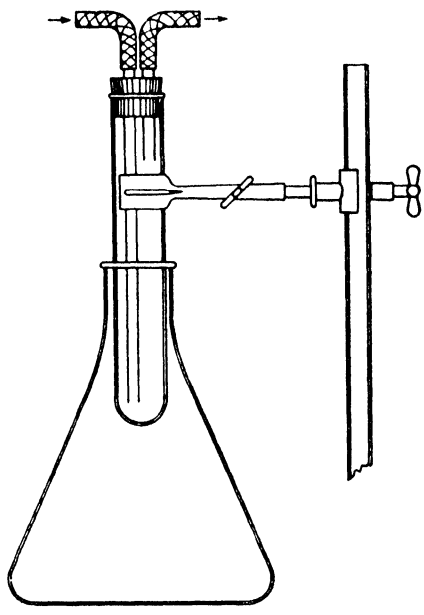

Fig. 27. A Test-Tube Condenser.

3. If the residue has not been appreciably attacked by the $HClO_4$ and HNO_3 and is thought to consist only of silica, the mixture can be evaporated to dryness in a platinum crucible, after which the residue can be heated and weighed as directed in the second paragraph of *B* of the procedure above without filtering out the precipitate. If the residue dissolves completely in the perchloric acid, the absence of silica is shown.

If manganese is present, it may be oxidized to the dioxide by the fuming $HClO_4$. If a dark precipitate forms on fuming the $HClO_4$, add $HCHO_2$ dropwise to the warm (*but not fuming*) mixture as long as this precipitate is being dissolved. Chromium would also be oxidized to chromate by the $HClO_4$ and would be reduced by the $HCHO_2$.

4. The $HClO_4$ can be cooled rapidly by repeatedly immersing the lower portion of the crucible momentarily in a dish of cold water.

5. HF is an *extremely dangerous chemical.* It produces painful burns if spilled on the hands, especially if it gets under the fingernails; in such cases a paste of borax and dilute acetic acid should be applied immediately. The fumes are irritating to the nose and lungs, and all operations with HF solutions should be carried out under an efficient hood.

6. Solutions containing HF cannot be handled in glass vessels. The most convenient apparatus—funnels, beakers, graduates, and so forth—for handling this reagent are those made from "transparent bakelite." If these are not available, apparatus made of hard rubber, or glass vessels which have been thoroughly coated with paraffin, should be employed.

7. If no residue is apparent, the solution should be completely evaporated in order to see if silica has been the only constituent of the residue brought to this procedure.

8. Hydrochloric acid is preferable for general use since it causes the reduction of any MnO_2 or chromate formed during the fuming with $HClO_4$; but as these would liberate chlorine the residue is transferred from the platinum vessel before adding the HCl. However, if the preliminary tests of P. 3 have indicated the presence of silver, HNO_3 should be substituted for the HCl, and in this case the acid may be added directly to the residue in the crucible.

9. By the above procedure most of the salts of volatile acids are taken into solution, and Cr_2O_3 and $Cr_2(SO_4)_3$ are slowly attacked (the chromium being oxidized to chromate by the hot $HClO_4$). Upon adding the HF, most silicates are decomposed and silicon and most silicides are also dissolved by the HF and HNO_3, or hot $HClO_4$. The residue remaining will be mainly sulfates of barium, strontium, and lead, a few silicates such as cyanite (Al_2SiO_5) and beryl ($Be_3Al_2Si_6O_{18}$), and also graphite, carborundum (SiC), and part of some slowly dissolving substances such as Al_2O_3 or SnO_2.

10. If the paper were ignited without washing out all of the $HClO_4$, it would burn with explosions that might cause loss of material from the crucible.

11. If only a determination of the silica in a cement, limestone, or similar material is desired, proceed as follows:

> Weigh out samples of about 1 g into 250-ml beakers. Pour 5 ml of water over each and then slowly add 5 ml of 12 n. HCl and 1 ml of 16 n. HNO_3. Let the mixture stand until vigorous action ceases, add 10 ml of 9 n. $HClO_4$, cover the beaker with a clock glass supported on glass hooks, and evaporate until the perchloric acid fumes copiously. Lower the clock glass to the rim of the beaker and keep the mixture fuming for at least 10 min., adding more $HClO_4$ if the mixture tends to solidify. Dilute the mixture with 50 ml of water, heat almost to boiling, and filter through a quantitative paper filter. Wash the precipitate and the entire filter with 25 ml of 1.2 n. HCl and then with hot water until it is substantially free from chlorides (Note 10).
>
> Treat the precipitate as directed in the second paragraph of *B* of the procedure above. Discard the filtrate. Correct the weight of silica first found by the weight of "non-volatile residue" remaining.

Water is added to the sample, and the acids are first added slowly, to prevent loss by spattering when treating a carbonate; hydrochloric acid is used because of its solvent action on metallic oxides, and nitric acid is used because of its oxidizing action. Larger volumes of the perchloric acid and of solution are used here than in the procedure above to minimize coprecipitation. If

it is not desired to correct for the "non-volatile residue," a porcelain crucible may be used instead of a platinum one.

12. If the perchloric acid mixture were evaporated to dryness and heated, all of the silica would be eliminated as SiF_4 and the excess hydrofluoric acid would be volatilized, but the perchlorates remaining after volatilizing the excess perchloric acid would be converted to chlorides upon being heated, whereas it is necessary to weigh the residue as oxides; also, the decomposition of these perchlorates in contact with the platinum at high temperature might lead to damage to the crucible. By discontinuing the evaporation when a small amount of perchloric acid is still present, the decomposition of the perchlorates into chlorine or other oxidizing constituents which might attack the platinum is avoided. By then adding a large excess of oxalic acid and again heating the crucible, the small amount of perchloric acid remaining is eliminated, the excess oxalic acid is sublimed, and the perchlorates are apparently converted to oxalates, which, upon further raising the temperature, are rapidly converted to oxides. Sulfuric acid is generally used for this process of volatilizing the silica and the excess hydrofluoric acid, but it has the disadvantage that it leaves sulfates, which have to be heated to a very high temperature in order to decompose them to oxides.

An experimental study of this oxalic acid method[8] has shown that silica can be eliminated from residues containing iron, aluminum, and calcium and that these latter elements can be quantitatively converted to their oxides by this treatment. In most cases the loss in weight of the platinum crucible during the process did not exceed 0.2 mg.

P. 8. Fusion of the Sample with Sodium Carbonate

Discussion. In most cases, after the treatment with perchloric and hydrofluoric acids, there will be no residue; however, in order to insure complete decomposition of a few insoluble sulfates and of very resistant materials, a fusion with sodium carbonate is provided. This treatment will usually decompose these more resistant substances, so that upon treating the melt with water the acidic constituents are extracted and the carbonate-oxide residue of the more basic elements can be separately dissolved in an acid. For a discussion of the principles involved in the metathesizing action of sodium carbonate, see the discussion of P. 81. The water extract is acidified and the two solutions are separately evaporated in order to dehydrate silica; they are not united, since in some cases this would cause the reprecipitation of insoluble salts. The group precipitates later obtained from these solutions may be combined.

It has been shown by Caley and Burford[9] that many of the insoluble compounds which would have resisted the previous treatments

[8] Unpublished experiments by J. Billheimer.

[9] Caley and Burford, *J. Ind. Eng. Chem., Anal. Ed.*, **8**, 63 (1936).

and which would usually have to be fused with sodium carbonate are dissolved by concentrated hydriodic acid. Thus, either ignited or native tin dioxide, which is only slowly, and usually incompletely, brought into solution by fusion with sodium carbonate, is rapidly dissolved by being heated to 90° to 95°C. with concentrated hydriodic acid; the reaction taking place is as follows:

$$SnO_2 + 4HI = SnI_4 + 2H_2O.$$

The SnI_4 is insoluble in the concentrated acid, and the formation of the characteristic reddish precipitate affords a sensitive indication of the presence of tin. As this treatment is much shorter and more easily carried out than the fusion with sodium carbonate, its optional use is provided for in Note 5 below; it is recommended that it be employed when the residue is thought to consist wholly or partly of tin dioxide.

The concentrated hydriodic acid is also effective in dissolving insoluble sulfates. Thus lead and strontium sulfates are readily dissolved, and barium sulfate and chromium dihydroheptasulfate are attacked more slowly. This solvent action is due to the reduction of sulfate to hydrogen sulfide, the type reaction being as follows:

$$MSO_4 + 10HI = MI_2 + 4I_2 + H_2S + 4H_2O.$$

The evolution of H_2S affords a sensitive indication of the presence of a sulfate. The article by Caley and Burford should be consulted for further details of the action of hydriodic acid with various insoluble compounds.

Procedure 8: FUSION OF THE SAMPLE WITH SODIUM CARBONATE. Transfer the dry residue (Note 1, P. 6) from P. 7 to a clean agate mortar and grind it to a powder (Note 5). Mix it thoroughly with 1 to 3 g of the purest Na_2CO_3 available, and transfer the mixture to a platinum (or nickel) crucible (Note 1) which has 1 g of the Na_2CO_3 spread over the bottom. Spread 1 g of the Na_2CO_3 over the top of the mixture and gradually heat the crucible with the oxidizing flame of a blast burner (or a large burner of the Meker type) until the entire mass is a viscous liquid. If particles of undecomposed substance remain, or if dark particles seem to be formed, cool the crucible somewhat and add to it in small portions 0.2 to 0.5 g of a mixture of equal weights of Na_2CO_3 and $NaNO_3$, and then again heat the crucible as directed above.

When decomposition of the substance seems complete, allow the crucible to cool (Note 2). Place the crucible and melt in a 200-ml beaker, add 30 ml of water, and boil the mixture until the melt is completely disintegrated. Filter the hot mixture through an ashless paper filter and wash the residue with 5 to 10 ml of 3 n. Na_2CO_3, collecting the washings with the filtrate. Treat the filtrate as directed in the last paragraph of this procedure.

Transfer the residue to a casserole (igniting the paper), moisten it with 1 n. HCl (Note 3), and evaporate it just to dryness without overheating any part of the residue. Treat the residue by the third paragraph of P. 6 (Note 4).

Make the filtrate just acid with HCl (Note 3), taking care to avoid spattering, and evaporate it just to dryness without overheating any part of the residue. Treat the residue by the third paragraph of P. 6 (Note 4).

Notes:

1. A platinum crucible is to be preferred, as, when properly used, it is not appreciably attacked by the flux and no extraneous constituents are introduced into the analysis.

There are certain precautions to be taken in order to avoid damage to platinum ware: Fusions of the above type should not be made in platinum vessels if elements of the Hydrogen Sulfide Group are present; these elements are easily reduced and then alloy with the vessel. Compounds containing sulfur, phosphorus, or arsenic should not be heated with reducing agents, especially organic matter, as when reduced they react with the platinum. When platinum vessels are heated with a gas flame, care should be taken to secure an oxidizing flame, as, in a reducing flame, carbon is deposited on the vessel, forming carbides of platinum, and hydrogen gas from the flame penetrates the platinum; either of these results in causing the metal to become brittle and more rapidly attacked. Platinum vessels are very little affected by fused sodium carbonate, but are rapidly attacked by more alkaline fluxes—for example, the hydroxides of the alkali and alkaline earth metals and even sodium or potassium cyanide. Strongly oxidizing fluxes, such as sodium peroxide or nitrate, should not be used. Moderate amounts of $NaNO_3$ added to a Na_2CO_3 fusion do not rapidly attack the crucible, but only a minimum amount of the nitrate should be used. Solutions which evolve the free halogens should not be put into platinum vessels. Sharp implements should not be used to remove "cakes" from platinum vessels, as the surface is easily scratched and then more rapidly attacked.

If a platinum crucible is not available, one of nickel may be substituted. This metal is not so satisfactory, because its greater thickness makes complete fusion more difficult to obtain and because it is appreciably attacked by the flux, several milligrams of nickel being dissolved with each fusion.

For this reason, nickel cannot be tested for after such a fusion. However, if much $NaNO_3$ is to be used, or if a stronger oxidizing flux, such as Na_2O_2, is to be employed, a nickel crucible should be used.

2. Several methods of facilitating the removal of the melt from the crucible may be employed. While still quite hot, the lower part of the crucible may be immersed in a vessel of cold water until the melt is cooled. After this treatment the melt will usually separate from the crucible quite readily when treated with a solvent. Another effective method is to insert a platinum wire into the molten mass and then to let it cool until it is solid. Upon reheating the crucible, the outer edges of the melt soften and the mass of the melt can be removed.

3. If arsenic, antimony, or tin compounds are thought to be present, HNO_3 should be substituted for HCl.

4. The only residue remaining after these residues are treated by P. 6 should be silica, resulting from the decomposition of a silicate which had not been entirely dissolved by the acid-HF treatment, but which had been decomposed by the Na_2CO_3 fusion. If it is desired to estimate the amount present, this can be done as directed in P. 7. Owing to the large amount of Na_2CO_3 used, and to the fact that in nearly all cases they would have been previously brought into solution, the analysis for the Alkali Group metals should not be made on the solutions obtained from the above fusions.

5. If the residue is thought to consist wholly or partly of tin dioxide, treat it as follows:

> Transfer the mixture to the bottom of a large test tube and add 2 to 5 ml of concentrated HI (sp. gr., 1.70). Sweep the air from the tube with a stream of CO_2, and then heat the mixture almost to boiling. (Red precipitate, usually accompanied by a yellowish sublimate on the tube just above the solution, presence of tin. Evolution of hydrogen sulfide, presence of insoluble sulfates.) Keep the mixture almost boiling as long as a reaction appears to be taking place.
>
> Add to the mixture 25 ml of water, filter out any precipitate, wash it with 20 ml of water, and treat the solution by P. 11. Treat the residue as directed in the procedure above.

See the discussion above in regard to the reactions taking place. In the concentrated acid, less than 0.2 mg of tin will give an easily recognizable red precipitate, which dissolves upon dilution of the solution.

Separation of the Basic Constituents into Groups

General discussion of the group separations. In devising a scheme for the systematic detection and separation of a large number of constituents, either cations or anions, the first step is the consideration of means of separating these constituents into a smaller number of groups. These groups are composed of constituents having certain common characteristics, so that a single reagent effects the detection and separation of the entire group. It is obviously more efficient to detect and separate these groups first than to attempt to detect and isolate each constituent separately. Thus entire groups of constituents are frequently absent and their individual analysis is avoided. Also, methods of singly separating each element or constituent from all of those remaining in the solution are often not available; furthermore, the accumulation in the solution of the many reagents that would have to be added would finally seriously interfere with further operations.

Tabular Outline II shows the methods which are used in this system of analysis for the separation of the basic elements into groups. It will be seen that there are first precipitated those elements whose sulfides are insoluble in a solution approximately 0.3 n. in hydrogen ion and from 0.3 to 0.6 n. in chloride ion; these elements constitute the Hydrogen Sulfide Group. This group is still too large for individual separations to be made effectively, so it is further divided by a treatment with sodium disulfide reagent into two smaller groups, consisting of, first, those elements of the Hydrogen Sulfide Group whose sulfides are insoluble in the sodium sulfide reagent, called the Copper Group, and, second, those elements whose sulfides dissolve in the sulfide reagent; these constitute the Tin Group.

By making the filtrate from the Hydrogen Sulfide Group slightly alkaline with ammonium hydroxide and providing for the presence of an excess of ammonium sulfide, there is precipitated a second large group, composed of those elements which form sulfides or hydroxides which are insoluble in a slightly alkaline solution; this group is termed the Ammonium Sulfide Group.

This large group is subdivided by dissolving the precipitate in hydrochloric acid, extracting the iron with ether, and then dividing

TABULAR OUTLINE II

Separation of the Basic Constituents into Groups

Solution of the Original Material:
Make the solution 0.3 n. in H^+ and Cl^-. Treat with H_2S. (P. 11)

Precipitate:
Hydrogen Sulfide Group elements as sulfides
Treat with Na_2S-Na_2S_2 Reagent. (P. 12)

- **Residue:** Copper Group — Ag, Pb, Bi, Cu, Cd as sulfides — *Analyze by P. 21–30.*
- **Solution:** Tin Group — Hg, As, Sb — Sn as sulfo-salts — *Analyze by P. 41–49.*

Filtrate: *Treat with NH_4OH and $(NH_4)_2S$.* (P. 51)

Precipitate:
Ammonium Sulfide Group as sulfides and hydroxides
Dissolve in 6 n. HCl, treat with ether. (P. 52)

- **Ether solution:** Iron as chloride (P. 53)
- **Aqueous solution:** *Neutralize with $NaHCO_3$, add $(NH_4)_2C_2O_4$. Treat with H_2S.* (P. 55)
  - **Precipitate:** Zinc group — Zn, Ni, Co as sulfides — *Analyze by P. 61–66.*
  - **Filtrate:** Aluminum Group — Mn, Al, Cr as complex oxalates — *Analyze by P. 71–75.*

Filtrate: *Evaporate, add $(NH_4)_2CO_3$ and C_2H_5OH.* (P. 81)

- **Precipitate:** Alkaline Earth Group — Ba, Sr, Ca, Mg as carbonates — *Analyze by P. 81–89.*
- **Filtrate:** *Heat to expel ammonium salts.* (P. 91) — Alkali Group — K, Na as nitrates — *Analyze by P. 91–95.*

the remaining elements into two groups by a treatment with hydrogen sulfide in an almost neutral buffered solution containing a relatively high concentration of oxalate ion. Those elements which are precipitated as their sulfides from this solution constitute the Zinc Group; those remaining in the solution constitute the Aluminum Group.

The filtrate from the Ammonium Sulfide Group precipitation is treated (after evaporation) with ammonium carbonate, ammonium hydroxide, and ethyl alcohol. The elements thus precipitated as their carbonates constitute the Alkaline Earth Group.

Of the basic elements provided for in this system there now remain in the original solution only sodium and potassium, and these constitute the Alkali Group. Ammonia is tested for in a separate portion of the sample, as it has been introduced with the reagents in the course of the analysis.

The relative advantages of these separations, as compared with other methods which are at times used for effecting the same or similar separations, are discussed later in connection with these procedures.

Tabular Outline II shows the reagents used in these group separations and the elements which constitute each of the groups.

TABULAR OUTLINE III

Precipitation of the Hydrogen Sulfide Group and Separation of the Copper and Tin Groups

Solution of the Original Material (30 milli-equivalents of acid; volume 50 ml):
Add 30 milli-equivalents of NH_4Cl (no precipitate, absence of Ag).
Heat, saturate with H_2S.
Dilute to 100 ml, again saturate with H_2S. (P. 11)

Precipitate:	Filtrate:
Hydrogen Sulfide Group Ag_2S, PbS, Bi_2S_3, CuS, CdS Hg, HgS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2 S	Elements of the Ammonium Sulfide, Alkaline Earth, and Alkali Groups (to P. 51)

Treat with Na_2S-Na_2S_2 reagent. (P. 12)

Residue:	Solution:
Copper Group sulfides Ag_2S, PbS, Bi_2S_3 CuS, CdS *Analyze by P. 21–30.*	Tin Group as sulfo-salts $HgS_2^=$, $AsS_4^{\equiv}$, $SbS_4^{\equiv}$, $SnS_3^=$ *Add H_2SO_4.* (P. 13)

Precipitate:	Filtrate:
Tin Group HgS, As_2S_5, $Sb_2S_4 \cdot S$, SnS_2, S. *Analyze by P. 41–49.*	*Discard.*

Precipitation of the Hydrogen Sulfide Group and Separation of the Copper and Tin Groups

P. 11. Precipitation of the Hydrogen Sulfide Group

Discussion. A marked departure from conventional systems of qualitative analysis is found in the elimination of the so-called Silver Group, usually separated by filtering out the precipitate produced by the addition of chloride ion to the cold nitric or sulfuric acid solution of the original substance. This precipitate would contain, as chlorides, all of the silver and mercurous mercury, most of the lead when a large quantity is present, and, less frequently, part of any bismuth or antimony as the oxychloride. The instructional value of this treatment is apparent. The analytical value, which is in the quick detection and removal of silver, the information gained as to the state of oxidation of mercury, and some information as to the amount of lead present, is more than offset by the following facts: The information regarding the state of oxidation of mercury is obtained only rarely, as nearly all mercurous compounds are so insoluble as to require the action of oxidizing agents in their solution; lead has to be detected and removed from two places in the system of analysis; and any precipitate produced by the addition of the chloride causes the complete analysis of the Silver Group to be carried out, involving the detection and separation of lead, mercury, and possibly bismuth and antimony, all of which are then again tested for and separated in the analysis of the Copper and Tin Groups. Furthermore, the detection and estimation of silver and mercurous mercury, when they are precipitated together as chlorides, offer some difficulty. Again, as silver nearly always occurs, both native and in alloys, together with elements of either the Tin or the Copper Group, its previous separation usually does not obviate an analysis of these groups. Finally, an incidental, though usually conclusive, test for silver is made in this first procedure; if its presence is indicated, it is easily detected and removed immediately after dissolving the Copper Group sulfides, at which place it can advantageously be precipitated and coagulated in a hot solution; if it is shown to be absent, that procedure can be omitted entirely.

Sulfide Separations. Separations which are dependent upon the solubility of the sulfides of the elements are more commonly used

in qualitative analysis than any other method. This is true because so many of the elements form insoluble sulfides, because these sulfides vary through such a wide range of solubility, and because the sulfide ion concentration can be varied and controlled over such a wide range by controlling the hydrogen ion concentration of the solution. This range is shown in Table IX, where the hydrogen and sulfide ion concentrations, and also the concentration of the undissociated hydrogen sulfide, are shown for various solutions. The data for this table are taken mostly from the calculations of Knox[1] and are for solutions at 25°C.

TABLE IX

ION CONCENTRATIONS IN SULFIDE SOLUTIONS

Solution	H^+	H_2S	$S^=$
Solutions saturated with H_2S:			
HCl, HNO_3, 1 f.	1[a]	0.1	2×10^{-23}
$HC_2H_3O_2$, 1 f.	4.2×10^{-3}	0.1	6×10^{-19}
Water	9×10^{-5}	0.1	1.3×10^{-15}
Solutions of the following:			
NH_4HS, 1 f.	7×10^{-9}	0.07	1.6×10^{-7}
$(NH_4)_2S$, 1 f.	5×10^{-10}	5.5×10^{-3}	2.4×10^{-6}
NaHS, 1 f.	3.3×10^{-11}	3.6×10^{-4}	3.6×10^{-5}
Na_2S, 1 f.	1.3×10^{-14}	1.3×10^{-7}	0.09

[a] The activity coefficient of HCl is 0.83, and that of HNO_3 is 0.73 in 1 f. solutions.

The reason for this wide range in the sulfide ion concentrations is evident when the ionization of hydrogen sulfide as a dibasic acid is considered, thus:

$$\frac{[H^+]\,[HS^-]}{[H_2S]} = 9.1 \times 10^{-8} \qquad (1)$$

and

$$\frac{[H^+]\,[S^=]}{[HS^-]} = 1.2 \times 10^{-15}. \qquad (2)$$

If these two are combined, there is obtained the expression

$$\frac{[H^+]^2\,[S^=]}{[H_2S]} = 1.1 \times 10^{-22}, \qquad (3)$$

which more clearly shows the effect of the hydrogen ion concentration on the sulfide ion concentration. A solution saturated with hydrogen sulfide at atmospheric pressure and room temperature is

[1] Knox, *Trans. Faraday Soc.*, **4**, 47 (1908).

approximately 0.1 m. in H_2S, so that for a saturated solution there can be used the simplified expression

$$[H^+]^2 [S^=] = 1.1 \times 10^{-23} \quad (4)$$

The extreme difference which exists in the calculated solubility products of sulfides is shown in Table X, where the values of this constant for a few typical sulfides are given.

Using the value 1×10^{-24} for the solubility product of zinc sulfide, it is calculated that, in order to hold 100 mg of zinc in 100 ml of solution, the hydrogen ion concentration must be greater than approximately 0.4 m. Experimentally, more than 100 mg of zinc can be held for a reasonable length of time in 100 ml of a solution

TABLE X

THE SOLUBILITY PRODUCTS OF CERTAIN SULFIDES[a]

(Arranged in the Order of Their Precipitation as the Hydrogen Ion Is Decreased)

Sulfide	Solubility Product	Sulfide	Solubility Product
HgS	10^{-54}	ZnS (β form)	10^{-24}
CuS	10^{-42}	CoS	10^{-27}
Ag_2S	10^{-50}	NiS	10^{-27}
CdS	10^{-28}	FeS	10^{-22}
PbS	10^{-28}	MnS (flesh color)	10^{-16}
ZnS (α form)	10^{-25}	MnS (green)	10^{-22}

[a] The data for this table were taken from the calculations of Kolthoff, *J. Phys. Chem.*, **35**, 2711 (1931). Reference should be made to this article for a general treatment of the problem of the solubility products of the metallic sulfides.

0.3 m. in hydrogen ion, and this apparent discrepancy illustrates a fact which should be emphasized at this point, namely, that it is extremely hazardous to use these values indiscriminately in solubility calculations and to attempt to predict therefrom the conditions under which separations may be made. This can be done in certain cases, but often other factors, such as complex ion formation, rate of precipitation, and adsorption effects, may make such calculations of little value or even misleading. It is also impossible to derive reliable solubility products from the solubilities of the sulfides of arsenic, antimony, and tin, as, owing to their acidic nature and to their tendency to form complex ions, especially in chloride solutions, even an approximate estimate of the concentration of their

TABLE XI

THE PRECIPITATES FORMED BY THE COMMON ELEMENTS IN VARIOUS SULFIDE SEPARATIONS

Element and Oxidation State	Solution Saturated with H_2S							Sulfide Solutions	
	HCl, 9 n. 100°C.	H_2SO_4, 9 n. 100°C.	HCl, 3 n. 100°C.	HCl, 0.3 n. NH_4Cl, 0.3 n.	H^+, 10^{-2} m. (HSO_4^- and $SO_4^=$)[g]	H^+, 10^{-4} m. ($HC_2H_3O_2$ and $C_2H_3O_2^-$)	H^+, 10^{-7} m. (CO_2 and HCO_3^- oxalate present)	OH^-, 10^{-5} m. $(NH_4)_2S$[j] NH_4OH	Na_2S, 3 n. NaOH, 1 n.
As^{V}[a]	As_2S_5[f]	As_2S_5[f]	As_2S_5[f]	As_2S_5[f]	As_2S_5[g]	As_2S_5[g]	$(AsS_4^=)$	$(AsS_4^=)$	$(AsS_4^=)$
As^{III}	As_2S_3	As_2S_3	As_2S_3	As_2S_3	As_2S_3	As_2S_3	$(AsS_3^=)$	$(AsS_3^=)$	$(AsS_3^=)$
Hg^{II}[b]		HgS	HgS	HgS	HgS	HgS	HgS	HgS	$(HgS_2^=)$
Cu^{II}[c]		CuS	CuS	CuS	CuS	CuS	CuS	CuS[i]	CuS
Ag^{I}		Ag_2S	Ag_2S	Ag_2S	Ag_2S	Ag_2S	Ag_2S	Ag_2S	Ag_2S
Sb^{V}		Sb_2S_5	Sb_2S_5	Sb_2S_5	Sb_2S_5	Sb_2S_5	Sb_2S_5	$(SbS_4^=)$	$(SbS_4^=)$
Sb^{III}		Sb_2S_3	Sb_2S_3	Sb_2S_3	Sb_2S_3	Sb_2S_3	Sb_2S_3	$(SbS_3^=)$	$(SbS_3^=)$
Bi^{III}		Bi_2S_3		Bi_2S_3	Bi_2S_3	Bi_2S_3	Bi_2S_3	Bi_2S_3	Bi_2S_3
Sn^{IV}				SnS_2	SnS_2	SnS_2	SnS_2	$(SnS_3^=)$	$(SnS_3^=)$
Cd^{II}				CdS	CdS	CdS	CdS	CdS	CdS
Pb^{II}				PbS	PbS	PbS	PbS	PbS	PbS
Sn^{II}				SnS	SnS	SnS	SnS	SnS[k]	$(SnS_3^=)$
Zn^{II}				[h]	ZnS	ZnS	ZnS	ZnS	ZnS
Co^{II}					[h]	CoS	CoS	CoS	CoS
Ni^{II}						NiS	NiS	NiS	NiS
Fe^{II}[d]						[h]	FeS	FeS	FeS
Mn^{II}							$(Mn(C_2O_4)_2^=)$	MnS	MnS
Cr^{III}						[i]	$(Cr(C_2O_4)_3^=)$	$Cr(OH)_3$	$(Cr(OH)_4^-)$[m]
Al^{III}						[i]	$(Al(C_2O_4)_3^=)$	$Al(OH)_3$	$(Al(OH)_4^-)$
	Separation of As from Sb and Sn	Separation of Cu from Cd	Separation of Sb from Sn	Precipitation of the H_2S Group	Separation of Zn from Co, Ni, etc.	Separation of Zn, Co, Ni from Mn	Separation of the Zn and Al Groups	Separation of the Cu and Sn Groups[l]	Separation of the Cu and Sn Groups

Where no precipitate is indicated, it has been found that 1 mg of the constituent can be present in 50 to 100 ml of the solution without forming a precipitate under the conditions indicated; larger amounts may be partially precipitated. Formulas in parentheses show the complex ions formed in solution.

[a] The oxidation number of the elements is indicated by Roman numerals rather than by the charge on the ions—for example, Hg^{++}, As^{+++}—as is often done. The latter is likely to convey the impression that these simple ionic species predominate in the solution; whereas, because of hydrolysis to an acidic form, or to complex ion formation, this is often not the case.

[b] When a mercurous salt is treated with H_2S, HgS and Hg are precipitated.

[c] The solubility of cuprous sulfide is approximately of the same order of magnitude as that of cupric sulfide.

[d] Fe^{III} is reduced to Fe^{II} by H_2S in acid solutions; Fe_2S_3 is formed in alkaline solutions.

[e] This H^+ concentration is also frequently obtained by the use of the proper ratio of formic acid and a formate.

[f] Depending upon the temperature and other conditions, varying amounts of As_2S_3 and S are also formed.

[g] The rate of the precipitation is very slow. Also see Note *f*.

[h] Depending upon conditions, these elements may be coprecipitated by other sulfides.

[i] These elements will hydrolyze and precipitate if present in considerable amounts.

[j] CuS dissolves to a slight extent. See discussion of P. 12.

[k] SnS is only slightly soluble in $(NH_4)_2S$; it is oxidized and dissolves in $(NH_4)_2S_2$.

[l] By adding $(NH_4)_2S_2$ and a higher concentration of NH_4OH, the higher oxidation states of the sulfo-salts are formed; these conditions are frequently used for separating arsenic, antimony, and tin from mercury, lead, bismuth, copper, cadmium, and silver.

[m] $Cr(OH)_3$ dissolves in dilute alkali, owing to the formation of a stable colloidal system, and may be reprecipitated by boiling. It forms chromite in concentrated hydroxide solutions.

various ionic species cannot be made. Rate effects may also be of great importance; thus there is considerable evidence that the precipitation of zinc sulfide is an extremely slow process, and that, if an equilibrium were attained, zinc sulfide would precipitate from solutions 0.2 to 0.3 m. in hydrogen ion. Probably because of similar effects, nickel and cobalt sulfides cannot be precipitated from solutions in which the hydrogen ion is 0.1 m.; yet they are dissolved so slightly, or slowly, in 1 m. hydrochloric acid that this treatment is often used to separate them from the other elements of the Ammonium Sulfide Group—it is to be noted that the values given for their solubility products would lead one to predict that they would precipitate from more strongly acid solutions than does zinc. It is also to be seen that, by working in alkaline solutions and increasing the sulfide ion concentration, the insoluble sulfides of certain acidic and amphoteric elements are dissolved as a result of the formation of soluble sulfo-salts; this behavior is the basis for the very important separation of the so-called Copper and Tin Groups.

Because of the importance of the sulfide separations, and because of the difficulty in treating them from theoretical considerations, the behavior of the elements of the Hydrogen Sulfide and Ammonium Sulfide Groups under the conditions attained in certain of the various sulfide separations is presented in Table XI. In this table the precipitates or distinctive ions which are formed are shown; where no, or in some cases incomplete, precipitation is obtained under the conditions indicated, the space is left vacant. The elements have been arranged in the order of their precipitation as the hydrogen ion concentration of the solution is decreased.

This table emphasizes a very important principle, namely, that not only does the hydrogen ion concentration affect the precipitation of the sulfides, but that the anions present also exert a very decided effect. Thus it is seen that in 9 n. hydrochloric acid only the sulfides of arsenic are precipitated, but that from 9 n. sulfuric acid there are precipitated with these the sulfides of mercury, copper, silver, antimony, and bismuth. This difference could be attributed (1) to the abnormal activity of hydrochloric acid in solutions of this concentration (the activity coefficient having been found to be much greater than unity), (2) to the incomplete ionization of the hydrosulfate ion, which would correspondingly decrease the hydrogen ion activity of the sulfuric acid solution, or (3) to the formation of what are termed complex or coördination compounds. These compounds are in general formed because of the tendency of positive ions to attract negative ions or neutral groups around them. The

greater the positive charge on the ion, the more stable such compounds are likely to be, and the greater the number (termed the coördination number) of negative or neutral groups which can be held. As will be observed later, this tendency is of significance, especially in concentrated solutions, in determining the reactions of all of the metallic elements except those of the Alkali Group and the Alkaline Earth Group. The following are examples of some of the chloride complex ions of the Hydrogen Sulfide Group elements: $HgCl_4^=$, $CuCl_4^=$, $AgCl_2^-$, $BiCl_4^-$, $SnCl_6^=$, $SnCl_4^=$, $CdCl_4^=$, and $PbCl_4^=$. The other halogen acids tend to form similar compounds; the tendency is much less pronounced with sulfuric acid and practically inappreciable with nitric or perchloric acid.

In order to decide which of the three effects mentioned above is the most important, a study of the precipitation of the Hydrogen Sulfide Group elements from 9 n. perchloric acid was made. This acid was used because the hydrogen ion activity in the 9 n. solution has been found to be much greater than that in 9 n. hydrochloric acid, because its solutions do not oxidize hydrogen sulfide, even at this concentration (as would nitric acid), and because (as mentioned above) there is practically no tendency toward complex ion formation. It was found from these experiments that, in addition to the sulfides precipitated from 9 n. sulfuric acid, stannic sulfide also formed in the 9 n. perchloric acid. This shows that the predominant factor preventing the precipitation of these sulfides from 9 n. hydrochloric acid is the formation of the chloride complex ions; this conclusion is emphasized by the fact that bismuth and stannic sulfides are not precipitated from even 3 n. hydrochloric acid.

It would seem possible to effect the separation of a group of elements from the main solution by precipitation with hydrogen sulfide in a solution made 9 n. in sulfuric or perchloric acid, or even 3 n. in hydrochloric acid. However, the addition of sulfuric acid would cause the precipitation of lead and alkaline earth metals as sulfates; perchloric acid is somethat expensive and might cause partial precipitation of potassium, and, furthermore, these separations are so critical upon the adjustment of the acid concentration as to be unsatisfactory for general use. For these reasons the first group separation in this system of analysis is made by the precipitation of those elements which form sulfides insoluble in a solution approximately 0.3 n. in hydrogen ion and from 0.3 to 0.6 n. in chloride ion; these elements will be hereafter designated as the Hydrogen Sulfide Group.

In order to begin the precipitation of these elements under condi-

tions which lessen the tendency of certain other elements (especially zinc, nickel, and cobalt) to be precipitated with them, ammonium chloride is added to the solution of the original substance, which should contain 30 milli-equivalents of acid, and it is first heated and saturated with H_2S in a volume of 50 ml, the hydrogen ion concentration being 0.6 n. This, incidentally, causes certain of the sulfide precipitates to coagulate into a more easily filtered form, and to precipitate more completely small quantities of arsenic when it is present in the quinque-positive state. The solution is finally diluted to 100 ml, cooled, and again saturated with H_2S in order to precipitate more completely the sulfides of lead and stannous tin.

The experiments of Noyes and Bray[2] show that under conditions similar to those of this procedure 1 mg of any of the metals of the Hydrogen Sulfide Group will give a perceptible precipitate, and that even 500 mg of zinc, nickel, and cobalt, the more readily precipitated of the other elements, remain in solution. Noyes and Bray (*loc. cit.*) also show that with 500 mg of certain elements of the Copper Group even 1 mg of zinc, nickel, and cobalt pass into the filtrate in sufficient quantity to be detected.

The work of Feigl[3] indicates that with large quantities of the Ammonium Sulfide Group elements coprecipitation may be expected to occur to an appreciable extent. Feigl found that, when mercuric sulfide was precipitated from an acid solution containing zinc chloride, it carried with it 2 to 3 per cent of the zinc, and that, when stannic sulfide was precipitated from a hydrochloric acid solution with cobalt present, it contained considerable cobalt sulfide. In experiments made to study this effect it was found that, upon taking 250 mg of mercury (as mercuric chloride) and 250 mg of zinc (as zinc nitrate) in 100 ml of a solution containing 30 milli-equivalents of nitric acid and saturating the cold solution with hydrogen sulfide, about 50 mg of the zinc were coprecipitated with the mercuric sulfide. However, when the precipitation was made under the conditions of the procedure below less than a milligram of zinc was coprecipitated; the coprecipitation of cobalt with stannic tin was also shown to be negligible. Kolthoff and Pearson[4] have shown that under certain conditions zinc is carried down by copper sulfide; this is apparently due to the adsorption of zinc on the surface of the copper sulfide,

[2] Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 188 (1907); Noyes and Bray, *Qualitative Analysis for the Rare Elements*, Macmillan, 1927, p. 374.

[3] Feigl, *Z. anal. Chem.*, **65**, 25 (1924).

[4] Kolthoff and Pearson, *Z. phys. Chem.*, **36**, 549 (1932).

with the subsequent formation of zinc sulfide. Since they found that other active surfaces would cause the same effect, it was assumed that the solution was supersaturated with respect to zinc sulfide. Experiments have shown that under the conditions of this procedure less than a milligram of zinc is carried out when 250 mg each of copper and of zinc are present. (For a detailed discussion of the precipitation of the sulfides of zinc, nickel, and cobalt, see the discussion of P. 61.)

The precipitation of quinque-positive arsenic by hydrogen sulfide from acid solutions has been extensively studied,[5] and the experimental facts are as follows: A cold solution of an arsenate in *dilute acid* will absorb considerable hydrogen sulfide gas before any precipitation takes place; after some time, a precipitate of arsenious sulfide is formed. From cold *concentrated hydrochloric acid* arsenic pentasulfide is precipitated; if the solution is hot, a mixture of trisulfide and pentasulfide is obtained. From the investigations which have been made it appears that the first reaction taking place in a cold dilute acid solution is the formation of sulfo-arsenic acids (of the type H_3AsO_3S), which then slowly decompose to give sulfur and arsenious acid. Arsenious acid then rapidly reacts with hydrogen sulfide to give arsenious sulfide. In a cold concentrated acid solution the basic ionization of the arsenic into ions such as AsO_2^+ takes place to a much larger extent, and these react directly with hydrogen sulfide to give the pentasulfide. When the solution is heated, there appears to be a much more rapid decomposition of the sulfo-arsenic acids, producing sulfur and arsenious sulfide, and there may also be a direct oxidation of hydrogen sulfide by the arsenic acid, represented by the equation

$$H_3AsO_4 + H_2S + 3H^+ = As^{+++} + S_{(s)} + 4H_2O.$$

Thus a mixture of the two sulfides and sulfur is often obtained. It is seen that the rate of precipitation is favored by increasing the concentration of the hydrogen ion and of the hydrogen sulfide, and

[5] McCay, *Am. Chem. J.*, **9**, 174 (1887), **10**, 459 (1888); *Z. anorg. allgem. Chem.*, **29**, 36 (1910); *J. Am. Chem. Soc.*, **24**, 661 (1902); McCay and Foster, *Z. anorg. allgem. Chem.*, **41**, 452 (1904). Bosek, *J. Chem. Soc.*, **67**, 515 (1895), and Brauner, *ibid.*, **67**, 527 (1895), have shown that, when hydrogen sulfide is passed into a solution of quinque-positive antimony, rapid precipitation occurs but the ratio of Sb_2S_5 to Sb_2S_3 is greater the more rapid the treatment with H_2S, the colder the solution, and, up to 3 to 4 n. HCl, the greater the acidity; only under very carefully controlled conditions can pure Sb_2S_5 be precipitated; above 95°C., largely Sb_2S_3 is obtained.

by raising the temperature. Under the conditions of this procedure, precipitation would be incomplete even after saturating the solution at 90° to 100°C. with H_2S at atmospheric pressure for an hour. Rapid precipitation can be obtained by increasing the hydrochloric acid concentration to 6 n. or greater, but this is not desired, as the solution is to be next neutralized. Precipitation can also be obtained by evaporating the solution to dryness, dissolving the residue in 6 n. hydrochloric acid, and precipitating the arsenic from this solution. However, the evaporation of such a large volume of solution without danger of loss is time-consuming, and, in addition, considerable amounts of sulfate are formed, causing possible loss of barium and strontium. The addition of hydriodic acid to the solution, which catalyzes the reduction of arsenic acid by hydrogen sulfide, was tried under various conditions and did increase the rate of precipitation of the arsenic, but not sufficiently to justify its use. Finally, the effect of heating the solution with hydrogen sulfide under pressure was investigated, and experiments have shown that all but 1 or 2 of 500 mg of arsenic, when heated with H_2S under pressure as directed in the procedure below, will be precipitated in 15 min. and that precipitation is practically complete in 30 min.

Procedure 11: PRECIPITATION OF THE HYDROGEN SULFIDE GROUP. The solution of the sample, prepared by P. 5 to P. 8, should be in a 200-ml flask and should contain 30 milli-equivalents of acid in a volume of 50 ml.

Heat the solution of the sample almost to boiling (Note 1), and, if HCl has not been used in the preparation of the solution, add to it drop by drop, 1 ml of 3 n. NH_4Cl. (No precipitate, absence of silver. Note 2.) Add to the solution 10 ml of 3 n. NH_4Cl, heat it almost to boiling, and saturate it with H_2S (Note 3); add slowly 50 ml of water, cool, and again saturate with H_2S. (Black or colored precipitate, presence of the Hydrogen Sulfide Group. Note 4.)

If there is no precipitate, immediately pour the solution into a 500-ml flask (Note 5), boil it until the H_2S is completely expelled (Note 1, P. 51), and treat it by P. 51 (Note 6).

If there is a precipitate, let it settle and filter the mixture with the aid of suction through an asbestos filter (Note 7), decanting as much as possible of the clear solution (Note 8).

Wash the precipitate (Notes 9, 11) with three to six 5-ml portions of 0.12 n. HNO_3 (Note 12), add these washings to the filtrate, and treat it as directed in the next paragraph (Note 13). Wash the precipitate thoroughly with hot water (or, if it begins to run through the filter, with 0.12 n. HNO_3 saturated with H_2S), discarding these washings (Note 14). Treat the precipitate by P. 12, after combining with it any further precipitate obtained in the next part of this procedure.

Heat the filtrate almost to boiling and again saturate it with H_2S (Note 15). If no further precipitate forms, immediately pour the solution into a 500-ml flask (Note 5), boil it until the H_2S is completely expelled (Note 1, P. 51), and treat it by P. 51 (Note 6).

If a precipitate forms, transfer the solution, with the aid of as little 0.3 n. HNO_3 as possible, to a stout 200-ml large-mouth pyrex bottle or short-neck, round-bottom flask. Cool the mixture, saturate it with H_2S, insert a clean rubber stopper into the mouth of the flask, and tie it into place with wire or stout cord. Immerse the mixture in a beaker of boiling water for 15 min. Remove the flask and allow the contents to cool before removing the stopper. If a large precipitate has formed, again saturate the cool mixture with H_2S, stopper it, and heat it as before for 10 min. Filter and wash the precipitate as directed in the third paragraph of this procedure. Immediately pour the filtrate into a 400-ml flask (Note 5), boil it until the H_2S is completely expelled (Note 1, P. 51), and treat it by P. 51.

Notes:

1. When it is directed that a solution be heated "almost to boiling," it should be brought to 80° to 90°C. only. In the above case, if the solution is heated to boiling, it frequently superheats, so that, when it is shaken (or when H_2S is passed into it), such a rapid evolution of steam takes place as to cause loss by spattering.

When it is directed that a solution be heated "just to boiling," it should be brought to the boiling point but not heated so as to cause rapid loss of volume by evaporation.

2. If no precipitate is produced here, the absence of silver is shown, and, if no oxidizing agents have been used in the preparation of the solution, the absence of mercurous mercury. A local precipitate which redissolves does not prove the presence of these elements, as it may be caused by a large quantity of lead, bismuth, or antimony; the precipitate produced by the latter substances is likely to be more crystalline or granular, and differ in

appearance from the more "curdy" silver chloride; even a large quantity of lead will remain in the hot solution. The formation of a permanent precipitate upon later adding the additional NH_4Cl indicates the presence of these elements; such a precipitate should not be filtered out, as it will be metathesized by the H_2S. Only 1 ml of NH_4Cl is added at this point in order to minimize the possibility of precipitating lead chloride; also the solubility of AgCl is increased by a large excess of chloride ion.

If desired, an approximate estimate of the amount of silver present can be made by adding the ammonium chloride from a 1-ml measuring pipet and noting the volume added when the next drop no longer produces a perceptible precipitate. The solution should be vigorously shaken after each drop, and the precipitate should be allowed to settle somewhat so that the effect of the next portion can be observed.

If mercurous mercury is known to be absent, the silver may be precipitated and removed at this point by carefully avoiding an excess of ammonium chloride, filtering the solution while keeping it hot, and washing the precipitate with hot 0.3 n. HNO_3.

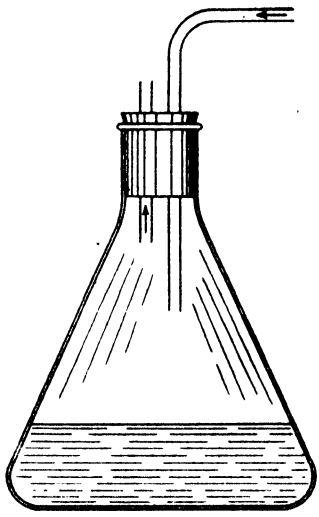

Fig. 28. Precipitation with Hydrogen Sulfide.

3. When a solution is to be saturated with H_2S, the flask should be fitted with a tight-fitting two-hole rubber stopper with an inlet tube in one hole extending about one-half the distance to the solution and a shorter tube in the second hole (see Fig. 28). Then pass the gas into the flask at the pressure of the generator until the air has been swept out, and close the second tube by holding a finger over it or by providing it with a short piece of rubber tubing carrying a pinch clamp. The solution should be carefully swirled until it is saturated; this is indicated when the gas no longer bubbles through the wash bottle. If the H_2S is generated by the use of iron sulfide and acid, it may also contain some hydrogen and volatile hydrocarbons formed from the iron and carbon usually present in commercial ferrous sulfide. Because of this, it is advisable occasionally to let the gas escape for a few seconds so that these gases do not accumulate in the flask. It is not recommended that the gas be bubbled directly into the solution and allowed to escape; this practice is wasteful of the gas, causes spattering of the solution, and often causes difficulty in removing the precipitate which forms on and inside the inlet tube.

4. If only a fine, entirely white precipitate is obtained by the treatment with H_2S, it is due to the oxidation of H_2S to S by some oxidizing substance, such as ferric iron or permanganate, present in the solution. Such a precipitate should be ignored, and the mixture should be treated as if no precipitate were obtained.

The color of the various sulfides is as follows: Ag_2S, black; PbS, black (the first precipitate produced in hydrochloric acid solutions may be orange-

red; this changes to dark brown, and then to black; the first precipitate is mainly Pb_2SCl_2, lead sulfodichloride; the subsequent precipitates are mixtures of this and lead sulfide in varying proportions); Bi_2S_3, brown to black; Cu_2S, black; CuS, black; CdS, yellow; HgS, black (the precipitate first produced in hydrochloric acid solutions is white mercury sulfodichloride, Hg_2SCl_2; this changes to yellow, brown, and then black; in solutions above 3 to 4 n. in hydrochloric acid, the intermediate colors, which are mixed compounds similar to those formed by lead, may persist for a considerable period of time); As_2S_3, yellow; As_2S_5, yellow; Sb_2S_3, orange-red, changing to black on long standing or on heating; Sb_2S_5, orange-red; SnS, brown; and SnS_2, yellow.

5. When a solution is poured from one vessel to another, or through a filter, it should be guided with a stirring rod in order to prevent it from splashing or running down the underside of the lip of the vessel from which it is poured. The solution adhering to the sides of the original vessel should be carefully drained off, and then the sides should be washed down with several successive small portions of water or other suitable wash solution (in this case two to four portions of 2 or 3 ml of water).

6. The H_2S should be expelled from the solution as soon as possible, as it tends to become oxidized on standing in air. This increases the amount of sulfate which may be subsequently formed and increases the possibility of the loss of barium or strontium in later procedures.

7. Asbestos filters are frequently used in these procedures where it has been found that the precipitate can be more readily dissolved from the asbestos than from paper and where successive operations would lead to an accumulation of pulp, which makes more difficult the subsequent operations. Asbestos filters are also more readily used with suction. The general discussion of the filtering of precipitates accompanying P. XVIII, "The Gravimetric Standardization of a Hydrochloric Acid Solution," should be consulted.

An asbestos filter for use here is made by placing in a medium-size glass funnel (or a funnel such as is used in quantitative determinations for holding perforated porcelain crucibles) a perforated porcelain plate (the so-called Witte plate) about 2 cm in diameter, and preferably having a beveled edge, and then pouring through this a water suspension of acid-washed asbestos fibers until a layer 1 to 2 mm thick is formed. The layer should be built up slightly thicker around the edges of the plate. The mat should then be washed until the wash water is free from fibers in order that a clear filtrate may be obtained. The asbestos should be prepared for use according to the directions in the Appendix.

Suction flasks (heavy conical flasks with thick walls and a side neck) of the conventional type may be used with the asbestos filters. As these are often available only in large sizes and as solutions cannot be safely heated in them, it is at times convenient to filter directly into the conical flask in which the filtrate is next to be treated. This can be done by selecting a stout flask and fitting it with a two-hole rubber stopper, carrying the funnel in one hold and an outlet tube connected to the suction in the other. Flexible rubber tubing and not the more rigid vacuum or pressure tubing should be used, as the latter will often tend to overturn the lighter flask; also, the

lighter tubing, even if collapsed, will carry as large a volume of air as can be safely used. As an additional precaution the funnel should be supported in a funnel stand. When a water aspirator is used for the suction, a water trap should be provided consisting of a flask with a two-hole stopper fitted with an outlet tube to the aspirator and an inlet tube from the filter flask outlet; the possibility of tap water being sucked into the filter flask is thus eliminated.

The first portion of any solution poured upon an asbestos filter should be added with great care in order not to stir up the mat, and a slight suction is generally advisable at this time as it helps to keep the filter in place. When flocculent or gelatinous precipitates are being filtered, a very thin layer of asbestos should be used and a second plate placed on top of this mat to keep it in place. Suction should be applied only as it is needed to keep the solution moving through the filter, for otherwise the first part of the precipitate will be tightly packed against the filter and may completely clog it.

It is possible to use a paper filter for this filtration; however, owing to the accumulation of paper pulp which occurs in the operations of P. 12 and P. 21, filtrations and washings are made difficult. Moderate suction may be used with a paper filter if the lower portion of the filter is supported in the funnel by a smaller (5-cm) filter of hardened paper, a perforated platinum cone, or a small cloth support. If a paper filter is employed, see Note 1, P. XVIII *C*, and the discussion of filtering media, p. 133, for suggestions in regard to its use.

8. In general, precipitates should be allowed to settle before being filtered, and then as much as possible of the clear solution should be decanted through the filter. In this manner, it is often possible to filter a mixture completely and then to wash the precipitate without removing it from the flask. This is termed *filtering by decantation* and should be practiced whenever the nature of the precipitate permits. In this case, if the precipitate settles rapidly, it need not be brought upon the filter but can be washed in the flask, the wash solution can be decanted through the filter, and the precipitate can then be treated directly in the flask with the sodium sulfide reagent with which it is to be treated in P. 12. Any precipitate carried onto the filter can be treated there or transferred to the flask with the aid of the sodium sulfide reagent.

9. Many precipitates have a tendency to become colloidal and to run through the filter when they are being washed, so that it is advisable to remove the filtrate before beginning to wash the precipitate, especially if the volume is large, and to collect the washings separately. Then, if a break occurs in the filter or the precipitate becomes colloidal, a much smaller volume of solution will have to be refiltered.

10. When washing a precipitate, the original solution and then each successive portion of wash water should be allowed to drain from it before the next portion is added. It can be shown that the amount of wash solution required will be determined largely by the volume of solution left with the precipitate and filter each time. However, a precipitate should never be allowed to dry or cake before or during the washing. It can also be shown that it is more effective to wash with several small portions of wash water than with one portion of the same total volume. See p. 137 for a general discussion of the washing of precipitates.

11. When limiting amounts of wash solution are specified, the volume used should be adjusted to the size of the precipitate to be washed. As a 1-g sample (0.5 g for alloys) is used, it is assumed that not more than 500 mg of any one constituent will be found.

12. It is not essential that this wash solution be accurately 0.12 n. in HNO_3; 0.1 n. would be satisfactory. However, as the more common dilute acids and bases are usually prepared to be 6 n., it is seen that 0.12 n. acid can be conveniently made by diluting 2 ml to 100 ml. Likewise, 0.6 n. wash solutions are often specified where 0.5 n. would be equally satisfactory but could not be so conveniently made from a 6 n. solution.

13. Experiments have shown that six washings with 5 ml of wash solution should leave less than 0.1 mg of elements of other groups in even a large sulfide precipitate. Thus, with 500 mg of iron present, less than 0.1 mg of it was left in a precipitate containing 500 mg of arsenic as As_2S_3. Accordingly, in order not to dilute the filtrate unduly, only the volume of the solution used to wash the precipitate is added to it. Any additional wash solution, which serves to remove traces of elements which might interfere in the group analysis, is accordingly discarded.

The precipitate is washed with dilute acid to prevent possible precipitation of any Ammonium Sulfide Group elements and to diminish the tendency of the precipitate to become colloidal; it is also advantageous to saturate the wash solution with H_2S.

14. The washing of a precipitate should in most cases be continued until portions of the wash solution give no test for the most easily detected of the substances originally present. In this case, if the washing is done with water, the washings as they come from the funnel can be tested for hydrogen ion with litmus paper.

15. The second treatment with H_2S is to provide for detecting any quinque-positive arsenic not already precipitated. See the discussion.

P. 12. Separation of the Copper Group from the Tin Group

Discussion. The Hydrogen Sulfide Group precipitate contains such a large number of elements that it is advisable to separate it into two smaller groups, rather than to make a large number of individual separations. In considering the possibilities of making such a separation, an inspection of Table XII shows that certain of the elements comprising this group are acidic, or at least distinctly amphoteric in nature and therefore tend to dissolve in alkaline solutions with the formation of acidic ions. Thus arsenic and antimony, especially when in their higher oxidation states, are predominantly acidic in character, and tin and lead are amphoteric, tending to form soluble acidic ions in alkaline solutions. The other elements of the group—namely, copper, mercury, cadmium, bismuth, and silver—form ions which are successively more basic in their reactions and precipitate relatively insoluble hydroxides in

TABLE XII

THE BEHAVIOR OF THE HYDROGEN SULFIDE GROUP ELEMENTS IN SOLUTIONS OF VARIOUS HYDROXYL (AND HYDROGEN) ION CONCENTRATIONS

Element and Oxidation State	(OH^-), 2 to 4 m.	(H^+), (OH^-), approx. 10^{-7} m.	(H^+), 10^{-5} to 10^{-6} m.
Ag^I	Ag_2O[c]	(Ag^+)[c]	(Ag^+)
Pb^{II}	$(Pb(OH)_4^-)$	$Pb(OH)_2$[d]	(Pb^{++})
Bi^{III}	$Bi(OH)_3$[a]	$Bi(OH)_3$[a]	$BiO(OH)$[i]
Cu^I	$Cu(OH)$, Cu_2O[c]	(Cu^I)[c,k]	(Cu^I)[k]
Cu^{II}	$Cu(OH)_2$, CuO[b,c]	(Cu^{++})[c,e]	(Cu^{++})
Cd^{II}	$Cd(OH)_2$[c]	(Cd^{++})[c]	(Cd^{++})
Hg^I	Hg_2O	(Hg_2^{++})[f]	(Hg_2^{++})
Hg^{II}	HgO	(Hg^{++})[g]	(Hg^{++})
As^{III}	$(HAsO_3^-)$	(H_3AsO_3)[h]	(H_3AsO_3)
As^V	$(AsO_4^{=})$	$(HAsO_4^-)$	$(H_2AsO_4^-)$
Sb^{III}	$(HSbO_3^-)$	Sb_2O_3	Sb_2O_3
Sb^V	$(SbO_4^{=})$[j]	$Sb_2O_5\cdot(H_2O)_x$	$Sb_2O_5\cdot(H_2O)_x$
Sn^{II}	$(Sn(OH)_4^{=})$	$Sn(OH)_2$	$Sn(OH)_2$
Sn^{IV}	$(Sn(OH)_6^{=})$	$SnO_2\cdot(H_2O)_x$	$SnO_2\cdot(H_2O)_x$

The composition of the so-called hydroxides varies with the conditions of formation, such as the concentration of the salt and of the hydroxyl ion, the temperature of the solution, the anions present (basic salts being formed), and the time for which they are allowed to stand in solution or in the air. They often separate from the solution with considerable amounts of adsorbed water, and can be dried without their temperature-vapor pressure curves showing the abrupt breaks characteristic of definite hydrate formation. Because of this uncertainty, the term *hydrous oxides*, or, where definite hydrates obviously exist, *hydrous hydrated oxides*, has been used (Weiser, *The Hydrous Oxides*, McGraw-Hill, 1926); however, the term *hydroxide* will be retained in this book, but with the limitation that an exact formula is not implied.

The ions which are formed when the amphoteric elements are dissolved by an excess of hydroxyl ion are usually assigned dehydrated structures (such as PbO_3^- and SnO_3^-), not because it was thought that these were necessarily the predominating species, but because the correct formula was not known, and frequently an equilibrium between two or more forms may exist. However, there now seems to be justification for assigning to these ions more specific formulas, not only because of evidence from work on the crystal structures of their compounds and from the principles applying to coördination-compound formation,* but also because the analogy with other coördination compounds is more clearly demonstrated and, in addition, in many cases a more adequate explanation of their chemical behavior is thereby obtained.†

[a] $Bi(OH)_3$ dissolves to a very slight extent in concentrated (6 f. or more) hydroxide solution.

[b] $Cu(OH)_2$ dissolves slightly in concentrated hydroxide solutions, forming the blue CuO_2^- ion.

[c] Complex ammino ions are formed when ammonia is present.

[d] $Pb(OH)_2$ dissolves to an appreciable extent.

* For a discussion of the formulas of the antimonates and the anions of a number of other elements see Pauling, *J. Am. Chem. Soc.*, **55**, 1895 (1933).

† Hammett, *Solutions of Electrolytes*, McGraw-Hill, 1936, pp. 105–113, discusses the reactions of certain amphoteric hydroxides.

[d] $Cu(OH)_2$ may be incompletely precipitated, depending upon temperature, concentration, and anions present.

[f] Ammonia causes a mixed precipitate composed of finely divided metallic mercury and $HgNH_2Cl$ or $HgO \cdot HgNH_2 \cdot NO_3$, depending upon the anion present.

[g] Ammonia in chloride solutions forms $HgNH_2Cl$; in nitrate solutions it forms $HgO \cdot HgNH_2NO_3$.

[k] As_2O_3 is only moderately soluble in water.

[l] This is usually a mixture of basic salts.

[i] In less alkaline solutions the ion $Sb(OH)_6^-$ probably predominates.

[k] Cuprous ion is unstable in aqueous solution, tending to give copper and cupric ion, unless stabilized by the formation of a complex ion.

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such solutions. Therefore it is seen to be theoretically possible to treat a solution containing all of these elements with sodium or potassium hydroxide in large excess, and thus to precipitate the last five named and to dissolve the first four. Practically, owing to the solubility of certain of the precipitates in strongly alkaline solutions and to the tendency of certain of the soluble acidic elements to be carried out with those precipitated, such a separation is not generally applicable.

Separations by Alkaline Sulfide Solutions. If, instead of the tendency of these acidic elements to form the oxygen acids, advantage is taken of their tendency to form the analogous sulfur acids, a very similar effect is obtained; thus an inspection of Table XI shows that, when their sulfides are treated with ammonium sulfide, arsenic, antimony, and tin form sulfo-salts analogous to their oxy-salts, and that with a higher concentration of sulfide (provided by using a sodium sulfide solution containing sodium hydroxide to repress the hydrolysis of the sulfide) mercury also forms a sulfo-salt.[6] It has been found experimentally that the use of these sulfide reagents gives group separations of these elements which are more quantitative than those obtained by the use of hydroxide solutions. The reagent most commonly used for this purpose is one containing ammonium sulfide, ammonium disulfide, and ammonium hydroxide. The disulfide is provided in order to oxidize stannous tin, as stannous sulfide is but slightly soluble in ammonium monosulfide, and as, in general, the acidic nature of the element becomes more pronounced the higher the oxidation state. Although arsenious sulfide, As_2S_3, and antimonous sulfide, Sb_2S_3, are soluble in a mono-

[6] Knox, *Trans. Far. Soc.*, **4**, 29 (1908), from a study of the solubility of HgS in sodium sulfide and disulfide solutions, gives for the dissociation constant

$$K = \frac{[Hg^{++}][S^{=}]^2}{[HgS_2^{=}]},$$

the value 1.96×10^{-55}.

sulfide reagent, they are oxidized by disulfide ion and are present in such solutions in their higher oxidation states as the ions $AsS_4^{\equiv}$ and $SbS_4^{\equiv}$, respectively. In this system a sodium sulfide reagent, which is approximately 3 n. in sodium sulfide, 1 n. in sodium disulfide, and 1 n. in sodium hydroxide, is used in place of the more commonly used ammonium sulfide reagent[7] for separating the Tin Group from the Copper Group sulfides.

An experimental study of the behavior of the elements of the two groups when their sulfide precipitates are treated with the sodium sulfide reagent as directed in the procedure below has been made, and the results of these experiments are shown in Tables XIII and XIV.[8]

TABLE XIII

EXTRACTION OF SMALL AMOUNTS OF THE TIN GROUP SULFIDES FROM THE COPPER GROUP SULFIDES BY THE SODIUM SULFIDE REAGENT

Copper Group Element	Tin Group Elements Amount Dissolved by Na_2S Reagent					
500 mg Taken	1 mg Taken					2 mg Taken
	Hg^{II}	As^{III}	Sb^{III}	Sn^{II}	Sn^{IV}	Hg^{II}
Ag^{I}	0.5	1	1	1	1	1.5
Pb^{II}	tr.	1	1	1	1	1
Bi^{III}	0.5	0.5	1	1	1	1
Cu^{II}	tr.	1	1	1	1	1.5
Cd^{II}	0	0.5	1	1	1	0.5

It is seen that, when the sodium sulfide reagent is used as directed, 1 mg of any element of the Tin Group, except mercury, will be extracted in sufficient quantity to give a satisfactory test even when present with 500 mg of any element of the Copper Group. When 1 mg of mercury is present with large amounts of lead or copper, its detection is uncertain; with a large amount of cadmium it fails. When 2 mg of mercury is present, enough is always extracted to insure its detection. When larger amounts of the Tin Group elements (250 mg) are extracted, considerable mercury and antimony are left if a large amount of cadmium is present. If desired, these

[7] Both the ammonium and sodium sulfide reagents are more complex in their composition than is indicated. On dissolving sulfur in alkaline sulfide solutions, thiosulfate, $S_2O_3^{=}$, trisulfide, $S_3^{=}$, and even higher sulfides are formed. These latter compounds appear to be present in appreciable amounts even if the amount of sulfur added is inadequate to convert the sulfide to disulfide; for this reason these reagents are frequently termed "polysulfide" solutions.

[8] Unpublished experiments by R. C. Aussieker.

elements can be recovered from the residue resulting when the Copper Group sulfides are dissolved in nitric acid and do not interfere with the analysis of that group. Of the elements of the Copper Group 20 ml of the sodium sulfide reagent dissolves about 1 mg of bismuth and only a trace of copper. Occasionally, small amounts of the Copper Group sulfides may pass into the sodium sulfide solution in colloidal form.

In comparison, the ammonium sulfide reagent, which is commonly used for this separation, leaves mercuric sulfide with the Copper Group, where its detection and separation are much more difficult, especially when silver is included in the Copper Group. Furthermore, the data of Noyes and Bray[9] on the behavior of the Copper

TABLE XIV

EXTRACTION OF LARGE AMOUNTS OF THE TIN GROUP SULFIDES FROM THE COPPER GROUP SULFIDES BY THE SODIUM SULFIDE REAGENT

Copper Group Element 250 mg Taken	Tin Group Elements 250 mg Taken Amount Found with the Residue			
	Hg^{II}	As^{III}	Sb^{III}	Sn^{II}
Ag^{I}	0.5–1	tr.	1–3	tr.
Pb^{II}	1	2–3	5	1
Bi^{III}	1–2	tr.	1	5
Cu^{II}	1	tr.	1	1
Cd^{II}	20	0	10	tr.

and Tin Group sulfides with ammonium mono- and polysulfide, show that, when tin is present with large amounts of any of the Copper Group elements, it may remain undetected in amounts as large as 3 to 5 mg, and even 15 mg of stannous tin may be wholly left with 500 mg of cadmium. Finally, 10 ml of the ammonium sulfide reagent dissolves 5 to 10 mg of copper, 1 mg of mercury, and 0.1 to 0.3 mg of cadmium.

Procedure 12: SEPARATION OF THE COPPER GROUP FROM THE TIN GROUP. Combine the H_2S precipitate on the filter (Note 1) with that remaining in the flask and treat it there with 5 to 20 ml of sodium sulfide reagent (Note 4). Heat the mixture to 60° to 80°C. (Note 2) for 5 min., stirring it and disintegrating any residue (Note 3). Add to the mixture 5 to 20 ml of hot 0.6 n. NaOH and filter it at once through an asbestos filter, catching the filtrate in a 200-ml flask. Wash the precipitate with two to four 10-ml portions

[9] Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 192 (1907).

of a solution made by diluting 1 volume of the sodium sulfide reagent with 3 volumes of water and heating it to 60° to 80°C. Add these washings to the original filtrate (Notes 9, 10, P. 11). Treat the filtrate by P. 13. Wash the residue thoroughly with hot water (or, if it begins to run through the filter, with a hot solution made by diluting 1 volume of the sodium sulfide reagent with 9 volumes of water) and treat it by P. 21.

Notes:

1. A precipitate on an asbestos filter can be transferred by tilting the funnel containing it and then scraping away the precipitate with any part of the filter to which it adheres, or by inverting the funnel in a casserole and pushing out the entire filter and precipitate with a thin glass rod inserted through the stem of the funnel. Any precipitate adhering to the funnel can then be loosened with a stirring rod or policeman and washed with the solution with which the precipitate is next to be treated—in this case sodium sulfide reagent.

If only a small precipitate has been obtained, or if only a small portion of a larger precipitate has been carried onto the filter, it may be treated directly by pouring the sodium sulfide reagent repeatedly through it. After treating the precipitate in the flask with the reagent, the same filter may be used for filtering the mixture.

2. A flask or casserole at 60° to 80°C. can be held in the hand for only a second or two without discomfort. The mixture should not be boiled.

3. When a precipitate is treated with a solution which is intended to dissolve all or part of it, any residue or solid material left after adding the solution should be carefully broken up and disintegrated with a stirring rod; one which has been heated and flattened at one end is advantageous for this purpose.

4. When limiting volumes of a reagent are specified, the amount used should be adjusted to the size of the precipitate or residue to be treated. It is advantageous to use as little of the sulfide reagent as possible because of the large amount of sulfur which is precipitated when the solution is made acid in P. 13.

P. 13. Precipitation of the Tin Group

Discussion. Upon acidifying the sodium sulfide solution, which contains the Tin Group elements as sulfo-salts, the sulfide present is converted into H_2S and the polysulfides are converted into H_2S and S, and at the same time the Tin Group elements are reprecipitated as sulfides. The reactions occurring may be represented as follows:

$$S^{=} + 2H^{+} = H_2S_{(g)}$$

$$S_2^{=} + 2H^{+} = H_2S_{(g)} + S_{(s)}$$

$$2AsS_4^{=} + 6H^{+} = As_2S_{5(s)} + 3H_2S_{(g)}.$$

Sulfuric, rather than hydrochloric acid is used, because, first, these sulfides are more soluble in high concentrations of chloride ion (see the discussion of P. 11) and, second, by adding an excess of the sulfuric acid to the sulfate already formed by the neutralization, a "buffered" sulfate-hydrosulfate solution (see the discussion of P. XII and P. 61) is obtained in which the hydrogen ion concentration is sufficiently high to cause complete decomposition of the sulfosalts without danger of dissolving the sulfides. Arsenic, tin, and mercury are precipitated as the higher sulfides, As_2S_5, SnS_2, and HgS; with antimony there is evidence that a precipitate of the tetrasulfide, Sb_2S_4, and sulfur results.[10]

It has been found that heating the mixture while keeping it saturated with H_2S insures the complete and more rapid precipitation of the sulfides and their coagulation into a more rapidly filtered form.

In order to test the detection of the Tin Group sulfides when the sodium sulfide solution is acidified, 1 mg of each of the Tin Group elements was dissolved in 20 ml of sodium sulfide reagent, 20 ml of 0.6 n. sodium hydroxide and 20 ml of a solution made by diluting 1 volume of sodium sulfide reagent with 3 volumes of water were added, the solution was then slowly acidified with hydrochloric acid, and 2 ml more were added. The precipitate was then examined and compared with that produced by acidifying a similar sodium sulfide solution containing no Tin Group element. The mixture was then heated to 80° to 90°C. The blank solution, when first acidified, produced a finely divided pure white precipitate, which upon coagulation by heating acquired a very slight yellowish color; 1 mg of mercury produced a distinct gray precipitate, which coagulated into dark flocculent particles; 1 mg of arsenic first produced a precipitate only a little different from that of the blank solution, which upon coagulation became deeper yellow and more flocculent in nature; 2 mg of arsenic produced an easily recognized yellow flocculent precipitate; 1 mg of antimony produced an orange precipitate; 1 mg of tin produced a buff precipitate. A comparison with a blank would be necessary only in determining the presence of as little as 1 mg of arsenic.

Procedure 13: PRECIPITATION OF THE TIN GROUP. Slowly acidify the filtrate from P. 12 with 18 n. H_2SO_4 (Note 1), note the volume of the acid used, and then add one-half that volume more. Shake the mixture vigorously

[10] Currie, *J. Phys. Chem.*, **30**, 205 (1926).

and heat it to 80° to 90°C. If the precipitate is white (Note 2), discard the mixture.

If the precipitate is not entirely white, heat the mixture nearly to boiling, saturate it with H_2S, and allow the precipitate to settle. If the precipitate does not settle rapidly, add to the mixture 5 g of solid $(NH_4)_2SO_4$, shake it vigorously, and again heat it (Note 3). Filter the mixture through an asbestos filter (Note 4). It is not necessary to wash the precipitate; drain it as dry as possible (Note 5). Treat the precipitate by P. 41 (Note 6).

Notes:

1. Unless otherwise stated, when it is directed to acidify, neutralize, or make a solution alkaline, it is intended that litmus, in the form of test papers, be used as the indicator. Usually the necessary amount of acid or alkali can be estimated and most of this volume can be added at once, care being taken not to cause any loss through spattering of the solution in cases such as the above, where H_2S or CO_2 are liberated; then the remainder is added in gradually decreasing portions, the solution being shaken after each addition, and a drop of it held on a stirring rod being tested with a corner of a strip of litmus paper. The amount of solution used in making these tests is generally insignificant; however, if the volume of the solution being used is small, the litmus paper can be finally washed with a few drops of water. *It is bad practice to drop strips of litmus paper into the solution being tested.* The paper usually absorbs the strongly alkaline or acid solution and then responds slowly to changes in the solution when the neutral point is approached, the litmus is leached from the paper and may impart an undesirable color to the solution, and the paper may so disintegrate as to make it difficult to detect small precipitates which may be present.

Aid in making the above neutralization can be gained by observing the first appearance of the white, very finely divided, precipitate of sulfur—the precipitate first appearing being yellow; complete neutralization of the base present is also indicated when, after vigorous shaking of the mixture, bubbles of H_2S are no longer formed with further addition of acid. These indications are of value in this case, as the H_2S set free tends to cause a slight acid reaction of the litmus paper before all of the Na_2S has been decomposed.

2. A finely divided, uniformly white precipitate is always produced on acidifying this solution, and is caused by the liberation of sulfur from the disulfide present in the sodium sulfide reagent. The absence of any appreciable dark, yellow, orange, or brown precipitate with this sulfur indicates the absence of as much as 1 mg of any of the Tin Group elements. One not familiar with the type of precipitate produced by the sodium sulfide reagent should obtain a basis of comparison by acidifying the same volume of sodium sulfide reagent and NaOH as was used in the procedure, and comparing the color and nature of this precipitate with that obtained on acidifying the filtrate.

The precipitate produced with even 1 mg of mercury is unmistakably darkened, coagulating into dark grayish particles, that with antimony is orange, and that with tin is buff-colored. The precipitate produced by 1 mg of arsenic, while not as definite as those produced by the other three elements, has a more decided yellow tinge and coagulates into more flocculent particles than does the sulfur precipitate alone. Two mg of arsenic produces an easily recognized, flocculent, yellowish precipitate. See the discussion.

The precipitate may be darkened by the presence of Copper Group elements (see the discussion of P. 12). If this seems probable, or if there is doubt as to the presence of Tin Group elements, or if only a small precipitate is obtained and a quick identification of the elements is all that is necessary, the precipitate, after being filtered, should be treated as directed in Note 6.

3. If tin is present, the precipitate may not settle and the filtration may be very slow, as stannic sulfide tends to be colloidal. The addition of a large amount of an electrolyte, such as ammonium sulfate, usually assists in coagulating the precipitate.

4. If the precipitate is colloidal in nature, indicating the presence of tin, a paper filter may be used to advantage. See Note 1, P. XVIII *C*, and pp. 133–134, as to the characteristics, selection, and use of paper filters.

In general, the filtering and washing of precipitates will proceed more rapidly and efficiently with hot solutions; and advantage should be taken of this fact unless the precipitate is appreciably soluble or some undesirable reaction is caused by the higher temperature.

5. As the solution in this case contains nothing which will interfere with the subsequent treatment of the precipitate, the usual washing is not necessary. As the precipitate can be more easily transferred to the beaker to be used in P. 41, from the flask than from the filter, it should be filtered by decantation as much as possible.

6. If there is doubt as to the presence of any Tin Group elements, the precipitate can be rapidly analyzed by the optional method given in P. 41.

THE ANALYSIS OF THE COPPER GROUP

Residue from Sodium Sulfide Treatment. Copper Group Sulfides: Ag_2S, PbS, Bi_2S_3, CuS, CdS
Boil with HNO_3. (P. 21)

Residue: S (HgS, Sb_2O_5) | Filtrate: Ag^+, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, H^+; NO_3^-
Heat, add NH_4Cl. (P 22)

Precipitate: AgCl
Dissolve in NH_4OH.
Solution: $Ag(NH_3)_2^+$
Add KI.
Precipitate: AgI
Titrate the mixture with KCN
Solution: $Ag(CN_2)^-$
(P. 23)

Filtrate: Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, H^+; NO_3^-, Cl^-
Add H_2SO_4, evaporate to fuming, dilute. (P. 24)

Precipitate: $PbSO_4$
Dissolve in $NH_4C_2H_3O_2$. (P. 25)
Solution: $Pb(C_2H_3O_2)_2$
Add $HC_2H_3O_2$ and standard $K_2Cr_2O_7$.

Precipitate: $PbCrO_4$
Discard.

Filtrate:
$K_2Cr_2O_7$ (excess)
Add HCl and KI.
Solution:
I_3^-, Cr^{+++}
Add starch, titrate with $Na_2S_2O_3$.
Solution:
I^-, $S_4O_6^=$
(P. 25)

Filtrate: Bi^{+++}, Cu^{++}, Cd^{++}, H^+; $SO_4^=$, HSO_4^-
Add excess NH_4OH. (P. 26)

Precipitate: $Bi(OH)_3$
Dissolve in HCl. (P. 26)
Solution: $HBiCl_4$
Pour into boiling water; neutralize.

Precipitate: BiOCl | Filtrate: *Discard.*

Dissolve in HNO_3, add small excess of standard $AgNO_3$. Heat.
Precipitate: AgCl
Cool, add $Fe(NO_3)_3$. Titrate excess $AgNO_3$ with KSCN.
Precipitate: AgSCN
Solution: $Fe(SCN)_6^=$ (red)
(P. 27)

Filtrate: $Cu(NH_3)_4^{++}$, $Cd(NH_3)_4^{++}$, NH_3, NH_4OH
Blue color indicates Cu (Cu absent; omit P. 28)
Add H_2SO_4 and KI. (P. 28)
Precipitate: CuI. Solution: CuI_2^-, I_3^-, $CdI_4^=$
Add starch, titrate with $Na_2S_2O_3$. (P. 28)

Precipitate: CuI
Discard.

Filtrate: $CdI_4^=$, I^-, $S_4O_6^=$
CuI_2^- (small amount)
Add NH_4OH and KCN.
Pass in H_2S. (P. 29)

Precipitate: CdS
Wash with Na_2SO_4 and H_2SO_4.
Add $Fe_2(SO_4)_3$, H_2SO_4; heat.
Precipitate: S
Solution: Fe^{++}, excess Fe^{+++}, Cd^{++}
Cool, titrate with $KMnO_4$.
Solution: Fe^{+++}, Mn^{++}, Cd^{++}
(P. 30)

Filtrate: $Cu(CN)_3^=$, NH_4HS, NH_4OH
Discard.

The Analysis of the Copper Group

P. 21. Solution of the Copper Group Sulfides in Nitric Acid

Discussion. The first operation in the analysis of the Copper Group is to bring the sulfides into solution. Nitric acid is employed, as both hydrochloric and sulfuric acids cause the precipitation of certain elements of the group. Nitric acid is also a more effective solvent for sulfides; when hot and more than about 2 n., it acts as an oxidizing agent on sulfides and hydrogen sulfide, forming sulfur and smaller amounts of sulfate. In addition, when nitric acid is used, any mercuric sulfide not extracted by the sodium sulfide reagent will be left after the Copper Group sulfides are dissolved, and any antimony sulfide will be converted into antimonic oxide.

When ammonium sulfide is used for separating the Copper and Tin Groups, mercury remains with the Copper Group and such a treatment with nitric acid is used to separate it from the other elements; it is also sometimes used for the quantitative separation of mercury from these elements.[1] As is seen in Table XIV, mercury is likely to be found here in small amounts when large amounts of cadmium are present.

Dilute nitric acid is first used and the solution is gradually heated in order to expel as much as possible of the hydrogen sulfide without oxidation. If the sulfides were treated directly with concentrated nitric acid, or quickly heated, the hydrogen sulfide would be largely oxidized to sulfur, which would tend to enclose the remaining precipitate and prevent it from being dissolved. Solution could be obtained then only by using concentrated nitric acid, which would oxidize the sulfur to sulfate with possible precipitation of lead sulfate, even though, owing to the solubility of this salt in hot nitric acid, considerable amounts remain in solution. Upon treating 500 mg of silver (as freshly precipitated silver sulfide) by the procedure below, less than 2 mg of silver were found in the dark residue which remained. The nitric acid residue, which is very largely sulfur, is washed with dilute nitric acid in order to avoid the tendency of bismuth salts to hydrolyze and precipitate as oxy-salts when diluted with water. It should be noted that even if the residue is white it

[1] See Hillebrand and Lundell, *Inorganic Analysis*, p. 171, for a discussion of this method.

does not prove the absence of mercury; mercuric sulfide, on treatment with nitric acid, is often transformed into white compounds, such as $2HgS \cdot Hg(NO_3)_2$, which are difficultly soluble.

Procedure 21: SOLUTION OF THE COPPER GROUP SULFIDES. Treat the residue from the sodium sulfide treatment (P. 12) with 10 to 20 ml of chloride-free 3 n. HNO_3 (Note 1), and stir the mixture in such a way as to break up any lumps (Note 2). Slowly heat the mixture and boil it gently for 5 min. If there is a dark residue which seems to be slowly dissolving, add to the mixture 2 to 5 ml of chloride-free 16 n. HNO_3 and again boil it until no more of the residue appears to dissolve (Note 3). Prepare a paper filter (Note 4, P. 13) and filter out the residue while keeping the solution hot. Collect the filtrate in a 200-ml flask. Wash the residue with 5 to 10 (Notes 10, 11, P. 11) 5-ml portions of hot 1.2 n. HNO_3 (Note 4), adding these washings to the filtrate. Treat the filtrate by P. 22. Treat the residue as directed in Note 5 or discard it.

Notes:

1. If, in P. 12, the mixture has been filtered by decantation, the residue should be retained in the same flask and treated there with the acid, combining with it any precipitate on the filter.

The HNO_3 used should be tested in order to be sure that it is free from chloride; this would cause the partial or complete loss of any silver present by precipitating it as silver chloride, which would be filtered out with the residue and asbestos.

2. After adding the HNO_3, the mixture should be stirred and the residue disintegrated so that any solvent action taking place in the cold can proceed. The mixture should then be heated only as much as is necessary to keep the solution of the precipitate in progress. If there is a large sulfide precipitate, and especially if silver is present, it may dissolve only slowly in the dilute HNO_3; in this case the additional HNO_3 is added, and the solution is again heated as long as the precipitate seems to be dissolving. If the sulfide precipitate is large or if it is heated too rapidly, a spongy residue of sulfur, darkened by enclosed traces of the precipitate, will frequently form. This residue can be readily distinguished from the undissolved sulfides, and, as the amount of them which it contains is usually negligible, it should be filtered out, pressed free of solution with a stirring rod, and discarded.

3. During the boiling of the solution the flask should be covered with a watch glass to prevent loss of acid by evaporation. If, in spite of this precaution, considerable volume is lost, it should be replaced with 3 n. HNO_3; the volume of the mixture when filtered should be 10 to 15 ml.

4. The precipitate should be gently stirred up with each portion of wash

water, added with either a dropper or a wash bottle, depending upon the size of the precipitate and paper, and then the remainder of that portion should be applied dropwise or in a very fine stream around the upper edge of the filter, more being used on the triple-folded section of the paper (Note 10, P. 11).

5. This residue will usually consist of only sulfur and asbestos. However, under certain conditions some mercury or antimony (see the discussion) or some silver (Note 1) may be present. The silver may be detected by pouring 10 ml of warm NH_4OH repeatedly through the residue, adding to the clear solution 1 ml of 3 n. NH_4Cl, and acidifying it with HNO_3; a white precipitate, dissolving when the solution is again made alkaline, proves the presence of silver.

If desired, the mercury and antimony can be recovered as directed in the procedure for the rapid analysis of the Tin Group (P. 41*A*), or the mercury may be detected by treating the residue as directed in Note 1, P. 45.

P. 22. Detection and Precipitation of Silver

Discussion. Silver is separated from lead and the other Copper Group elements at this point by precipitation as the chloride. This separation depends upon the fact that silver chloride can be quantitatively precipitated from a boiling nitric acid solution; lead chloride is not precipitated; because an excess of chloride can be avoided, and because lead chloride is much more soluble in hot than in cold water. Owing to the moderately high concentration of nitric acid and to the small excess of chloride present, even 500 mg of bismuth do not cause a precipitate (of BiOCl), although hydrolysis, and, therefore, the tendency of bismuth to precipitate, is more pronounced in the hot solution. The precipitation of silver chloride and the factors affecting the solubility of the precipitate have been extensively discussed in P. XVIII, "The Gravimetric Standardization of a Hydrochloric Acid Solution."

Experiments have shown that the amount of silver present can be quite precisely estimated, even in the presence of large amounts of bismuth and lead, by titrating with a dilute standard solution of sodium or ammonium chloride until the formation of any precipitate ceases. This principle is the basis of a very precise volumetric method for the quantitative determination of silver.[2] While this method is precise, it is time-consuming and somewhat uncertain when carried out for the first time. In addition, if a large quantity of silver were titrated, a considerable volume of solution would be added, requiring the addition of more acid to prevent the precipita-

[2] See Treadwell-Hall, *Analytical Chemistry*, Vol. II, Quantitative, 7th Ed., p. 600, for a discussion of this method, known as the Gay-Lussac titration.

tion of oxy-salts of bismuth and increasing the volume of solution to be evaporated in P. 24. In order to avoid this dilution, an approximate estimate may be made using a 1 n. chloride solution. The results of tests of this method are shown in Table XV.[3] The sodium chloride solution used was prepared to be exactly 1 n.; the silver and other elements listed were added as solutions of their nitrates to 30 ml of 3 n. HNO_3; the time required for the titrations varied from 10 to 20 min. This method, while not adopted for general use in this procedure, may be employed at the judgment of the individual analyst, thus eliminating P. 23.

The precipitate is washed with HNO_3, and not pure water, to avoid precipitating oxy-salts of bismuth. It is washed first with sufficient solution to remove practically all of any other Copper

TABLE XV

THE TITRATION OF SILVER WITH 1 N. CHLORIDE SOLUTIONS

Experiment	Elements Taken (mg)	NaCl Used (ml)	Ag Found (mg)
1	Ag 50	0.45	49
2	Ag 100	0.92	99
3	Ag 250	2.38	257
4	Ag 500	4.72	509
5	Ag 250 Bi 250	2.40	259
6	Ag 250 Pb 250	2.35	254

Group elements present, and these washings are combined with the filtrate. It is finally thoroughly washed in order to remove any traces of bismuth or lead which might interfere with the subsequent determination of silver by forming precipitates when the silver chloride is dissolved in ammonia.

If a standard solution of potassium cyanide is not available, the estimation of silver can be made by one of the methods used in the gravimetric standardization of a hydrochloric acid solution—that is, by weighing the precipitated silver chloride. Because of the rapidity with which it can be carried out, the method in which the precipitate is dried by means of alcohol (P. XVIII *D*) is recommended. See pp. 129–131 of the discussion accompanying that procedure.

[3] Unpublished experiments by Everett G. Trostel.

Procedure 22: DETECTION AND PRECIPITATION OF SILVER. Evaporate the filtrate from P. 21 to a volume of 20 to 30 ml and add to the hot solution just 0.1 ml of 1 n. NH_4Cl solution. (White precipitate, presence of silver. Notes 1, 2; Note 6, P. XVIII.)

If there is no precipitate, treat the solution by P. 24.

If there is a precipitate, add 1 n. NH_4Cl, 0.5 ml at a time, until no more precipitate forms. Avoid adding more than 0.5 ml excess of the NH_4Cl by keeping the mixture hot, shaking it, and letting the precipitate settle after adding each portion of the reagent so that the effect of the next portion can be observed in the clear solution. (It should not be necessary to add more than 6 ml of the 1 n. NH_4Cl.) When no more precipitate forms, heat the mixture almost to boiling and shake it vigorously until the precipitate settles rapidly.

If a gravimetric estimation of the amount of silver present is desired, this can be carried out by any one of the optional methods given in P. XVIII, "The Gravimetric Standardization of an Hydrochloric Acid Solution." Method *D*, involving the use of a sintered-glass filter and the use of alcohol for drying the crucible and precipitate is recommended. The precipitate is washed as directed in the paragraph below.

Prepare a small paper filter, not larger than 7 cm, and, with the aid of a stirring rod, decant the hot solution through the paper, receiving the filtrate in a 200-ml flask (Note 3). Carefully drain the solution from the precipitate, carrying as little of the precipitate as possible onto the paper. Wash the precipitate remaining in the flask with three 5-ml portions of hot 1.2 n. HNO_3, heating each portion just to boiling after adding it to the precipitate, and then again decanting (Note 4). When decanting the solution, direct it to the lower part of the filter paper with a stirring rod. Add these washings to the filtrate and treat it by P. 24. Wash the precipitate on the filter paper and that in the flask with 0.6 n. HNO_3 and treat it at once by P. 23 (Note 5).

Notes:

1. If silver is found present, direct sunlight should be avoided in carrying out the remainder of P. 22 and P. 23. The silver halides are decomposed

by sunlight, and the metallic silver formed would dissolve in either the NH_4OH or KCN used in P. 23 only as it was oxidized by any oxygen present.

2. It is recommended that an approximate estimation of the silver present be made at this point by slowly adding a standard 1 n. NH_4Cl or NaCl solution from a graduated pipet or buret and noting when no more precipitate forms. The NH_4Cl should be added in successively smaller portions as the rate of precipitation is seen to be decreasing, until finally the effect of each drop is noted. After the end-point is obtained by this method, an excess of 0.1 to 0.2 ml of NH_4Cl should be added in order to insure complete precipitation. The necessity of carrying out P. 23 can often be eliminated by this process (see the discussion).

If a precipitate which appears to contain less than 10 mg of silver is obtained, it should be estimated by comparing it with what is thought to be an equal amount of silver which has been precipitated under similar conditions. With such small quantities of an element, this method is in general more trustworthy than a titration.

3. It should be an invariable practice to test either the clear solution above the precipitate or the first portion of the filtrate to see that an excess of the precipitant has been added. In this case a few drops of ammonium or sodium chloride should be added to the clear filtrate and the solution examined for any evidence of further precipitation.

4. When it is noted that the next operation to be carried out with the precipitate can be performed in the vessel in which it is already contained, it is better not to transfer the precipitate to the filter but to wash by decantation, as was done in this case. The small amount of precipitate unavoidably carried onto the filter can then be much more easily dissolved or transferred, as the case may be. In this case, if a large silver chloride precipitate were transferred to the filter, it would be difficult to dissolve it in the ammonia used in P. 23.

5. If the AgCl precipitate is allowed to stand for a considerable length of time, it dissolves slowly when treated by P. 23.

P. 23. Estimation of Silver

Discussion. The method used here for the estimation of silver is based upon the classical Liebig[4] method for determining cyanide. The principles involved are as follows: A silver chloride precipitate, although very slightly soluble in water, dissolves in an ammonia solution, owing to the formation of the complex ion, $Ag(NH_3)_2^+$, called the diammino silver ion. Silver iodide is even less soluble in water than the chloride and dissolves scarcely at all in ammonia solutions; therefore, upon the addition of an iodide to the ammonia solution, silver iodide precipitates. Still less dissociated than the diammino silver ion is the complex ion which silver forms with cyanide, having the composition $Ag(CN)_2^-$. Therefore, when KCN is added to an alkaline solution containing both the diammino ion

[4] Liebig, *Liebig's Ann. d. Chem.*, 77, 102 (1851).

and a silver iodide precipitate, there is a quantitative conversion of first the ammino ion and then the iodide precipitate into the soluble cyanide ion. If a standard cyanide solution is used and the point at which the silver iodide precipitate disappears is noted, the amount of silver present can be calculated. Because the silver iodide acts only as an indicator for the titration, it is not necessary to measure exactly the amount of iodide that is added; for a very precise determination, this quantity, as well as the volume of the solution and the amount of ammonia present, should be closely controlled, as they each affect the end-point.[5] As, under the conditions of this procedure, the silver chloride precipitate may so coagulate as to dissolve slowly in an equivalent amount of cyanide, a sharper end-point is obtained by adding a slight excess of cyanide and then back-titrating with standard silver nitrate solution to the appearance of the characteristic yellowish turbidity of the silver iodide precipitate.

In an experimental study[6] of the procedure used here, it was found that, if (in P. 22) the silver chloride precipitate was thrown on the filter, it collected into large particles which dissolved very slowly in even concentrated ammonia, thus causing results which were from 1 to 2 per cent low. This loss, as well as the time required for the process, was reduced by carefully filtering by decantation. The table at the right shows the results obtained by treating solutions containing silver and lead by P. 22 and P. 23.

TABLE XVI

THE TITRATION OF SILVER WITH STANDARD CYANIDE SOLUTION

Experiment	Elements Taken (mg)	Silver Found (mg)
1	Ag 500	499
2	Ag 250	249
3	Ag 54.8 Pb 400	54.6
4	Ag 164.2 Pb 300	164.1
5	Ag 331.4 Pb 100	331.0

This method of estimating the silver present has been adopted because the titration can be made directly in the ammonia solution of the silver chloride precipitate. Other more commonly used methods for estimating silver, such as the titration with standard thiocyanate in nitric acid solution with ferric salt as indicator (the Volhard method), would require a rather difficult preliminary separation of the silver from the chloride.

[5] For a detailed discussion of the conditions affecting the Liebig method for determining cyanide, see Kolthoff and Furman, *Volumetric Analysis*, Vol. 1, pp. 40–64 and Vol. II, pp. 238–240.

[6] Unpublished experiments by Robert J. Coulter.

Procedure 23: ESTIMATION OF SILVER. Place the flask, which should still contain most of the precipitate, under the filter through which the filtrate has been passed. Pour, drop by drop, 5 ml of warm (40° to 60°C.) 6 n. NH_4OH through the filter (moistening thoroughly every portion of it) into the flask (Note 1). Wash the paper in the same manner with 10 ml of water, collecting these washings in the flask. (Discard the paper.) Shake the mixture in the flask; crush any undissolved particles of precipitate with a stirring rod and add to it 1 ml of 1 n. KI solution. Take in a clean 50-ml buret (Note 7, P. V; Notes 4, 5, 6, P. VI) what is thought to be a sufficient volume of standard 0.2 f. KCN solution for the titration (Notes 2–5) and note the reading of the meniscus. Add this solution to the mixture in the flask in 0.5-ml portions until the precipitate dissolves (Notes 3, 4), shaking the mixture vigorously and breaking up any lumps of precipitate present after adding each portion of the KCN solution. Then titrate the solution with standard 0.1 n. $AgNO_3$, added drop by drop with constant shaking, until a permanent yellowish turbidity is produced. From the volume of the KCN and $AgNO_3$ solutions used calculate the amount of silver present (Note 5).

Notes:

1. The small quantity of finely divided precipitate which is carried onto the filter is readily dissolved by the ammonia. It is essential that most of the silver chloride be kept in the flask, since it is difficult to dissolve a large precipitate from the filter even with concentrated ammonia. If much precipitate has been carried to the filter, it should be returned, by means of a stirring rod, to the flask; the ammonia should be poured repeatedly through the filter and then collected in the flask. The precipitate in the flask, if large, may not completely dissolve in the ammonia, and, although this is desirable, it is not necessary, as it will dissolve in the KCN. The titration with the KCN can be carried out more rapidly, however, if a clear ammonia solution is obtained before adding the iodide.

2. It is an extravagant waste to fill a buret for every titration. Estimate the required amount of the standard solution from the size of the precipitate and take only slightly more than that amount.

3. Under certain conditions, and especially if it has been allowed to stand, particles of the silver chloride precipitate may dissolve slowly upon addition of the KCN. Accordingly, they should be carefully broken up, preferably with a stirring rod which has been heated and flattened out at one end. A small, flocculent, white precipitate, caused at times by traces of bismuth or lead which have been incompletely washed from the AgCl

precipitate or by small amounts of aluminum in the reagents, should not be mistaken for the more granular silver chloride particles or for the very characteristic, usually colloidal, yellowish silver iodide.

4. If the silver chloride precipitate completely dissolved in the NH_4OH, it is often possible to avoid the back-titration with $AgNO_3$ by adding the KCN in successively smaller portions as the precipitate of AgI begins to diminish, and then drop by drop until the precipitate dissolves. Even if the end-point is slightly overrun, the few drops of $AgNO_3$ needed for the back-titration then can be added with sufficient accuracy from a 1-ml measuring pipet or even with a dropper from a small graduate. The appearance (or disappearance) of the precipitate is best noted by using a black background.

5. The potassium cyanide solution should be standardized each day it is used, as its concentration gradually decreases. Proceed as follows:

> Pipet 25 ml of the cyanide solution into a 200-ml flask, add 5 ml of 6 n. NH_4OH and 1 ml of 1 n. KI, and dilute to 50 ml. Titrate the solution as directed above with standardized $AgNO_3$ (prepared in P. V) until the first yellowish turbidity is obtained.

The 0.2 f. KCN solution is prepared by dissolving approximately 13 g of KCN and 5 g of KOH in 1 l of solution. The KOH represses the hydrolysis of the KCN and makes the solution more stable.

P. 24. Precipitation of Lead

Discussion. After silver has been detected and removed, the next separation in the analysis of the Copper Group is made by precipitating the lead as sulfate. This is accomplished by adding sulfuric acid and evaporating the mixture to fuming in order to remove the nitric acid and any chloride present. As is seen from the solubility-product principle, any factor which decreases either the sulfate or the lead ion concentration will increase the solubility of lead sulfate. Nitric acid, or any strong acid, has this effect because it tends to convert $SO_4^=$ into HSO_4^-; hydrochloric acid has a still greater effect, as, in addition to the hydrogen ion effect, the chloride ions tend to combine with the lead to form complex ions of the type $PbCl_4^=$. The solubility of lead sulfate in increasing concentrations of sulfuric acid at first decreases, owing to the expected common ion effect, but the decrease is less than would be calculated, because of the decrease in the activity of the sulfate ion as the result of inter-ionic attraction forces. Then there is a concentration range (from somewhat less than 1 f. to approximately 11 f. acid at 25°C.) throughout which there is very little change in the solubility and in which the minimum solubility is found. Finally, as the concentration of the sulfuric acid is increased (and the concentration of the water becomes relatively small), the fraction of the acid ionized into

sulfate decreases to such a small value that in very concentrated acid there is a marked increase in the solubility of the lead sulfate.[7]

This separation of lead, as the sulfate, from copper and cadmium is very satisfactory. The separation from bismuth is somewhat less so, for, although the sulfates of copper, cadmium, and bismuth are readily soluble, bismuth ion tends to hydrolyze, as shown by the equation

$$Bi^{+++} + H_2O = BiO^+ + 2H^+.$$

On standing, the bismuthyl ion[8] may precipitate from sulfuric acid solutions as bismuthyl sulfate, $(BiO)_2SO_4$, or under certain conditions as a compound having the formula $(BiO)_2S_2O_7 \cdot 3H_2O$, hydrated bismuthyl pyrosulfate. These compounds ordinarily remain in the solution largely because of the formation of supersaturated solutions; however, with a large amount of bismuth, or when lead sulfate forms, they may precipitate in considerable amounts. As the result of an experimental study of this difficulty,[9] the procedure below was developed, whereby, if a large precipitate is obtained, the solution is decanted from it and the precipitate dissolved in hydrochloric acid and again fumed with a smaller portion of sulfuric acid. It was found that, under the conditions of the procedure below, if 250 mg each of lead and bismuth were present, from 30 to 50 mg of bismuth would precipitate with the lead; that, after decanting, adding 3 ml of 36 n. sulfuric acid, and again fuming, 7 to 10 mg of bismuth still remained; but that, after adding 5 ml of 12 n. hydrochloric acid and then fuming with the sulfuric acid, only 1 to 1.5 mg of bismuth remained. The concentrated hydrochloric acid almost completely dissolves or metathesizes the precipitates, thus facilitating the extraction of the bismuth.

Other details of the separation are as follows: Experiments have shown that the concentrated sulfuric acid should not be diluted by pouring it into water, as is often done in qualitative systems for reasons of safety, since the first portions of acid are thereby so diluted as to favor the precipitation of the bismuth oxy-salt. The solution should be kept cold when the sulfuric acid is being diluted, in order to minimize the hydrolysis of the bismuth and to decrease the solubility of the lead sulfate, which increases rapidly as the tempera-

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[7] For the solubility of lead sulfate in sulfuric acid of various concentrations, see Creckford and Brawley, *J. Am. Chem. Soc.*, **56**, 2600 (1934).

[8] Such hydrolyzed or "oxy" ions are frequently designated by the suffix *yl*. For example, the antimonyl ion is SbO^+; the vanadyl ion is VO^{++}.

[9] Unpublished experiments by Randal Maass.

ture is raised. As lead sulfate also forms supersaturated solutions, the mixture is allowed to stand for 5 min. after it is diluted; upon standing much longer, bismuthyl compounds tend to precipitate. The precipitate is washed first with 1.2 n. H_2SO_4, and not with water, to remove any bismuth sulfate without causing it to hydrolyze. The H_2SO_4 is then washed out in order to make the precipitate more soluble in the ammonium acetate later used.

In spite of these precautions, if lead and bismuth are both present in considerable amounts, a small amount of bismuth may precipitate with the lead; however, it does not interfere with the determination of lead in P. 25.

A volumetric method for estimating the lead in the precipitate is provided in P. 25. However, if standard solutions are not available, a rapid gravimetric estimation can be made by collecting the lead sulfate on a previously weighed sintered-glass filter, drying it by means of alcohol, and then weighing the filter and precipitate. See pp. 129–131 for a discussion of this method and for data concerning it.

Procedure 24: PRECIPITATION OF LEAD. Cool the solution from the silver chloride precipitation (P. 22), slowly add to it just 3 ml of 36 n. H_2SO_4 (Note 1), and evaporate it on a sand bath or hot plate (or directly over a burner if it is continuously kept in swirling motion) until the H_2SO_4 gives off copious dense white fumes (Note 2). Allow the mixture to stand until it cools somewhat (Note 3), cool the flask to room temperature with running water, and, while continuously cooling the flask, pour slowly into it, 1 ml at a time, 20 ml of water. Allow the solution to stand for not less than 5 min. and not longer than 10 min. (White precipitate, presence of lead.)

If a gravimetric estimation of the amount of lead present is desired, the precipitate should be collected on a sintered-glass filter, treated and washed as directed in the following paragraphs, and dried with alcohol as directed in Optional Method *D* of P. XVIII, "The Gravimetric Standardization of an Hydrochloric Acid Solution."

If only a small precipitate forms, decant the solution through a paper filter (Note 4), collecting the filtrate in a 200-ml flask. Wash the precipitate by decantation with three 5-ml portions of 1.2 n. H_2SO_4, taking care to retain as much as possible of the precipitate in the flask, and add

these washings to the original filtrate. Treat the filtrate by P. 26. Wash the precipitate with two 5-ml portions of cold water and treat it by P. 25.

If considerable precipitate forms (Note 5), decant the solution through a paper filter, retaining as much as possible of the precipitate in the flask, and collect the filtrate in a 200-ml flask. Add to the precipitate in the flask 5 ml of 12 n. HCl and 2 ml of 36 n. H_2SO_4, evaporate the solution as directed above until the H_2SO_4 fumes, allow the mixture to cool, and add to it in the manner directed above 15 ml of water. Treat the mixture as directed in the preceding paragraph, using the same filter, and combine the filtrates.

Notes:

1. The acid should be added slowly and the solution kept cool; otherwise spattering may result.

In general, concentrated sulfuric acid should be added *to* an aqueous solution, not in the reverse order. Elsewhere in this procedure this order is reversed, because a better separation results and because transferring of a precipitate from one vessel to another is thereby avoided. This mixing should be carried out very slowly and the solution constantly cooled.

2. It is essential that the H_2SO_4 be made to fume in order to expel all of the HNO_3 and HCl. The more transparent HNO_3 fumes produced as the solution becomes concentrated should not be mistaken for the dense white fumes of H_2SO_4. The latter can be recognized by the choking sensation which even a very small amount causes. It is to be noted also that the H_2SO_4 will not begin to fume until the solution is reduced to about the volume of 36 n. H_2SO_4 added.

3. The flask should be allowed to cool somewhat before it is cooled further with tap water, or it is likely to crack.

4. If a precipitate corresponding to only a few milligrams is obtained, the presence of lead should be confirmed and a visual estimation should be made as directed in Note 4 of P. 25.

5. The precipitate need not be treated by this last paragraph unless it is thought to contain a considerable amount (50 mg or more) of bismuth, and unless the analyst desires to make a precise estimation of the lead or bismuth present.

P. 25. Estimation of Lead

Discussion. Lead is estimated in this procedure by dissolving the lead sulfate precipitate in an ammonium acetate solution, reprecipitating the lead as chromate from an acetic acid–acetate solution by adding a measured volume of standard chromate solution, and then determining the excess of chromate iodometrically.

Lead sulfate dissolves in an ammonium acetate solution because of the formation of the slightly ionized lead acetate molecule.[10] If a highly ionized acid, such as nitric, is added to this solution, the acetate concentration would be so greatly decreased (the ionization constant for acetic acid being 1.8×10^{-5}) that the lead sulfate might be at least partially reprecipitated; for this reason, the solution is acidified with acetic acid before precipitating the chromate. Although chromic acid is not a highly ionized acid and is converted into dichromate by hydrogen ion according to the reaction

$$2CrO_4^{=} + 2H^+ = Cr_2O_7^{=} + H_2O$$

(see the discussion of P. 82), extensive investigations[11] have shown that lead chromate is so very insoluble that it can be almost quantitatively precipitated from acetate and acetic acid solutions. Confirmatory experiments[12] have shown that for the estimation of lead the precipitate should be formed in an acid solution, or low results are obtained, owing probably to the formation of basic lead chromates. The precipitation of the yellow lead chromate serves as a sensitive confirmatory test for the presence of lead as well as providing a means for its indirect determination. Bismuth, even if dissolved by the ammonium acetate, would not give a precipitate because of the acidity of the solution.

The lead chromate precipitate could be dissolved in hydrochloric acid and directly treated with potassium iodide, and the resulting iodine could be titrated. Even large amounts of lead chromate are readily dissolved by hydrochloric acid and by concentrated chloride solutions, owing to the formation of complex ions of the type $PbCl_4^{=}$. This procedure is recommended for use when a small amount of lead is present. With considerable amounts of lead it was found that the yellowish lead iodide precipitate which usually formed interfered with the determination of the end-point and also that it required considerable time to wash the lead chromate precipitate free of the excess chromate.

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[10] Noyes and Whitcomb, *J. Am. Chem. Soc.*, **27**, 747 (1905); Fox, *J. Chem. Soc.*, **95**, 878 (1909).

[11] Patten, *J. Assn. Off. Agr. Chem.*, **4**, 217 (1920); Goode and Summers, *Soc. Chem. Ind., Victoria, Proc.*, **32**, 689 (1932); Fairhall and Akatsuka, *J. Am. Chem. Soc.*, **56**, 14 (1934); Huybrechts and Degard, *Bull. Soc. Chim. Belg.*, **42**, 331, (1933); Guzelj, *Z. anal. Chem.*, **104**, 107 (1936).

[12] Unpublished experiments by R. W. Hoeppel.

The chromate-iodide reaction and the subsequent titration are carried out under conditions similar to those which have been used in standardizing the thiosulfate solution against potassium dichromate (P. XIV); that procedure should be consulted for the details of the method.

Procedure 25: ESTIMATION OF LEAD. Place the flask containing most of the $PbSO_4$ precipitate (from P. 24) under the funnel and with a stirring rod carefully tear a small hole in the bottom of the filter. Wash through as much of the precipitate as possible with 5 ml of water, and then pour dropwise over every portion of the filter 5 to 20 ml of 3 n. $NH_4C_2H_3O_2$ (Note 1). Discard the filter.

Dilute the filtrate to 50 ml, heat it to boiling, and add to it 2 to 10 ml of $HC_2H_3O_2$ (about one-half the volume of $NH_4C_2H_3O_2$ used above). Add to the hot solution from a buret or pipet (Note 2) standard 0.1 n. (oxidizing equivalents) $K_2Cr_2O_7$ solution, 5 ml at a time, until no more precipitate appears to form. The mixture should be heated almost to boiling, swirled vigorously, and then allowed to settle before each addition so that it can be observed if more precipitate is formed (Note 3). When no more precipitate forms, heat the mixture and frequently swirl it until the precipitate settles rapidly (Note 4); if the solution does not show a distinct orange-red color, more $K_2Cr_2O_7$ should be added.

If less than 40 to 50 mg of lead are thought to be present, cool the mixture to room temperature and filter the solution through a small paper filter. Wash the precipitate and filter with cold water, added dropwise, until the wash solution runs through colorless. Discard the filtrate. Dissolve the precipitate by pouring dropwise through it a solution made by adding 10 ml of HCl to 50 ml of water and saturating the solution with NaCl. Collect the solution in a 400-ml flask and treat it as directed in the second paragraph below.

If more than 40 to 50 mg of lead are thought to be present, cool the mixture to room temperature, transfer it with the aid of cold water to a 250-ml volumetric flask (Note 5), and dilute it exactly to the mark. Mix the solution thoroughly and then, while the precipitate settles, prepare a small

paper filter (Note 6). Decant 10 to 15 ml of the supernatant solution through the filter into a 100-ml flask. Use this portion to rinse the filter and flask and then discard it (Note 7). Decant 60 to 70 ml of the solution through the filter into the flask, pipet 25 ml of it into a 400-ml flask, add to it 10 ml of HCl and 25 ml of water, and treat it as directed in the next paragraph.

Add to the solution 2 to 3 g of KI dissolved in 40 ml of water. Close the flask and allow it to stand for 3 min. in a dark place. Dilute the solution to 300 to 400 ml and titrate it at once with standard 0.1 n. $Na_2S_2O_3$ solution until the iodine color becomes indistinct (Note 8), and then add 5 ml of starch indicator solution and again titrate until the blue color just disappears. From the volume of standard dichromate solution used to precipitate the lead, and from the volume of standard thiosulfate solution used in this titration, calculate the amount of lead present.

Notes:

1. The volume of $NH_4C_2H_3O_2$ used should be adjusted to the size of the precipitate, noting that $PbSO_4$ is a compact, heavy substance. As an aid to judging the volume of $K_2Cr_2O_7$ to be later used, a visual estimate of the amount of lead present should be made. If experience with this type of precipitate is lacking, a known amount of lead, obtained from the test solution provided in the laboratory, should be fumed with H_2SO_4, the mixture then diluted as in P. 24, and the precipitate carefully compared with that already obtained.

The minimum amount of $NH_4C_2H_3O_2$ required should be added; the solubility of $PbCrO_4$ becomes appreciable in very concentrated acetate solutions.

2. The approximate volume of 0.1 n. $K_2Cr_2O_7$ required for the amount of lead judged to be present should be calculated, as, when this is known, a pipet can be used more quickly than a buret. An excess of at least 3 ml of the $K_2Cr_2O_7$ should be added.

3. The $PbCrO_4$ precipitate tends to remain suspended until an excess of the dichromate has been added, and then it settles much more rapidly. This behavior is so characteristic that one familiar with the precipitation can judge very closely when the equivalent amount of dichromate has been added.

4. If less than about 5 mg of lead are thought to be present, it is usually more satisfactory to make the estimation by comparing the size of the precipitate with known amounts of lead which have been precipitated under similar conditions; the latter is essential, as the conditions of the precipitation may markedly affect the character and apparent size of the precipitate.

5. Hot solutions should not be poured into volumetric measuring flasks.

These flasks are usually calibrated for use at room temperature (20°C.) and return slowly to their original size after being heated.

6. If the mixture can be conveniently left until the precipitate completely settles, the clear supernatant solution may then be pipeted directly from the flask and a filtration can be avoided. Care should be taken not to stir up the precipitate. The error introduced by the volume of the precipitate is so small that it can be neglected.

7. It is more convenient to rinse the paper and the collecting flask and then discard the first portion of the solution than to use a dry filter and flask. Also, in more precise quantitative work this procedure would be advisable, as the filter paper may adsorb an appreciable quantity of the constituents from the first portion of the solution passing through it.

8. One accustomed to this method can carry the titration to within a few drops of the end before adding the starch. This is quite desirable, for starch, when used as an indicator, should not be added to a solution which contains a considerable quantity of iodine, as it then tends to coagulate, making the end-point much less definite.

P. 26. Precipitation of Bismuth and Detection of Copper

Discussion. After silver and lead have been removed from the solution of the Copper Group, the separation of bismuth from copper and cadmium is next made by adding an excess of ammonium hydroxide to the sulfuric acid solution. Bismuth hydroxide is relatively insoluble, exhibits no appreciable amphoteric tendency in the low hydroxyl ion concentration provided by an excess of ammonia in the presence of ammonium salts, and does not form an ammino complex ion; therefore, it is quantitatively precipitated. As the solution is neutralized, the bismuth ion hydrolyzes and is precipitated as a basic salt, probably $(BiO)_2SO_4$. This may not be completely converted into the hydroxide by an excess of ammonia, and therefore the precipitate varies in its composition, so that bismuth cannot be precisely determined by attempting to ignite this precipitate to the oxide (Bi_2O_3) and weighing it as such.

In the presence of an excess of ammonia, copper and cadmium form the tetrammino ions $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$. These ions remain in solution, as their hydroxides and salts are soluble. The tetrammino copper ion has an intense blue color, which serves as a distinctive means for detecting copper. In this procedure the solution is evaporated to a small volume in order to make this detection more sensitive; the blue color given by $\frac{1}{3}$ mg of copper is readily perceived under these conditions.

Experiments carried out under the conditions of the procedure below have shown this separation to be very satisfactory; with 250

mg of bismuth and 250 mg of copper or cadmium, not more than 1 mg of copper or cadmium was found in the precipitate. For a more detailed discussion of the separation of various other elements by the use of an ammonia precipitation, see the discussion of P. 55.

The precipitate is washed with only an amount of 1.2 n NH_4OH which will remove practically all of any copper and cadmium present, and these washings are added to the filtrate. It is not further washed, as none of the constituents of the solution interfere with the subsequent estimation of bismuth.

Procedure 26: PRECIPITATION OF BISMUTH AND DETECTION OF COPPER. Evaporate the filtrate from P. 24 to about 15 ml (Note 1) and cool it with running water. Add slowly with a dropper 15 n. NH_4OH until it is alkaline (Note 2) and then add 2 ml more. (White precipitate, presence of bismuth; blue solution, presence of copper. Note 3.)

Heat the solution almost to boiling and let the precipitate settle. Filter the solution through a paper filter, decanting as much as is possible, and wash it with two or three 5-ml portions of hot 1.2 n. NH_4OH, adding these washings to the filtrate. Treat the filtrate by P. 28 if copper is present, or by P. 29 if copper is absent. Treat the precipitate by P. 27.

Notes:

1. Solutions can be safely and rapidly evaporated from conical flasks by giving the contents a continuous rapid swirling motion while the flask is heated directly over the flame until the solution boils rapidly. Vigorous boiling without keeping the flask and contents in motion is dangerous with most solutions, because of the danger of "bumping."

2. The solution is cooled and the concentrated ammonia is added slowly to the acid solution in order to avoid danger of spattering.

When a solution is made alkaline with ammonia, the approximate volume to be added can, in general, be estimated, and the solution can then be added in small portions until the smell of ammonia can be detected. Avoid splashing the ammonia on the sides of the flask and mix the contents thoroughly by swirling.

3. When the solution is intensely colored, it should be examined in a bright light so that a small bismuth precipitate will not be overlooked. If the presence of copper is doubtful, owing to the presence of a precipitate or the indefiniteness of the blue color, the solution, after being filtered, should be compared against a white background with the same volume of water in a similar flask. Under these conditions the blue color caused by $\frac{1}{3}$ mg of copper can be readily detected.

P. 27. Estimation of Bismuth

Discussion. The volumetric method used for determining bismuth depends upon precipitating the oxychloride (bismuthyl chloride, BiOCl), dissolving this in nitric acid, precipitating the chloride ion with an excess of a standard silver nitrate solution, and then titrating the excess of silver with a standard thiocyanate solution, using ferric nitrate as the indicator. This titration has been discussed in P. VI.

The volumetric determination of bismuth is usually not attempted, the BiOCl precipitate being filtered, washed, dried at 100° to 110°C., and weighed; if desired, this procedure can be followed here. However, a study of the advantages of the two methods, especially as regards rapidity and accuracy, has indicated that the volumetric procedure is the more satisfactory, as it can be carried out in about one-half the time and with comparable accuracy.[13] If standard solutions of silver nitrate and potassium thiocyanate are not at hand, the gravimetric method is more expedient for a single determination; a procedure for its optional use is provided.

The bismuth hydroxide precipitate is dissolved in hydrochloric acid, as the precipitate dissolves much more readily in it than in nitric or sulfuric acids, it having been shown that the ions $BiCl_4^-$ and $BiCl_5^=$ are formed;[14] also, the chloride for the subsequent precipitation is thereby provided.

When the hydrochloric acid solution of the bismuth hydroxide is sufficiently diluted, bismuthyl chloride precipitates; that this should occur is shown by the following equations:

$$BiCl_4^- + HOH = BiOCl_{(s)} + 2H^+ + 3Cl^- \qquad (1)$$

$$BiCl_5^= + HOH = BiOCl_{(s)} + 2H^+ + 4Cl^-. \qquad (2)$$

The precipitation reaction is often represented as follows:

$$Bi^{+++} + Cl^- + HOH = BiOCl_{(s)} + 2H^+. \qquad (3)$$

However, an inspection of the equilibrium expression for this reaction shows that, except for activity effects, it should be independent of dilution, as the concentrations of the reactants occur to the same power in both the numerator and the denominator; it is also seen that dilution should markedly favor the formation of the precipitate

[13] Unpublished experiments by Roland C. Hawes (1928). Migray, *Chem. Ztg.*, **57**, 744 (1933), has recently investigated the same method.

[14] Noyes, Hall, and Beattie, *J. Am. Chem. Soc.*, **34**, 2526 (1917).

by either of the first two reactions. Since an excess of acid has been used in dissolving the ammonia precipitate, and as this (with the acid formed from the precipitation of a large quantity of bismuth) would tend to prevent complete precipitation of the oxychloride, the acidity of the solution is finally adjusted with the aid of methyl orange. Methyl orange is used because it is desirable that the solution not become actually alkaline during this adjustment, for BiO(OH) might then precipitate and not be metathesized to oxychloride during the subsequent boiling. Heating the solution favors the hydrolysis reaction. Experiments have shown that, under the conditions of this precipitation, 1 mg of bismuth can be detected; that with 500 mg not over 0.1 mg remained in the filtrate; and that with 50 mg of lead no precipitate was produced. The precipitation of the bismuthyl chloride also serves as a distinctive confirmatory test; any lead not precipitated as sulfate (in P. 25) would be precipitated with the bismuth by the ammonia but would not precipitate with the bismuthyl chloride.

The precipitate is dissolved in nitric acid and the chloride is precipitated with standard silver nitrate, a large excess being avoided by noting when precipitation ceases (see the discussion of P. 22). For determining this excess, the titration with thiocyanate is used (see P. VI). As the method is used here, the excess of silver nitrate is titrated in the presence of the silver chloride precipitate. This may lead to some error, for silver thiocyanate is less soluble than silver chloride, and therefore the thiocyanate may be removed from the solution by the metathetical reaction

$$AgCl_{(s)} + SCN^- = AgSCN_{(s)} + Cl^-.$$

This causes the end-point to fade and an excess of thiocyanate to be added. While this titration of silver with thiocyanate in the presence of a precipitate of AgCl is theoretically inaccurate, it has been shown[15] that, if the AgCl precipitate is thoroughly coagulated, the rate at which it reacts with the excess of thiocyanate necessary for the end-point is so slow that quite accurate results can be obtained.[16]

If standard solutions of thiocyanate and silver are not available, it is recommended that the bismuth be estimated gravimetrically

[15] Rothmund and Burgstaller, *Z. anorg. Chem.*, **63**, 330 (1909).

[16] Caldwell and Moyer, *J. Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935), have suggested that 1 ml of nitrobenzene be added to the solution before making the back-titration. This is adsorbed on the precipitate, causes it to coagulate, and further decreases the rate of the metathesis; this method has been found to be very effective and its use is recommended.

by collecting the bismuthyl chloride precipitate on a weighed sintered-glass filter, drying it with alcohol, and again weighing. See pp. 129–131 for a discussion and for data relative to this method.

Procedure 27: ESTIMATION OF BISMUTH. Dissolve the BiO(OH) precipitate (P. 26) remaining in the flask with 5 to 15 ml of warm HCl (Note 1), and then pour this solution dropwise through the precipitate on the filter, collecting the solution in a 400-ml flask. Wash the flask and filter with 10 ml of hot 1.2 n. HCl. Cool the solution and add NH_4OH until a slight permanent precipitate is produced (Note 2); then add HCl, 0.1 ml at a time and shaking vigorously after each addition, until the precipitate just dissolves.

Heat the solution almost to boiling, slowly add to it 100 ml of boiling water (Note 3), and boil the mixture until the precipitate settles rapidly. Add to the boiling solution 2 or 3 drops of methyl orange indicator solution and then NH_4OH, drop by drop, until the pink color first begins to change to yellow (Note 4), and then just 3 drops more than enough HCl to restore the distinct pink color. Add to the mixture 100 ml of boiling water and again heat it just to boiling until the precipitate settles rapidly (Note 5).

If a gravimetric estimation of the bismuth is to be made, dry and weigh a sintered-glass filtering crucible as directed in Optional Method *D* of P. XVIII. Collect the precipitate on the filter, and wash as directed in the next paragraph. Dry and weigh the precipitate and crucible by the same procedure used with the empty crucible.

Filter the hot mixture through a paper filter and wash the precipitate, by decantation, with 10-ml portions of hot water, retaining as much of the precipitate as possible in the beaker until the wash water no longer gives a pronounced test for chloride (Note 6). Discard the filtrate and washings.

Tear a small hole in the bottom of the filter with a stirring rod and wash most of the precipitate through the funnel into the original flask with 10 ml of water. Dissolve the precipitate remaining on the filter by pouring dropwise through it 5 to 25 ml of HNO_3 (chloride-free), and then dis-

solve the precipitate remaining in the flask with this solution (Note 7).

Add standard 0.1 n. $AgNO_3$ from a buret to the HNO_3 solution, 1 ml at a time, until no more precipitate forms. After adding each portion of the $AgNO_3$, shake the mixture vigorously and let the precipitate settle so that the effect of the next portion can be observed in the supernatant liquid (Note 8; Notes 2, 3, P. 22). Carefully note and record the amount of $AgNO_3$ used.

When no more precipitate forms, heat the mixture just to boiling and shake it vigorously until the precipitate coagulates into lumps and settles rapidly. Cool the mixture to room temperature, add to it 5 ml of 1 n. $Fe(NO_3)_3$, and titrate it with 0.1 n. KSCN until the first pink color, permanent for 15 to 20 sec., can be observed in the solution. Calculate the amount of bismuth present from the volumes of standard $AgNO_3$ and KSCN used.

Notes:

1. A small precipitate may be due to aluminum, silica, iron, or elements of the Tin Group. These constituents may have been introduced in the reagents or may be present owing to incomplete washing of the sulfide precipitates in P. 11 and P. 12. Such a precipitate should be compared with known amounts of bismuth, similarly precipitated. The following confirmatory test should then be made on both precipitates:

To 0.5 ml of $SnCl_2$ reagent add 2 ml of water and (cooling the solution) NaOH until the precipitate first produced is dissolved. By means of a dropper, treat the precipitate on the filter with this solution. (Immediate blackening of the precipitate, presence of bismuth.)

The bismuth hydroxide is *immediately* converted into intensely black metallic bismuth by the alkaline sodium stannite solution. A slow darkening of the residue is of no significance, as the stannite slowly decomposes into stannate and metallic tin. Because of this, one unfamiliar with the test should also apply it to the known bismuth hydroxide precipitate.

2. A volume of ammonia nearly equivalent to the acid present can be rapidly added, and smaller portions can be added until a transitory precipitate appears; it should then be added dropwise until the last drop forms a permanent precipitate.

3. If the solution is rapidly diluted, the resulting precipitate may be so finely divided as to be difficult to filter or wash.

4. It is essential that the addition of the NH_4OH be stopped when the pink color first *begins* to change. Enough HCl should then be immediately added to restore an unmistakably pink color to the solution. With 3 drops

of methyl orange indicator solution these changes can easily be seen even in the presence of a large precipitate.

5. The BiOCl at times separates in such a finely divided state that it will pass through the filter unless it is coagulated by boiling, as is directed.

6. These tests should be made by adding a few drops of HNO_3 and then a few drops of 0.1 n. $AgNO_3$ to the 10-ml filtrate to be tested. It is suggested that a standard be prepared containing the amount of chloride which would correspond to not more than 0.5 mg of bismuth, and that the washings be continued until not more than this amount is found in a 10-ml portion of wash water. The test for chloride with silver ion is so sensitive that it is unnecessary and time-consuming to wash until a perfectly clear solution is obtained.

7. If the precipitate on the filter or in the beaker dissolves slowly, the HNO_3 can be heated to 40° to 50°C., thereby increasing the rate of solution. It should not be heated more than this or oxidation of the chloride by the nitric acid may occur.

8. If it is desired, the estimation of bismuth can be made by this titration, as suggested in Note 3, P. 22. In general, if a standard thiocyanate solution is available, the end-point can be more quickly obtained as directed in the next paragraph of the procedure.

P. 28. Precipitation and Estimation of Copper

Discussion. If copper has not been found present in P. 26, this procedure for its estimation should be omitted.

Upon adding an excess of a soluble iodide to a solution containing cupric copper, a precipitate of cuprous iodide is formed and an equivalent amount of iodine is set free. By titrating this iodine with standard thiosulfate, an estimation of the copper present is obtained.

From an inspection of the potentials (see Appendix) of the electronic reactions

$$Cu^{+} = Cu^{++} + E^{-}$$

and

$$3I^{-} = I_3^{-} + 2E^{-},$$

it is obvious that the equilibrium of the reaction

$$2Cu^{++} + 3I^{-} = 2Cu^{+} + I_3^{-}$$

should greatly favor the formation of the products on the left side of the equation. If, however, the effect of the solubility of cuprous iodide is considered, it is seen that it may have a large effect in shifting the equilibrium toward the right by keeping the concentration of the cuprous ion at a very low value. In fact, from the potential for the reaction

$$CuI_{(s)} = Cu^{++} + I^{-} + E^{-}$$

it is seen that the equilibrium for the reaction

$$2Cu^{++} + 5I^- = 2CuI_{(s)} + I_3^-,$$

should favor the formation of the products on the right; and a calculation of the equilibrium constant enables the prediction to be made that the reaction should proceed to an extent well within the usual quantitative limits, especially if an excess of iodide is present in the solution.

This method for the determination of copper is extensively used commercially and has been the subject of numerous investigations.[17] These have shown that the solution should contain approximately 4 per cent by weight of potassium iodide, that the cuprous iodide may absorb iodine, and that in an acid solution there may be some iodine liberated by the oxygen of the air; these latter effects are not large and are compensating, thereby permitting results precise to 0.1 to 0.2 per cent to be readily attained.

Cuprous iodide is very slightly soluble in water, so that all but a few milligrams of the copper is precipitated; this amount remains in solution, owing mainly to the formation of the CuI_2^- ion. The precipitate is filtered out and this small amount of copper is left in the solution, as it does not interfere with the test for cadmium under the conditions of P. 29. Experiments have shown that no cadmium is carried out by the precipitate.

The copper can be precipitated as cuprous thiocyanate[18] by the addition of an excess of a soluble thiocyanate before the titration of the liberated iodine. An extensive series of experiments[19] have shown that under very closely regulated conditions the precipitation of the copper can be made so complete that no precipitate is obtained upon passing hydrogen sulfide into the filtrate, and, consequently, the later use of cyanide to prevent the precipitation of cuprous sulfide in the precipitation of cadmium as sulfide is avoided. The accuracy of the method was proved by confirmatory experiments made with various amounts of copper, both alone and in the presence of cadmium. However, experience with the procedure in the hands

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[17] Gooch and Heath, *Am. J. Sci.*, **24**, 65 (1907); Bray and McCay, *J. Am. Chem. Soc.*, **32**, 1199 (1910); Peters, *ibid.*, **34**, 422 (1912); Popoff, *ibid.*, **51**, 1299 (1929); Whitehead and Miller, *J. Ind. Eng. Chem., Anal. Ed.*, **5**, 15 (1933).

[18] Bruhns, *Chem. Zeit.*, **42**, 301 (1918); Kolthoff, *ibid.*, **42**, 609 (1918); Kruger and Tschirch, *Z. anal. Chem.*, **97**, 161 (1934).

[19] Unpublished experiments by Karl A. Ganslee (1927).

of persons unfamiliar with the method showed that often the proper conditions were not obtained, and the test for cadmium was obscured by a black copper sulfide precipitate. This fact made the use of an additional confirmatory test necessary, and, as the precipitate of cuprous thiocyanate was no more readily filtered and washed than that of cuprous iodide, the use of the thiocyanate was abandoned. However, if it is desired to avoid the use of potassium cyanide in P. 29, this method is available and instructions for its use are provided in Note 4 of this procedure and Note 1 of P. 30. Foote and Vance[20] have shown that the iodine adsorbed on the cuprous iodide precipitate is removed by the addition of thiocyanate *just before* the completion of the titration with thiosulfate. While possible error caused by the reaction between the iodine and thiocyanate is thus eliminated and the end-point is made much more distinct, especially for one not accustomed to the titration, it was found in the series of experiments mentioned above that the precipitation of the copper was not so complete as when the thiocyanate was added before the titration was begun. The effect may be caused by a slow precipitation of the CuI_2^- ion. When the complete precipitation of copper is not necessary, it is recommended that thiocyanate be added just before taking the end-point.

A rapid determination of the copper could be made by titrating the ammoniacal solution with a standard cyanide solution until the disappearance of the blue color. This method is capable of giving fairly consistent results when the amount of copper being determined does not vary widely, when the conditions as to temperature, volume, and concentration of ammonia and ammonium hydroxide are closely regulated, and when the cyanide solution is standardized with copper under these same conditions. However, as the reaction taking place, which is essentially represented by the equation

$$2Cu(NH_3)_4^{++} + 7CN^- + H_2O = 2Cu(CN)_3^= + CNO^- + 2NH_4^+ + 6NH_3,$$

depends appreciably upon the conditions existing in the solution and is, moreover, influenced by the presence of cadmium, which likewise forms a complex cyanide ion, this method is not as reliable as the iodometric titration, and, therefore, it is not generally advised.

[20] Foote and Vance, *J. Am. Chem. Soc.*, **57**, 845 (1935).

In case only a quick approximate estimation is desired, it may be used.[21] As is mentioned above, the iodometric method is extensively used commercially for determining the copper in alloys and ores. The only elements commonly occurring in copper ores which would oxidize iodide are arsenic, antimony, and ferric iron. It has been shown that the effect of the iron can be eliminated by adding fluoride (which forms the complex ion FeF_6^{---}),[22] and oxidation by the arsenic and antimony is prevented by buffering the solution to a *p*H of approximately 3.3; this buffering effect can be obtained by providing the proper ratio of fluoride and hydrofluoric acid in the solution.[23] A procedure for the direct determination of copper in ores is given in Note 8 below. The copper in alloys may usually be determined by dissolving the metal in nitric acid and then following P. 24, P. 26, and P. 28.

Procedure 28: PRECIPITATION AND ESTIMATION OF COPPER. If in P. 26 copper was found to be present (Note 1), carefully neutralize (Note 2) the NH_4OH solution with H_2SO_4 and then add just 2 ml more. Have available a buret containing standard 0.1 n. $Na_2S_2O_3$ solution. Add to the acidified solution 2 to 3 g of solid KI (Note 3), swirl the mixture until the KI dissolves, and titrate it immediately with the $Na_2S_2O_3$ solution (Note 4). Add the thiosulfate rapidly until the color of the iodine becomes indistinct, add 5 ml of "starch solution," and again titrate just to the disappearance of the starch color (Note 5). Note the buret reading and from the volume of standard thiosulfate used calculate the amount of copper present.

Shake the mixture vigorously for several minutes, let the precipitate settle, and filter it out on a paper filter (Note 6). Wash the precipitate with two or three 5-ml portions of cold water, adding these washings to the filtrate. Treat the filtrate at once by P. 29 (Note 7). Discard the precipitate.

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[21] See Treadwell-Hall, *Analytical Chemistry*, Vol. II, Quantitative, 7th Ed., p. 616.

[22] Mott, *Chem. Analyst*, **5**, 7 (1912).

[23] Park, *J. Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931); Crowell, Hillis, Rittenberg, and Evenson, *ibid.*, **8**, 9 (1936); Foote and Vance, *ibid.*, **8**, 119 (1936); Crowell, Silver, and Spiher, *ibid.*, **10**, 80 (1938).

Notes:

1. If the amount of copper present is thought to be less than 10 to 15 mg, it can be estimated by adding to the same volume of solution, in a similar flask containing the same amount of ammonium sulfate and of ammonia, a standard solution of copper, until, when compared as directed in Note 3, P. 26, the intensity of the blue color in the two solutions is the same. If it is estimated that only this amount of copper is present, the remainder of this procedure can be omitted, as it will not interfere with the detection of cadmium.

2. The disappearance of the intense blue color due to the tetrammino copper ion may be used to indicate the neutralization of the solution.

3. The solution should be titrated as soon as the KI is dissolved in order to avoid possible loss of iodine vapors from the flask.

4. If it is desired to avoid the use of KCN in P. 29, after dissolving the KI add to the mixture 2.5 g of KSCN. Care should be taken to obtain an absolutely clear filtrate when the mixture is later filtered.

If only the titration of copper is involved, it is recommended that the thiocyanate be added just before the end-point is taken (see the discussion).

5. One accustomed to this titration can carry it to within 1 to 2 ml of the end-point before adding the starch; however, the presence of the buff-colored precipitate usually confuses one unfamiliar with the process. The addition of the starch can be deferred and the final end-point approached more closely by letting the mixture in the flask come to rest, and then holding the tip of the buret close to the surface of the solution and noting if the next drop of thiosulfate bleaches the solution locally as it is added. If it is doubtful whether or not the end-point has been passed, it should be noted if an additional millimeter of starch darkens the solution.

6. Unless Note 4 has been followed, it is not essential that a perfectly clear filtrate be obtained, as a small amount of CuI will be held in solution in P. 29 by the KCN added there. Should the iodine color reappear, it should be removed by additional $Na_2S_2O_3$ before proceeding to P. 29; an excess of the thiosulfate should not be added.

7. Upon standing in an acid solution for a considerable length of time, the tetrathionate may decompose into, among other products, sulfurous acid. This will cause a precipitate of sulfur when the solution is treated with H_2S in P. 29.

8. If only the determination of the copper in an ore is desired, proceed as follows:

> Weigh out a 0.3 to 0.4 g sample into a 200-ml flask, add 10 ml of 18 n. H_2SO_4 and, slowly, 10 ml of 16 n. HNO_3 and 5 ml of 12 n. HCl. Cover the flask with a watch glass and heat the mixture so that the reaction continues until decomposition of the ore appears complete and sulfur is no longer present. Remove the watch glass and evaporate just to fuming. Add 10 ml of 16 n. HNO_3 and 5 ml of 12 n. HCl and evaporate to fuming. Cool the solution (Note 3, P. 24), add 20 ml of water (Note 1, P. 24, second paragraph), and then add NH_4OH until its odor is distinct above the solution. Add 1.5 g of ammonium acid fluoride, $(NH_4)HF_2$, and titrate as

directed in the procedure above, beginning with the second sentence. Add 2 g of KSCN just before the end-point.

P. 29. Detection of Cadmium

Discussion. Cadmium is detected and precipitated as the sulfide. The formation of the yellow precipitate is a very distinctive test for this element, especially when the precipitation is made from an ammoniacal solution, in which the sulfides of arsenic, antimony, or tin are soluble. As copper sulfide is less soluble than cadmium sulfide, copper has to be absent or its precipitation prevented. The latter is accomplished in this procedure by carrying out the precipitation in an alkaline solution to which cyanide has been added; the complex ion $Cu(CN)_3^-$ is so stable that the concentration of the copper ions left in the solution is not sufficient to exceed the solubility product of the sulfide.[24] Experiments have shown that 0.5 mg of cadmium will form an easily visible precipitate, while a large quantity of copper will remain in the solution to which NH_4OH and KCN have been added. It is an advantage to have removed most of the copper in P. 28, for, although even 500 mg of this element would not cause an immediate precipitate of cuprous sulfide upon passing H_2S into the solution, a red precipitate of hydrorubianic acid, $(CSNH_2)_2$, is sometimes formed. Since ammonium sulfide solutions usually have a yellowish color (because of the presence of polysulfides), the test for cadmium is made by passing hydrogen sulfide into the ammoniacal solution for a short time only. The solution should not be saturated with hydrogen sulfide, as the large amount of ammonium sulfide formed would be partially oxidized to polysulfides and these would impart a yellow color to the solution, and as the excess of hydrogen sulfide would convert the cyanide into the slightly ionized hydrocyanic acid, thus permitting the precipitation of any copper present.

Cadmium sulfide, when precipitated from neutral or slightly acid solutions, usually tends to be colloidal and is filtered with difficulty, but, under the conditions of this procedure, separates in a form that is readily coagulated.

Procedure 29: DETECTION OF CADMIUM. Make the filtrate from P. 28 alkaline with NH_4OH, and then add 5 ml

[24] Bonner and Kaura, *Chem. Met. Eng.*, **34**, 84 (1927), and Glasstone, *J. Chem. Soc.*, **1929**, 702, have shown that $Cu(CN)_3^-$ is the predominant ion obtained when cuprous cyanide is dissolved in an excess of cyanide.

more (if P. 28 has been omitted, treat the ammoniacal filtrate from P. 26 as next directed). Add 2 ml of 1 n. KCN (*Caution:* Note 1); filter, wash, and discard any precipitate which forms, collecting the washings with the filtrate (Note 2). Pass a moderate current of H_2S into the filtrate for 20 sec. (Yellow precipitate, presence of cadmium. Notes 3, 4.) If a yellow precipitate is obtained, add to the mixture 5 ml of NH_4OH and again pass a slow current of H_2S into it for 5 min. (do not saturate the solution). Shake the mixture vigorously for 2 or 3 min., heat it to boiling (Note 5), and allow the precipitate to settle. Treat the mixture by P. 30.

Notes:

1. KCN is a deadly poison. Solutions containing it should not be acidified unless under a well-ventilated hood. Care should be taken in the disposal of such solutions that they are not inadvertently mixed with acids.

If, in order to avoid the use of cyanide, thiocyanate has been used in P. 28, an additional 5 ml of NH_4OH should be added here in place of the KCN.

2. A precipitate forming upon addition of the ammonia is probably due to lead or mercury, or to iron or aluminum introduced by reagents or apparatus. As any of these, except aluminum, would cause a dark sulfide precipitate with H_2S, they should be carefully filtered out, washed with a minimum of water, and discarded.

3. Even 0.5 mg of cadmium will produce a distinct yellowish, opalescent precipitate of CdS, so that, if no precipitate forms after passing in the H_2S, the solution may be discarded. The H_2S should be passed into the solution for only 20 sec., and under no conditions should the solution be saturated with the gas. Occasionally a moderate amount of sulfur will be liberated when H_2S is passed into the alkaline solution; this may be due to incomplete reduction of iodine by the $Na_2S_2O_3$ in P. 28 or to the presence of sulfite resulting from the decomposition of thiosulfate or tetrathionate. This sulfur redissolves, forming disulfide and imparting a yellowish color to the solution which should not be mistaken for the yellowish turbidity caused by small amounts of cadmium sulfide.

4. If a black precipitate forms, so that a small yellow precipitate also present might be obscured, collect it on a small filter and transfer it to a casserole with the aid of 25 ml of 1.2 n. H_2SO_4. Boil the mixture gently for 10 min. Filter out any residue through a small paper filter, wash it, and discard it. Collect the filtrate in a 200-ml flask, dilute it to 100 ml, and saturate it with H_2S. If cadmium is present, a yellow precipitate should be obtained.

By this procedure, lead, mercury, or copper are discarded in the residue. Iron sulfide is not precipitated from sulfuric acid solutions.

5. Except when only a small amount of cadmium is present, the precipitate is effectively coagulated by boiling the mixture.

P. 30. Estimation of Cadmium

Discussion. The amount of cadmium present is estimated by treating the cadmium sulfide precipitate under suitable conditions with an excess of ferric sulfate, with the result that an equivalent amount of ferrous salt is produced, according to the reaction

$$2Fe^{+++} + CdS_{(s)} = 2Fe^{++} + Cd^{++} + S_{(s)}.$$

The ferrous iron is titrated with permanganate, since the precipitated sulfur does not react sufficiently rapidly with either the excess of ferric sulfate or with permanganate to cause serious error. Although cadmium can be detected and precipitated as the sulfide, the precipitate is usually of uncertain composition. This is usually stated to be due to the fact that it contains a considerable proportion of double salts of the type $CdCl_2 \cdot CdS$; however, studies have indicated that the effect is probably caused by the adsorption of cadmium salts by the precipitate.[25] Because of this, it is not generally recommended that the precipitate be weighed or used as the basis for volumetric methods. An experimental study[26] of the method used here has indicated that, if the precipitation is made from an alkaline solution in the presence of cyanide, the precipitate is more uniform in composition; for this reason it is recommended that cyanide be added in P. 29, even if copper is absent.

Before being treated with the ferric salt, the cadmium sulfide precipitate is heated and washed with a hydrosulfate-sulfate solution in order to remove any adhering ammonium sulfide without at the same time dissolving any of the cadmium. The "buffering" of a solution by means of hydrosulfate and sulfate is discussed in P. 61. Before titrating with the permanganate, phosphoric acid is added to diminish the color caused by the large amount of ferric salt present, thus making the end-point more distinct. Experiments have shown that the results obtained are usually high, the error ranging from 0.3 to 2 per cent; that complete washing of the precipitate is necessary even with the hydrosulfate-sulfate treatment; and that the greater the amount of cadmium present and the longer the calcium sulfide is heated with the ferric sulfate the greater the error.

The precise determination of cadmium is usually effected either (1) electrolytically, or (2) by precipitating the element from an acid solution as the sulfide (after having separated it from other elements

[25] Weiser and Durham, *J. Phys. Chem.*, **32**, 1061 (1928).
[26] Unpublished experiments by F. N. Laird.

that would be similarly precipitated), dissolving the sulfide in hydrochloric acid, evaporating this solution to dryness with an excess of sulfuric acid, and heating to 500°C. until the anhydrous cadmium sulfate thus obtained is constant in weight.

Procedure 30: ESTIMATION OF CADMIUM. Filter the mixture from P. 29 by decantation through an asbestos filter. Sprinkle about 1 ml of solid Na_2SO_4 on the precipitate and wash it by decantation with a 50-ml portion of boiling water (Note 1). Add to the precipitate in the flask 50 ml of a solution made by adding 3 g of solid Na_2SO_4 and 1 ml of 6 n. H_2SO_4 to 100 ml of water, and heat the mixture almost to boiling (Note 2). Again decant the solution and wash the precipitate with the remainder of the sulfate solution. If the precipitate does not coagulate readily, add solid NH_4Cl.

Transfer the precipitate and filter to a 400-ml flask and add to it a solution made by dissolving 4 g of solid $Fe_2(SO_4)_3$ in 50 ml of boiled water. Slowly heat the mixture to boiling, add to it 3 ml of 6 n. H_2SO_4, and heat it on a water bath until the CdS has dissolved and only a coagulated sulfur precipitate remains (usually 5 to 10 min., depending upon the size of the precipitate).

Immediately cool the solution, add to it 3 ml of 85 per cent H_3PO_4 and 10 ml of 6 n. H_2SO_4, and dilute it with 150 ml of water. Titrate the solution with standard $KMnO_4$ solution, stirring continuously, until a drop of the permanganate causes a pink color to persist throughout the solution for 15 to 20 sec. (Note 3). From the volume of $KMnO_4$ used, calculate the amount of cadmium present (Note 4).

Notes:

1. Adding the Na_2SO_4 and heating the mixture for 1 to 2 min. usually causes the precipitate to coagulate, so that after 2 to 5 min. most of the solution can be readily decanted. If the precipitate is small, most of it may have to be caught on the filter.

2. The precipitate is treated with H_2SO_4-Na_2SO_4 solution in order that any adsorbed sulfide may be extracted from it and expelled as H_2S. The hydrogen ion concentration of the hydrosulfate-sulfate solution is so low that there is no appreciable solution of the CdS upon expelling the H_2S.

3. Although the end-point is not permanent, it is easily noted; the permanganate is rapidly decolorized, and the entire solution is not colored until the end-point is reached, especially if the solution is continuously stirred.

4. The $Fe_2(SO_4)_3$ should be tested for ferrous iron by titrating 4 g of it with $KMnO_4$ under the conditions of this procedure.

The Analysis of the Tin Group

General discussion of methods for the analysis of the Tin Group. The satisfactory separation of the elements of the Tin Group when these are present in moderately large amounts was found to offer considerable difficulty. Some systems of qualitative analysis attempt the separation of antimony and tin from arsenic and mercury by treating the precipitate of the Tin Group sulfides with 12 n. hydrochloric acid. By such treatment antimony and tin sulfides, when present alone, can be dissolved, while, if the solution is kept saturated with hydrogen sulfide, arsenic sulfide is insoluble. However, it has also been found that considerable amounts of mercury are dissolved by the concentrated hydrochloric acid, and that, if a mixture containing considerable amounts of these sulfides is treated, the extraction of antimony from the arsenic sulfide is incomplete. Attempts were made to separate mercury from the other elements of this group by adding an excess of an ammonium salt to the sodium sulfide solution of the Tin Group sulfides. This causes the precipitation of mercuric sulfide, which, as was mentioned in the discussion of P. 12, is insoluble in an ammonium sulfide reagent. It was found that by this means even small amounts of mercury could be detected and that its precipitation was complete when it was present alone or even when it occurred with arsenic or antimony. When tin was present in even moderate amounts, the precipitation of mercury was incomplete; also, the precipitate contained a considerable amount of tin and was so colloidal that filtration was often impossible. Because of these facts the above methods are not used in this system of analysis.

As a result of an extensive investigation by Dr. Chester E. Wilson, a process has been developed in which the sulfide precipitate is dissolved in a hydrochloric acid solution with the aid of bromate as an oxidizing agent; the arsenic is then reduced and distilled as the relatively volatile trichloride, the mercury is reduced to the metallic form by means of phosphorous acid, and the antimony is then precipitated as the sulfide from a solution in which the acid and chloride concentrations are carefully controlled.

The tin is precipitated as sulfide by making the solution alkaline, passing in hydrogen sulfide, and then making the solution again

TABULAR OUTLINE V

The Analysis of the Tin Group

(Method for the More Quantitative Separation and Estimation of the Elements of This Group)

Precipitate of the Tin Group Sulfides (from P. 13): As_2S_5, HgS, Sb_2S_4, SnS_2, S
Treat with HCl and $KBrO_3$. (P. 41)

Residue: S

Solution: H_3AsO_4, H_2HgCl_4, $HSbCl_6$, H_2SnCl_6, Br_2
Add HBr and H_3PO_3. *Heat.*
Solution: $AsCl_3$, $HSbCl_4$, H_2HgCl_4, H_2SnCl_6, Br^-, H_3PO_3, H_3PO_4
Distill. Collect distillate in water.

Distillate: $AsCl_3$, HCl
Neutralize with $NaHCO_3$

Titrate with KI_3 *solution, starch indicator.*

(H_3AsO_4, I^-) (P. 43)

Solution: H_2HgCl_4, $HSbCl_4$, H_2SnCl_6, Br^-, H_3PO_3, H_3PO_4
Add H_2SO_4 *and dilute. Heat.* (P. 44)

Precipitate: Hg_2Cl_2, Hg
Treat with Na_2HPO_3 *and NaOH.*
(Hg_2O, Hg)

Dissolve in HNO_3.
(Hg^{++})

Add $Fe(NO_3)_3$, *titrate with KSCN.*
Solution: $Hg(SCN)_2$, un-ionized; $Fe(SCN)_6^=$ (red) (P. 45)

Solution: $HSbCl_4$, H_2SnCl_6, H_3PO_4, H_3PO_3, HSO_4^-, Br^-, H^+Cl^-.
Dilute to 75 ml. Heat. Saturate with H_2S. (P. 46)

Precipitate: Sb_2S_3
Dissolve in HCl. Add tartaric acid. Neutralize.
($HSbOC_4H_4O_6$)

Add $NaHCO_3$, *titrate with* KI_3 *solution, starch indicator*
Solution: $HSbO_2C_4H_4O_6$, I^- (P. 47)

Solution: H_2SnCl_6, etc.
Neutralize, pass in H_2S, *make just acid.*

Precipitate: SnS_2

Dissolve in HCl. Heat with Ni foil.
(H_2SnCl_4, $NiCl_2$)

Cool, dilute, add starch, titrate with KI_3 *solution.*
Solution: H_2SnCl_6, I^- (P. 49)

Filtrate: *Discard.*

acid. It was found that, because of the phosphoric and phosphorous acids present, the precipitation of the tin by saturating even a very slightly acid solution with hydrogen sulfide was very slow; by forming the sulfo-salt in an alkaline solution and then acidifying, rapid precipitation is obtained. The details of these procedures are shown in Tabular Outline V; the results obtained from a series of test analyses[1] are shown in Table XVII.

TABLE XVII

TEST ANALYSES OF THE METHOD FOR THE ANALYSIS OF THE TIN GROUP ELEMENTS

Amount of Each Element Taken and Found (mg); *S* Denotes a Satisfactory Detection

Experiment	Arsenic		Mercury		Antimony		Tin	
	Taken	Found	Taken	Found	Taken	Found	Taken	Found
1	500	490	1	*S*	1	*S*	1	*S*
2	1	*S*	500	481	1	*S*	1	*S*
3	1	*S*	1	*S*	500	499	1	*S*
4	1	*S*	1	*S*	1	*S*	505	504
5	250	245	250	232	253	251	255	220[a]

[a] Twenty mg of tin were found in the sulfur residue (P. 41); probably as a result of too rapid addition of $KBrO_3$ in that procedure.

However, this method for the more quantitative separation of these elements was found to require such an expenditure of time and the use of such special technique that it was decided to offer a simpler and more rapid optional method for the analysis of this group. This method can be used when there is question as to whether or not any Tin Group elements are present in the precipitate obtained on acidifying the sodium sulfide solution, or when only small amounts (50 mg or less) of these elements are present and only a rapid qualitative analysis is desired. When larger amounts are present and when a more quantitative separation and estimation of these elements is required, the use of the longer but more exact method is recommended.

[1] These test analyses were part of the investigation carried out by Dr. Chester E. Wilson.

TABULAR OUTLINE V-A

OPTIONAL METHOD FOR THE ANALYSIS OF THE TIN GROUP
(For Use When Only a Rapid Qualitative Analysis Is Desired)

Tin Group Precipitate (from P. 13): HgS, As_2S_5, Sb_2S_4, SnS_2, S
Treat with NH_4OH and $(NH_4)_2S$

Residue: HgS, S	Solution: $AsS_4^{=}$, $SbS_4^{=}$, $SnS_3^{=}$, HS^-, HS_2^-, NH_4OH *Heat with 6 n. HCl.*
Residue: As_2S_5, S	Solution: $HSbCl_4$, H_2SnCl_6 *Dilute, treat with H_2S.*
Precipitate: Sb_2S_3	Solution: H_2SnCl_6 *Partly neutralize, treat with H_2S.*
Precipitate: SnS_2	Solution: *Discard.*

P. 41A. Optional Method for the Analysis of the Tin Group (For Use When Small Amounts of the Tin Group Elements Are Present and Only a Rapid Qualitative Analysis Is Desired)

Discussion. In this method, which is shown in detail in Tabular Outline V-A, the sulfide precipitate (from P. 13) is treated with ammonium hydroxide and a small amount of an ammonium sulfide reagent. These dissolve the sulfides of arsenic, antimony, and tin but leave mercuric sulfide (and any Copper Group sulfides) in the residue, where a confirmatory test for the presence of mercury can be made. Only a small amount of the ammonium sulfide is used in order not to dissolve much of the sulfur; thus, upon acidifying this ammonium sulfide solution the detection of the presence of any Tin Group sulfides is made more certain. By then adding an equal volume of 12 n. hydrochloric acid to this acid mixture and heating, most of any antimony and tin will be dissolved, leaving arsenic sulfide in the residue. The acid concentration of the filtrate is then suitably adjusted, and the filtrate is treated with hydrogen sulfide, which precipitates the antimony as sulfide. Thus, only tin is left in the filtrate, from which it is precipitated as sulfide by partial neutralization of the acid.

Although this method gives very imperfect separations when considerable amounts (50 mg or more) of these elements are present, it is recommended for use with smaller amounts for the following reasons: It is very much more rapidly and easily carried out than

are the more exact procedures; it provides an even more sensitive detection of traces of these elements; and, by comparison of the precipitates obtained with known amounts of the element precipitated under similar conditions, an approximate estimate of the amount of the elements present can be made.

Procedure 41A: OPTIONAL METHOD FOR THE ANALYSIS OF THE TIN GROUP. Transfer the sulfide precipitate (from P. 13) to a casserole, add to it 10 ml of NH_4OH and 2 ml of ammonium monosulfide reagent, and heat the mixture to 60° to 70°C.; disintegrate any residue. (Dark residue, presence of mercury or of Copper Group sulfides.) Filter out the residue, and, if it is darkened, treat it as directed in Note 1, P. 45, to confirm the presence of mercury.

Collect the filtrate in a 100-ml flask (do not add any wash water to it) and boil it vigorously for 5 min. (Note 1). Acidify the solution with 12 n. HCl, adding 1 ml in excess. (Colored precipitate, presence of arsenic, antimony, or tin.)

If a colored precipitate is obtained, transfer the mixture to a graduated cylinder, add an equal volume of 12 n. HCl, return the mixture to the flask, and heat it just to boiling for 10 min. (Note 2). Pass a few bubbles of H_2S into the mixture, again heat it to boiling, and filter the hot solution through a small paper filter which has been moistened with 6 n. HCl. (Yellow residue, presence of arsenic.) Do not add any wash water to the filtrate. Treat the residue by Note 9, P. 42, to confirm the presence of arsenic.

Dilute the filtrate to just three times its volume with water, heat it almost to boiling, and again saturate it with H_2S. (Orange precipitate, presence of antimony.) Filter out the precipitate (Note 1, P. 47).

Add to the filtrate a volume of 15 n. NH_4OH just two-thirds that of 12 n. HCl originally added (the solution should be acid), again saturate the hot solution with H_2S, close the flask, and allow it to stand for 15 min. (Yellow precipitate, presence of tin. Note 2, P. 48.)

Notes:

1. The solution is boiled in order to expel most of the ammonia and thus reduce the volume of acid required to make it acid.

2. By adding an equal volume of 12 n. HCl, the solution is made approximately 6 n. in hydrochloric acid. This is the composition of the constant-boiling solution, so that its concentration is not changed by boiling. This is important as it permits a close adjustment of the acid for the subsequent separation of antimony from tin.

P. 41. Solution of the Tin Group Sulfides

Discussion. In the more exact method for the analysis of the Tin Group elements, the first step involves the complete solution of the sulfide precipitates. In the procedure below, the antimony and tin sulfides are dissolved by concentrated hydrochloric acid alone, and then arsenic and mercury sulfides are brought into solution by the addition of an oxidizing agent, such as potassium bromate (potassium chlorate or nitric acid may also be used). Bromate is used in preference to chlorate as it was found to be much more effective in dissolving the sulfur which is always precipitated upon acidifying the disulfide reagent. The use of liquid bromine was found to be equally effective in this respect, but it formed large amounts of sulfur monobromide, S_2Br_2, a red liquid which retained considerable amounts of arsenic. This was probably due to the formation of a compound containing arsenic, sulfur, and bromine, analogous to the chlorine compound $As_4S_5Cl_2$, which is produced under similar conditions. When bromate is used and when a large amount of arsenic is present, a reddish residue containing a few milligrams of arsenic will frequently be left. Usually, after the treatment with bromate, there remains only a small residue, which is composed mostly of elementary sulfur with small amounts of undissolved sulfides and of sulfur monobromide enclosed within it. Experiments have shown that when 500 mg of each element of the Tin Group as the sulfide is treated separately by this procedure, there remain in these residues less than 2 mg of mercury, 3 mg of arsenic, not over $\frac{1}{2}$ mg of antimony, and an insignificant amount of tin.

Although arsenic trichloride is readily volatilized from hot hydrochloric acid solutions, the use of the bromate, which is required to dissolve arsenic sulfide, insures the complete oxidation of this element to the quinque-positive state. The solution cannot be boiled or unduly heated, as quinque-positive arsenic is reduced by the bromide resulting from the reduction of the bromate and would then volatilize.

Procedure 41: Solution of the Tin Group sulfides. Transfer the sulfide precipitate (from P. 13) to a 100-ml

beaker with the aid of 20 ml of 12 n. HCl (Note 1). Cover the beaker with a glass and warm the mixture (*do not boil*) for 2 to 3 min. (or longer if the precipitate seems to be dissolving). Disintegrate the residue frequently and thoroughly with a stirring rod. If the precipitate is not all dissolved, cool the beaker and add to the mixture, in 0.1-ml portions, solid $KBrO_3$ (Note 2) until the sulfides appear to be dissolved and a permanent orange color is obtained (Note 3). Carefully disintegrate the residue before each addition of the $KBrO_3$ (Note 4), and add a fresh portion only after the previous one stops reacting.

Cool the mixture and filter it through an asbestos filter which has been moistened with 12 n. HCl and drained, collecting the filtrate in a 200-ml distilling flask which has also been washed with 12 n. HCl (Notes 5, 6). Wash the beaker and residue with 10 ml of 12 n. HCl, added in small portions, and collect these washings with the filtrate. Treat the filtrate by P. 42. Discard the residue.

Notes:

1. Only 12 n. HCl (and no water) should be used to aid this transfer, as the later distillation of the arsenic depends upon having concentrated acid present. The precipitate is most easily transferred by inserting a thin glass rod through the stem of the funnel and pushing the perforated plate and asbestos into the beaker; any precipitate adhering to the sides can be washed through the funnel with the acid. A beaker is used in preference to a casserole to avoid the danger of loss by spattering during the addition of the bromate.

If a paper filter has been used and only a small amount of the precipitate has been carried onto the filter, this precipitate may be transferred by pushing a hole through the paper with a stirring rod and then washing it off the paper and through the funnel with the HCl. It is also possible to open the filter against the side of a larger funnel and wash the precipitate from it by squirting the HCl repeatedly against it with a dropper. The filter and funnel can then be washed with the HCl. If a large amount of precipitate has been carried onto the filter, it is usually better to transfer as much of the precipitate to the beaker as is possible with a stirring rod or porcelain spatula; the precipitate adhering to the paper can then be treated as suggested above.

2. As long as the precipitate appears to be dissolving in the HCl alone, the $KBrO_3$ should not be added, as it causes the liberation of considerable sulfur; this mechanically encloses undissolved particles of the sulfides, which then dissolve more slowly. Of the sulfides of the Tin Group, antimony and tin dissolve readily in concentrated HCl alone, mercury dissolves to a slight extent, and arsenic dissolves scarcely at all. When treated with HCl under

certain conditions, mercuric sulfide changes into a white residue which still contains mercury; a dark precipitate changing in this way should be further treated with $KBrO_3$.

3. When properly used, 2 g of the bromate are adequate to dissolve 500 mg of arsenic sulfide, even when the latter is present with the sulfur resulting from the using of the maximum amount of the disulfide reagent. When the sulfides have been dissolved, the addition of bromate will give a permanent orange color to the solution; a large excess of the bromate should be avoided, as it oxidizes the phosphorous acid later to be added.

4. When a large sulfide precipitate is treated, there usually remains a small dark or colored residue of sulfur enclosing small amounts of undissolved precipitate; after being treated as directed, these residues generally contain insignificant amounts of antimony or tin and not over 2 mg of mercury or 3 mg of arsenic, even when these elements are present in very large quantities. If the $KBrO_3$ is added rapidly, if the mixture is boiled, or if the residue is not continually kept broken up, larger amounts of the sulfides may remain undissolved. Therefore, if it is desired to recover this amount of these elements, the solution should be completely decanted, the residue should be heated with 1 to 2 ml of 6 n. NaOH and evaporated almost to dryness, and 5 ml of 12 n. HCl and then sufficient $KClO_3$ to dissolve the sulfide present should be added. After this solution has been boiled to expel any Cl_2 left, it can be filtered and collected with the main filtrate or can be treated separately. In this treatment the sulfur is dissolved by the hydroxide, forming sulfide and thiosulfate, and any Tin Group elements again dissolve as the sulfo-salts. Upon acidifying the solution, the sulfides are reprecipitated and it can be noted if an appreciable amount of arsenic or mercury is present. If there is, the precipitate is then in a form which readily dissolves on treatment with $KClO_3$.

5. The filter and flask are moistened with HCl to prevent the precipitation of antimonyl chloride when large quantities of antimony are present, and to prevent dilution of the solution before the distillation of arsenic.

6. The distilling flask should be of resistance glass and should preferably have the side arm bent as shown in Fig. 29.

P. 42. Separation and Detection of Arsenic

Discussion. After a solution of the Tin Group sulfides has been obtained by means of the treatment with hydrochloric acid and bromate, methods for separating the individual elements are to be considered. Arsenic can be precipitated as its sulfides from a solution 9 to 12 n. in hydrochloric acid, and a quantitative separation from antimony and tin can thus be obtained. It was found, however, that mercury, when present in considerable quantities, would divide between the precipitate and the solution; if the acid concentration was reduced sufficiently to precipitate the mercury completely (to less than 6 n.), antimony would be coprecipitated by the arsenic sulfide precipitate.

A method often used for the quantitative separation of arsenic from all the other common basic elements consists in the distillation of the trichloride from a hydrochloric or hydrobromic acid solution. This method can be advantageously applied at this point, as the distillation is most effectively made from a concentrated acid solution; however, as all of the Tin Group elements are present in their higher oxidation states, a means of reducing the arsenic has to be provided. This could be done by the addition of considerable bromide to the solution, but the rate of the reduction is somewhat slow, and the bromine which is evolved reoxidizes the arsenic in the distillate. By the addition of phosphorous acid, which is to be used later to reduce the mercury, the liberation of the bromine is prevented, because it is reduced by the phosphorous acid as fast as it is formed. Phosphorous acid alone would not serve the purpose, as the reduction of arsenic acid by phosphorous acid proceeds at an extremely slow rate.

In the procedure which has been adopted, 7 ml of 6 f. phosphorous acid and 1 ml of 9 f. hydrobromic acid are added to the 30 ml of 12 f. hydrochloric acid, and the resulting solution is distilled to a volume of 15 ml. In the development of this process it was found that, with 500 mg of arsenic present, about 90 per cent of it passes over with the first 10 ml of distillate, and not over 1 mg remains after the distillation. When two 5-ml portions of hydrochloric acid are subsequently added and distilled, the amount of arsenic remaining (approximately 0.1 mg) is so small that it does not interfere with the detection of antimony. Under these same conditions, with 500 mg of each of the other elements, 10 to 12 mg of mercury, 3 to 5 mg of antimony, and only a trace of tin are distilled. When the distillation is carried to 7 ml, an additional 4 to 6 mg of mercury are distilled, but only a trace of either antimony or tin is distilled; when it is continued until only 5 ml remain, 6 to 8 mg more of mercury, but no appreciable amount of antimony or tin, come over.

From the fact that the boiling point of arsenious chloride is 130°C., while that of stannic chloride is 114°C., it is obvious that the behavior of these elements in this distillation is not due entirely to a difference in the volatility of the various chlorides. However, arsenious chloride exists as such to a large extent in hydrochloric acid solutions, while stannic chloride is converted into the very stable chlorostannate ion, $SnCl_6^=$. Quinque-positive arsenic does not volatilize, because it is largely hydrolyzed to arsenic acid; the antimony chlorides are likewise to a large extent converted into complex ions or hydrolyzed. Mercuric chloride is not appreciably

ionized in aqueous solutions but forms a complex ion, $HgCl_4^=$, with an excess of chloride ion; the mercury which distills over does so as metallic mercury because of a slight reduction by the phosphorous acid.

Procedure 42: SEPARATION AND DETECTION OF ARSENIC. Add to the solution in the distilling flask 7 ml of 6 f. H_3PO_3 and 1 ml of 9 f. HBr (Note 1). Close the end of the side-arm outlet tube with a short piece of rubber tubing fitted with a clamp or glass bead, and insert in the neck of the flask a closely fitting test tube filled with cold water and wet with 12 n. HCl on the outside. Heat the solution to 80° to 90°C. until any bromine color disappears (Note 2), and then cool the solution. Remove the rubber tubing and the test tube, rinsing the latter with 1 to 2 ml of 12 n. HCl, and clamp the flask in position (see Fig. 29) with the side arm extending to the bottom of a 100-ml volumetric flask containing 40 ml of cold water and immersed in a large beaker of ice water. Insert an "ebullition tube" (Note 3) and close the distilling flask with a cork stopper carrying a glass tube 7 mm in diameter and about 70 cm long which extends to the bottom of the flask. Heat the solution and distill until just 15 ml of solution remain in the flask (Notes 4, 5).

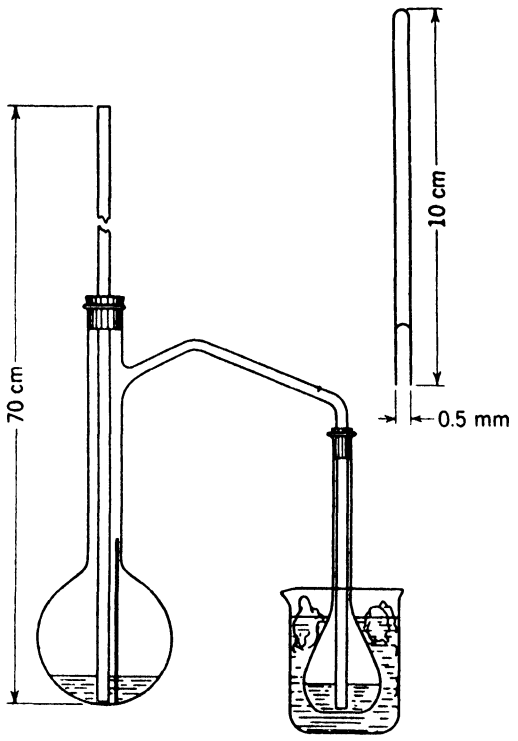

Fig. 29. Apparatus for the Distillation of Arsenic Trichloride.

Add 10 ml of 12 f. HCl to the distilling flask through the safety tube by means of a dropper and again distill until only 15 ml of solution remain (Note 4).

Remove the flask with the distillate, rinsing the delivery tube, cool to room temperature, dilute with water to the mark on the flask, and thoroughly mix the contents (Note 6).

Pipet 25 ml of the distillate into a 200-ml flask, add 10 ml of 12 n. HCl, saturate the solution with H_2S, and then heat it almost to boiling while continuing the flow of H_2S. (Yellow precipitate, presence of arsenic, Notes 7, 8, 9, 10.)

If arsenic is present, treat the remainder of the distillate by P. 43.

Treat the residual solution in the distilling flask by P. 44.

Notes:

1. Hydrobromic acid can be obtained as the 48 per cent solution, which is 9 f., or as the 42 per cent solution, which is 7.2 f. If only the less concentrated solution is available, an equivalent amount should be added.

2. After adding the hydrobromic acid, there will probably be a yellowish color due to bromine in the solution, because in the concentrated acid both arsenic and antimonic acids are reduced by bromide. If the distillation were started immediately, this bromine would pass into the distillate and would reoxidize the arsenic, introducing an error in the subsequent estimation of arsenic; therefore the solution is heated until the bromine is reduced by the phosphorous acid. To prevent loss of arsenic, a test tube of cold water is inserted in the neck of the distilling flask. When antimony is present, a slight yellowish color may remain after the bromine has been reduced; otherwise the solution becomes colorless. It has been found that, when the solution is heated to between 80° and 85°C., the arsenic and bromine are completely reduced in less than 5 min. Care should be taken not to boil the solution, or arsenious chloride will be lost.

3. "Bumping" and irregular boiling of the solution during the distillation can be minimized by the use of an "ebullition tube" in the flask. Such tubes are made as follows: Heat a piece of soft glass tubing of 8 to 10 mm in diameter and draw from it a long capillary of approximately 0.5 mm in diameter. Cut this capillary into lengths somewhat shorter than the height of the distilling flask. Heat one end of each of these lengths until it seals, and then heat at a point about 1 cm from the other end until the capillary constricts and closes, thus leaving a capillary space about 1 cm long in that end.

"Bumping" is caused by the lower portion of the solution superheating and not maintaining an equilibrium with its vapor phase, until, when finally gas formation does start, there is a sudden formation of a large volume of vapor. The ebullition tube is placed in an upright position in the flask with the open end down and just above the heating flame. When the solution is heated, the air is expelled from the capillary, the tube fills with the vapors of the liquid, and thus, as long as the solution is boiled, a vapor phase

is kept in contact with the hottest part of the solution; superheating is thus minimized. It is desirable that the solution should not completely stop boiling at any time during the distillation, because, if the vapor condenses and the tube completely fills with liquid, it ceases to function.

A supply of these tubes can be readily made and kept available in the laboratory.

4. In order to avoid distilling over considerable amounts of mercury, the solution should not be distilled below 10 ml. Furthermore, in order that an exact adjustment of the acid present in the subsequent procedures may be made, the amount of solution remaining in the flask should be just 15 ml. This volume is best estimated by pouring 15 ml of water into a similar flask and making a direct comparison.

5. To avoid possibility of loss through the safety tube, it should be occasionally cooled during the distillation by adding 0.1 to 0.2 ml of 12 n. HCl to it with a dropper.

6. A small gray or black precipitate floating on the surface of the distillate or collected on the bottom of the flask is probably mercury. In this case, before the solution is diluted, it should be filtered through a tightly packed asbestos filter which has been washed with 6 n. HCl and the precipitate and filter should then be washed with 3 to 5 ml of 6 n. HCl added dropwise. This filter should be reserved and the mercury obtained in P. 44 should be collected on it. The HCl is used on the filter and in washing to prevent the precipitation of antimony.

7. As the arsenic may be present in the quinque-positive state, the mixture is heated to boiling in order to hasten the formation of the precipitate and to coagulate the precipitate more effectively.

8. If no precipitate (or only a very small one) is obtained, the remainder of the distillate should be added to the flask, a corresponding volume of 12 n. HCl should be added, and the solution should be treated with H_2S. The amount of arsenic in any precipitate thus obtained can be estimated by a comparison with standard precipitates.

9. If desired, the presence of arsenic in the precipitate may be further confirmed as follows:

> Filter and wash the yellow precipitate. Transfer it to a small casserole with the aid of 10 ml of NH_4OH. Evaporate the ammonia solution almost to dryness, add to it 5 ml of 16 n. HNO_3, and again evaporate just to dryness. Treat with 5 ml of 3 n. HNO_3, and then filter out and discard any insoluble residue. Make the solution alkaline with NH_4OH, add 1 ml excess, and then add 5 ml of 1 n. $Mg(NO_3)_2$ reagent. (White crystalline precipitate, presence of arsenic.)

The precipitate so obtained is $MgNH_4AsO_4$. For a discussion of its properties, see P. 88.

The precipitate may be further confirmed by collecting it on a small filter, washing it with 1 to 2 ml of cold water added dropwise, and then pouring dropwise over it a solution made by adding 5 drops of $HC_2H_3O_2$ to 15 drops of $AgNO_3$. (Red precipitate, presence of arsenic.) By this treatment the $MgNH_4AsO_4$ is metathesized to the less soluble Ag_3AsO_4, which is brick red in color.

10. Any antimony which may have distilled over may be recovered and estimated approximately by filtering out the arsenic precipitate, diluting the filtrate to 100 ml, adding 10 ml of 15 n. NH_4OH, and again saturating it with H_2S. An orange precipitate shows the presence of antimony; the amount present can be estimated by comparison with a standard precipitate.

P. 43. Estimation of Arsenic

Discussion. The method used here for the estimation of arsenic depends upon the oxidation of arsenious acid to arsenic acid in a neutral solution by means of a standard iodine solution. This method was discussed in detail in P. XII, p. 71, and was used there for standardizing an iodine solution. It was mentioned there that this reaction can be caused to proceed quantitatively in either direction by the proper adjustment of the hydrogen ion concentration, and the conditions for using the reverse reaction are treated in detail in the discussion of P. 89. As, in spite of the precautions taken in P. 41, traces of bromine may pass over into the distillate and oxidize an equivalent amount of arsenic, the reverse reaction is utilized here. Any quinque-positive arsenic is reduced before the titration with iodine by adding a small amount of iodide to the strongly acid solution; the iodine thus set free is reduced with thiosulfate, an excess being avoided, and the solution is then neutralized and buffered for the titration with standard iodine solution.

Procedure 43: ESTIMATION OF ARSENIC. Pipet 25 ml of the distillate (from P. 42) into a 200-ml flask. Add to it 10 ml of 6 n. HCl and, in 0.1 g portions, 1 g of solid $NaHCO_3$. Add just 0.5 g of solid KI, close the flask with a clean rubber stopper, swirl the mixture until the KI dissolves, and allow it to stand for 5 min. (Note 1). If there is a perceptible yellow color, carefully add 0.1 n. $Na_2S_2O_3$, a drop or half-drop at a time, until the solution becomes colorless (Note 2).

Dilute the solution at once to 50 ml, add to it 3 drops of phenolphthalein indicator solution and then sodium hydroxide until a pink color is obtained (Note 3). Add HCl until the pink color disappears, and then add 1 ml in excess. Cool the solution, add solid $NaHCO_3$, 0.2 g at a time, until rapid effervescence no longer occurs (about 0.5 g), and then add 3 g more (Note 4). Add 5 ml of starch indicator and titrate with standard iodine solution, swirling the mixture gently but not vigorously shaking it (Note 7, P. XII), until the first permanent blue (or purplish, Note 5) color is ob-

tained which persists for 30 sec. (Notes 8, 9, P. XII). From the volume of standard iodine used calculate the amount of arsenic present.

Notes:

1. $NaHCO_3$ is added to provide an atmosphere of CO_2 in the flask and thus prevent possible oxidation of iodide by the oxygen of the air. If too much KI is added, or if the HCl is too concentrated, a precipitate of yellowish arsenious iodide, AsI_3, may separate. As this will obscure the end-point, it should be dissolved by adding water, 5 ml at a time, until a clear colorless or yellow solution is obtained.

2. It is not necessary to note the amount of thiosulfate which is added, but great care must be taken not to add an excess, as it will cause a corresponding error in the subsequent titration. Not more than 5 to 10 drops should ever be required to decolorize the solution. Starch is not necessary in the small volume of solution used here and is not satisfactory as an indicator in strongly acid solutions, 4 n. or greater.

If large amounts of antimony are present, traces may be found in the distillate, imparting a slight yellowish color to the solution and causing the disappearance of the iodine color to be difficult to detect. In this case add 5 ml of CCl_4 to the mixture and titrate until the CCl_4 layer loses its iodine color.

3. The solution is neutralized with NaOH in order to avoid using a large amount of $NaHCO_3$, with the attendant danger of loss by spattering.

4. The following titration should be carried out in a flask (not in an open beaker) and the solution should be quite cold in order to prevent the loss of CO_2. If this occurs, the solution becomes more alkaline and, due to the reaction between iodine and hydroxyl ion, the end-point will fade. For very precise titrations it is advisable to pass a slow stream of CO_2 continuously through the solution.

5. Certain starch solutions, especially in hydrocarbonate solutions, give an intermediate purplish color with iodine.

P. 44. Precipitation of Mercury

Discussion. After arsenic has been distilled from the solution, the mercury is separated from antimony and tin by reduction with phosphorous acid; mercurous chloride and, finally, metallic mercury are formed.

In a *cold* dilute hydrochloric acid solution mercuric chloride is reduced only to a mercurous chloride by phosphorous acid, and the complete precipitation requires at least several hours. The reaction can be represented as follows:

$$2HgCl_4^{=} + H_3PO_3 + H_2O = Hg_2Cl_{2(s)} + H_3PO_4 + 2H^+ + 6Cl^-.$$

A gravimetric determination of mercury is often made by collecting

the mercurous chloride precipitate, drying it at 100° to 110°C., and weighing it.

However, if a large excess of phosphorous acid is provided and the solution is heated as directed in this procedure, 0.5 mg of mercury will cause a white precipitate of mercurous chloride within 5 min.; the reduction then proceeds to the formation of metallic mercury, and the precipitation of even 500 mg is complete within 10 min. As would be predicted from the above equation, the precipitation of mercury by phosphorous acid is markedly influenced by the concentration of the hydrochloric acid present; thus no appreciable precipitation takes place during the distillation of the arsenic, but, by diluting the residual solution, complete precipitation can be obtained. If the concentration of the hydrochloric acid is much greater than that provided for, approximately 1.5 n., the time required for the precipitation of the mercury is longer.

In order to prevent the precipitation of antimony as the oxychloride, the residual solution from the distillation is diluted with a sulfuric acid solution, and some additional hydrochloric acid is added to prevent the precipitation of tin when it is present in large amounts. The solution is heated on a water bath during the precipitation so as to avoid excessive loss of the acid by evaporation and loss of mercury by volatilization.

Procedure 44: PRECIPITATION OF MERCURY. Cool the residual solution (from P. 42), and transfer it from the distilling flask to a 200-ml flask with the aid of a solution made by adding just 20 ml of 6 n. H_2SO_4 and 5 ml of 6 n. HCl to 25 ml of water (Notes 1, 2). Add 1 ml of 6 f. H_3PO_3, cover the flask with a watch glass, heat the solution just to boiling, and immerse it for 5 min. in a beaker of boiling water. (White precipitate, turning to black, presence of mercury. Note 3.)

If no precipitate forms, add to the solution just 5 ml of 6 n. HCl and 5 ml of water and treat it by P. 46.

If a precipitate forms, heat the mixture in the boiling water for 5 min. more, remove it, heat it just to boiling for 15 to 30 sec., and allow the precipitate to settle (Note 4). Decant the solution through a compact asbestos filter (Note 5) which has been moistened with 6 n. HCl and drained. Wash the precipitate and filter by decantation with just 10 ml of 3 n. HCl aded in 2-ml portions (Note 6). Collect

these washings with the filtrate in a 200-ml flask. Treat the precipitate by P. 45 (Note 7). Treat the filtrate by P. 46.

Notes:

1. The solution is cooled to avoid the precipitation of mercury in the distilling flask when it is diluted. Even so, with large amounts of mercury a small precipitate may be formed, and extreme care must be taken that it is all transferred to the conical flask. The safety tube should be carefully washed.

2. Sulfuric acid has to be added with the water in order to avoid the precipitation of antimonyl chloride, SbOCl. A larger amount of HCl would cause the mercury to precipitate slowly. An additional amount of H_3PO_3 is next added in case most of that added in P. 42 has been oxidized by a large excess of bromate.

3. In order not to overlook a small precipitate of mercury, one should examine the solution in a bright light for finely divided suspended particles. Then, after being heated, the solution should be swirled, and the bottom of the flask should be carefully searched for small particles which should be collected near the center.

4. The heating of the solution and especially the final boiling cause the crystalline white precipitate of Hg_2Cl_2 which first forms to be changed into finely divided metallic mercury; this coagulates into compact black particles which quickly settle out or even coalesce into droplets of the metal. Accordingly, the solution can be quite completely decanted, and this precipitate can be washed with a small volume of solution. Care should be taken not to overlook or lose any of the precipitate because of its compactness and density.

5. Unless a compact filter is used, there is danger of loss of the finely divided mercury.

6. If a precipitate, usually gray, continues to form as the solution is being filtered, it indicates incomplete precipitation of the mercury, and the mixture should be again heated for 5 min. and refiltered.

7. The precipitation of mercury in this procedure gives no indication as to the state of oxidation of the mercury in the material being analyzed. If it is desired to obtain information in this regard, proceed as follows:

Introduce 0.5 g of the sample into a flask, add 50 ml of water, and heat to 40° to 50°C. for 3 min. Cool the solution, allow any residue to settle, and add to it first 3 drops (noting the result) and then 5 ml of HCl. (White crystalline precipitate, presence of mercurous compounds or of silver.) Filter the mixture through a small paper filter and wash the residue with 10 ml of hot water. Treat the filtrate as directed in the next paragraph. Pour 2 to 5 ml of NH_4OH through the residue on the filter. (Blackening of the white precipitate, presence of mercurous compounds.)

Add to the filtrate 0.1 ml of $SnCl_2$ reagent, allow it to stand for 1 to 2 min., and then add 5 ml more of the $SnCl_2$. (White crystalline precipitate, darkening on standing, presence of mercuric compounds.)

As mercurous compounds are unstable, tending to decompose into metallic mercury and mercuric compounds, it is not advisable to attempt to dissolve the material by boiling it with an acid; also, by so doing, mercurous compounds might be oxidized if certain oxidizing agents, such as nitrates, were also present. Because of this, the material is first treated with only warm water, and it should be noted, if the first few drops of HCl cause a precipitate; this would indicate the presence of a soluble mercurous compound. As many mercurous compounds, notably the halides, are insoluble, the residue remaining from the water treatment is not filtered out but is also treated with the ammonia. If it is desired to confirm further the presence of mercury in this residue, it should be treated as directed in Note 1 of P. 45.

Most mercurous compounds are darkened upon application of ammonia, because of the formation of finely divided metallic mercury. The reaction occurring with the chloride is as follows:

$$Hg_2Cl_{2(s)} + NH_3 = Hg_{(s)} + HgNH_2Cl_{(s)} + NH_4^+ + Cl^-.$$

Mercuric sulfide would not be affected by either the dilute HCl or the ammonia.

P. 45. Estimation of Mercury

Discussion. This estimation of mercury depends upon the fact that mercuric thiocyanate is an extremely un-ionized substance. Therefore, when a standard thiocyanate solution is added to a cold solution containing both mercuric and ferric ions, un-ionized mercuric thiocyanate is first formed; a sufficient amount of the ferric thiocyanate compound (see P. VI, p. 37) to give a detectable pink color will not form until an amount of thiocyanate closely equivalent to the mercury present has been added.

As mercuric chloride is also only slightly ionized, the presence of even a small amount of chloride in the solution makes the end-point very uncertain; and for that reason the precipitate from P. 42, which may consist partly of mercurous chloride, is treated with an alkaline phosphite solution, by which it is more completely reduced to metallic mercury and by which any mercurous chloride remaining is metathesized into mercurous oxide. After this treatment the precipitate is dissolved in concentrated nitric acid and the solution is heated in order to expel any nitrous acid present, as this substance rapidly reacts with thiocyanate, forming a transitory red compound and finally oxidizing it to hydrocyanic acid and sulfuric acid. In order to be sure that the mercury is all in the dipositive state and that the last traces of nitrous acid are removed, permanganate is added to the solution until a permanent color is produced. As permanganate also oxidizes thiocyanate, the excess is reduced by ferrous sulfate. The solution must be cold during the titration or the end-

point occurs prematurely; also, when considerable HNO_3 is present, oxidation of the thiocyanate may proceed at an appreciable rate.

The titration of mercuric ion with thiocyanate is a very precise method for the determination of mercury;[2] however, because of the loss of mercury by volatilization in P. 42, and possible mechanical loss in this procedure on account of the compact nature of the precipitate, the estimation of the amount of mercury present is usually lower than the correct value by from 1 to 5 per cent.[3]

Procedure 45: ESTIMATION OF MERCURY. Pour dropwise through the precipitate (from P. 44) on the filter a solution made by adding 1 ml of 6 f. H_3PO_3 to 5 ml of NaOH (Note 1). Collect the filtrate in the flask containing the remainder of the precipitate. Heat the mixture just to boiling for 2 to 3 min. and then slowly decant the solution through the same filter. Discard the filtrate (Note 2). Wash the precipitate by decantation with three 5-ml portions of hot water. Discard the wash water.

Dissolve the precipitate on the filter by pouring dropwise (and repeatedly if necessary) through every portion of it 10 ml of warm 16 n. HNO_3. Collect the acid with the precipitate in the flask and heat it just to boiling until the precipitate is completely dissolved. Wash the filter with two 10-ml portions of hot water, collecting the washings with the solution. Boil the solution vigorously for 2 to 3 min. and cool it to room temperature or below.

Add 0.2 f. $KMnO_4$ dropwise until the first perceptible permanent pink color (Note 3) is obtained, and then add 0.1 f. $FeSO_4$ dropwise until the solution is colorless, avoiding an excess. Add 2 ml of 1n.($\frac{1}{3}$ f.) $Fe(NO_3)_3$ and titrate the cold solution with 0.1 n. KSCN until the first permanent pink color is produced (Note 4).

Notes:

1. If only a very small precipitate (less than 5 mg) is obtained, it is preferable to omit this treatment and the volumetric estimation. In that case it is advisable to confirm the presence of mercury and visually estimate the amount present as follows:

Pour repeatedly through the filter 5 ml of HCl to which 1 or 2 drops of liquid bromine (hood) has been added; add more Br_2 if its

[2] Kolthoff and Lingane, *J. Am. Chem. Soc.*, **57**, 2377 (1935).

[3] For a discussion of the errors involved in the gravimetric estimation of mercury by reduction to the metal with various agents, see Willard and Boldyreff, *J. Am. Chem. Soc.*, **52**, 569 (1930).

color disappears. Add 5 ml of water and boil the solution until the bromine is expelled. Cool, add 2 ml of $SnCl_2$ solution, and let the solution stand for 5 min. (White precipitate, turning gray to black, presence of mercury.) Compare the precipitate with known amounts of mercury precipitated under similar conditions.

2. If this filtrate is not perfectly clear, it should be carefully refiltered.

3. As the permanganate may react somewhat slowly, the solution should be swirled for a few seconds after obtaining a perceptible pink color in order to be sure that it is permanent. An excess of permanganate should be avoided, or a precipitate of MnO_2 may result; should this occur, ferrous sulfate should then be added until it is completely dissolved.

4. When a large quantity of mercury is present, a precipitate of white crystalline $Hg(SCN)_2$ may appear during the titration, but this does not interfere with the detection of the pink color.

P. 46. Precipitation of Antimony

Discussion. The separation of antimony from tin by precipitation of the antimony as sulfide from a hydrochloric acid solution of the proper concentration has been shown by Noyes and Bray[4] to be satisfactory for the qualitative detection of the two elements, but experiments have shown that when both elements are present in considerable quantity and the antimony is completely precipitated, considerable amounts of tin are carried down with the precipitate. Thus, from a solution containing 250 mg of each element, about 25 mg of tin were found to be carried down with the antimony sulfide precipitate.

It has been found by Vortmann and Metzel[5] that a quantitative separation can be obtained under very similar conditions if phosphoric acid is present in the solution, and confirmatory experiments have shown that a similar effect is obtained with phosphorous acid. Thus under the conditions of this procedure, with 250 mg of each element present, less than 2 mg of tin were found with the antimony sulfide precipitate, and with 500 mg of tin and 1 mg of antimony the antimony was detected without precipitation of the tin. Therefore, regardless of whether or not any of the phosphorous acid added in P. 42 has been oxidized, satisfactory conditions are obtained for the quantitative separation of antimony from tin. The precipitate obtained under these conditions of acidity and temperature coagulates readily and often is darkened by the conversion of the orange modification of antimony sulfide to the black form.

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[4] Noyes and Bray, *J. Am. Chem. Soc.*, **30**, 481 (1908).

[5] Vortmann and Metzel, *Z. anal. Chem.*, **44**, 533 (1905).

Procedure 46: PRECIPITATION OF ANTIMONY. Heat the filtrate from P. 44, which should have a volume of 75 ml and contain approximately 120 milli-equivalents of HCl (Note 1), almost to boiling, saturate it with H_2S, and immerse the flask containing it in a large beaker of water at 75°C. Pass a slow current of H_2S (3 to 5 bubbles a second) through the solution for just 10 min., keeping the water in the beaker at 75°C. (Orange to black precipitate, presence of antimony.) Filter the hot solution immediately through an asbestos filter which has been washed with 3 n. HCl and drained, and wash the precipitate with three 5-ml portions of hot 1.2 n. HCl, adding the washings to the filtrate in a 200-ml flask (Note 2). Treat the filtrate by P. 48. Wash the precipitate thoroughly with 1.2 n. HCl and treat it by P. 47.

Notes:

1. It has been found that after the distillation the hydrochloric acid in the flask is not of constant-boiling composition (approximately 6 n.) but is about 4 n. This difference is due mainly to the presence of the phosphorous and phosphoric acids.

2. The solution is kept hot during the precipitation and filtration and is filtered immediately through an acid-washed filter in order to avoid the possible precipitation of tin should it be present in large quantities.

P. 47. Estimation of Antimony

Discussion. This method for the estimation of antimony is based upon the oxidation of antimony in a neutral solution from the trito the quinque-positive state by means of a standard iodine solution. The principles involved are very similar to those applying to the standardization of an iodine solution by means of arsenious oxide (P. XII) and to the estimation of arsenic (P. 43); in general, the discussions given in those procedures apply to the method for antimony. More time should be taken near the end of this titration, as the reaction between the iodine and the antimony is somewhat slow.[6]

The antimony, being in the form of sulfide, is dissolved in 6 n. hydrochloric acid, whereby the hydrogen sulfide set free insures the reduction of all of the antimony to the tripositive state; the hydrogen sulfide is then expelled by boiling. If the hydrochloric acid solution were diluted largely, or neutralized, precipitation of antimonyl chloride, SbOCl, or the hydrous oxide, would result and

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[6] For a study and very complete bibliography of various methods for the determination of antimony, see McNabb and Wagner, *J. Ind. Eng. Chem., Anal. Ed.*, **2**, 251 (1930).

the iodine would react only slowly with the precipitate. This precipitation is prevented by the addition of tartaric acid, which forms a soluble ion, $SbOC_4H_4O_6^-$. This allows the solution to be neutralized and the excess of hydrocarbonate required for the titration to be added without the formation of a precipitate. Antimonic oxide also dissolves in tartrate solutions, forming the ion $SbO_2C_4H_4O_6^-$.

The antimony in stibnite (native Sb_2S_3) materials may be determined by the procedure given below, provided no interfering elements, such as iron or arsenic, are present. As the native material is more resistant to solution, it may be necessary to use an additional amount of concentrated hydrochloric acid; in that case the solution process should be carried out in a flask fitted with a test-tube condenser to avoid possible volatilization of antimony as the trichloride; instructions for carrying out this determination are outlined in Note 6 below.

Hillebrand and Lundell[7] show that the loss of antimony is not significant when dilute hydrochloric acid solutions in covered vessels are boiled but not concentrated, but that upon evaporation to a small volume the loss is large. Thus over half of approximately 250 mg of antimony was lost when a solution of the trichloride in hydrochloric acid was twice evaporated to a syrup.

If a standard solution of potassium iodate is available, the antimony can be estimated by making use of the iodine monochloride end-point.[8] In this method the tripositive antimony is titrated in a hydrochloric acid solution with standard iodate until the iodine, which is the first reduction product of the iodate, is oxidized to colorless iodine monochloride and can no longer be detected in a small amount of carbon tetrachloride or similar solvent. The successive reactions taking place can be represented as follows:

Reduction of iodate to iodine and oxidation of the antimony:

$$5HSbCl_4 + 2IO_3^- + 12H^+ + 10Cl^- = 5HSbCl_6 + I_2 + 6H_2O. \quad (1)$$

Oxidation of the iodine to iodine monochloride by further addition of iodate:

$$2I_2 + IO_3^- + 6H^+ + 5Cl^- = 5ICl + 3H_2O. \quad (2)$$

Experiments have shown that, if the hydrochloric acid is much

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[7] Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929, pp. 221–222.

[8] See pp. 85–88; also Andrews, *J. Am. Chem. Soc.*, **25**, 756 (1903); Jamieson, *J. Ind. Eng. Chem.*, **3**, 250 (1911); Jamieson, *Volumetric Iodate Methods*, Chem. Cat. Co., 1926, pp. 7–17.

more concentrated than 3 n., the reaction apparently proceeds mainly as follows:

$$2HSbCl_4 + IO_3^- + 6H^+ + 5Cl^- = 2HSbCl_6 + ICl + 3H_2O, \quad (3)$$

and so little iodine is formed that the end-point is not distinct. If the hydrochloric acid concentration is much less than 2 n., precipitation of antimonyl chloride may result and the rate at which the reaction represented by Equation 2 takes place is so slow that an excess of iodate may be added before the end-point is obtained.

As the method can be readily applied to the hydrochloric acid solution of the antimony sulfide and as, when the hydrochloric acid concentration is properly regulated, it is so precisely and rapidly carried out, an optional procedure for its use is provided in Note 2 of the procedure below.

Procedure 47: ESTIMATION OF ANTIMONY. Transfer the precipitate from P. 46 (Notes 1, 6) to a 400-ml beaker, add to it 10 to 15 ml of HCl, cover the beaker with a clock glass, heat the mixture slowly just to boiling, and boil it gently until the H_2S is completely expelled (as shown by the failure of a strip of filter paper moistened with $Pb(C_2H_3O_2)_2$ solution to darken when held in the vapors). Cool the solution and add to it 2 g of finely powdered tartaric acid (Note 2).

If the amount of antimony present is estimated to be less than 100 to 150 mg (Note 3), dilute the solution slowly (Notes 4, 5) to 50 ml and treat the diluted solution as directed in the last paragraph of P. 43, "Estimation of Arsenic."

If the amount of antimony present is estimated to be more than 100 to 150 mg, transfer the solution to a 100-ml volumetric flask, dilute it slowly to the mark, and mix the contents thoroughly (Notes 4, 5). Pipet 25 ml of this solution into a 200-ml flask, add to it 2 g of powdered tartaric acid, dilute it to 50 ml, and treat it as directed in the last paragraph of P. 43, "Estimation of Arsenic." From the volume of standard iodine used calculate the amount of antimony present.

Notes:

1. In case only a small precipitate without the characteristic orange color of Sb_2S_3 was obtained, it should be treated as follows:

Transfer the precipitate to a 200-ml beaker, add 13 ml of HCl,

boil until slightly less than 10 ml are present, cool, transfer to a 10-ml graduate, and dilute with 6 n. HCl to just 10 ml. Transfer the mixture to a 100-ml flask, taking care not to dilute it, heat it just to boiling, and saturate it with H_2S. Filter out and discard any precipitate (As_2S_3). Dilute the solution to just 25 ml, heat it almost to boiling, and again saturate it with H_2S. (Orange-red precipitate, presence of antimony.)

Arsenic and mercury, but not antimony, are precipitated as sulfides from a solution 6 f. in HCl; antimony, but not tin, is precipitated from a solution 2.4 f. in HCl.

2. In case it is desired to titrate the antimony with a standard iodate solution, omit the addition of the tartaric acid and proceed as follows:

If less than 100 mg of antimony are thought to be present, dilute the solution with exactly an equal volume of water and transfer it to a 200-ml ground-glass-stoppered flask with the aid of 10 to 20 ml of 3 n. HCl. Treat it as directed in the second paragraph below.

If more than 100 mg of antimony are thought to be present, dilute the solution with exactly an equal volume of water, transfer it to a 100-ml volumetric flask, and dilute it to the mark with 3 n. HCl. Pipet out a 25-ml portion into a 200-ml ground-glass-stoppered flask and treat as directed below.

Add to the solution 5 ml of CCl_4 and titrate with a 0.1 n. (0.025 f.) iodate solution until the iodine color which first appears can no longer be observed in the CCl_4. Add 10 ml of 6 n. HCl with each 10 ml of the iodate solution. As the end-point is approached, stopper the flask and shake the mixture vigorously before observing the CCl_4.

The iodine color can be most effectively observed by stoppering the flask tightly, inverting it, and looking through the CCl_4 after it has collected in the neck of the flask. Loss of solution from the flask can be prevented by cooling the flask with tap water and then pouring 0.5 to 1 ml of 3 n. HCl around the stopper before it is withdrawn.

3. This estimation should be based upon the size of the Sb_2S_3 precipitate obtained in P. 46.

4. The solution should be diluted slowly to avoid precipitation of SbOCl. If this substance is precipitated locally (by too rapid dilution of the solution), it redissolves very slowly.

5. If all the H_2S has not been expelled by the previous boiling, an orange-colored precipitate will form when the solution is diluted. In this case the mixture should be immediately boiled, more acid being added if necessary, until this precipitate is dissolved, and the dilution should then be continued.

6. In case it is desired to determine the antimony in a native stibnite (Sb_2S_3), directly proceed as follows:

Weigh out a 0.5 to 1-g sample of the ore, transfer it to a 300-ml flask, and add 20 ml of 12 n. HCl. Provide the flask with a test-tube condenser (Note 2, P. 7), and treat the mixture as directed in the procedure above.

Arsenic and iron should not be present in significant amounts, as they would be reduced to their lower oxidation states by the above treatment and would be oxidized in the subsequent titration.

P. 48. Detection and Precipitation of Tin

Discussion. The conventional method of precipitating the tin as sulfide by partly neutralizing the filtrate from the antimony sulfide precipitate and saturating it with H_2S is modified here, because the presence of the phosphorous and phosphoric acids cause the precipitation of the tin to take place very slowly, probably because it exists largely as a complex molecule. However, by first making the solution alkaline and then treating it with H_2S, sufficient sulfide is formed in the solution to convert the tin into a soluble sulfo-salt, which, when the solution is then acidified, rapidly decomposes, with the precipitation of the tin as sulfide (see the discussion of P. 13).

Procedure 48: DETECTION AND PRECIPITATION OF TIN. Cool the filtrate from P. 46 and add to it 15 n. NH_4OH until it is alkaline, avoiding a large excess (Note 1). Saturate the solution with H_2S and then pass a slow current of the gas through it for 2 to 5 min. Heat the solution almost to boiling, slowly add H_2SO_4 until it is just acid, and then add 2 ml more. (Yellowish precipitate, presence of tin. Note 2.)

If a precipitate is produced, immerse the flask containing the mixture in a beaker of boiling water and pass a slow current of H_2S through it for 5 min. Let the precipitate settle and filter the solution by decantation, using suction if the precipitate is large. Add to the precipitate 0.5 g of solid NH_4Cl and wash it by decantation with a 15-ml portion of hot water. Discard the filtrate and washings (Note 3). Treat the precipitate by P. 49 (Note 4).

Notes:

1. A volume of 15 n. NH_4OH equivalent to the HCl present can be calculated and added at once. The additional ammonia required to complete the neutralization of the solution can then be added 1 ml at a time until the solution turns red litmus paper blue.

Phosphorous acid of commerce frequently contains iron, and this is precipitated from the alkaline solution as ferrous sulfide, causing the tin sulfide precipitate to be dark in color even after the solution is acidified. As iron does not interfere with the estimation of tin (in P. 49), it can be neglected in case a precipitate of considerable size (more than 10 to 20 mg) is obtained.

2. If a small dark precipitate is obtained which makes doubtful the decision as to the presence of tin, proceed as follows:

Filter out the precipitate on a paper filter and pour dropwise through it 2 ml of warm sodium sulfide reagent. Collect the solu-

tion in a flask, make the solution just acid with HCl, and then add just one-half its volume of 6 n. HCl in excess. Heat the solution to boiling and saturate it with H_2S. Filter out and discard any precipitate (Sb_2S_3). Collect the filtrate in a flask, dilute it with twice its volume of water, saturate it with H_2S, and allow it to stand for 10 min. (Yellow precipitate, presence of tin.)

3. The complete and rapid precipitation of the tin sulfide depends upon the formation of the sulfo-salt, and therefore, if a considerable precipitate has been obtained, it is advisable to repeat the first paragraph of this procedure with the filtrate before it is discarded.

4. The precipitation of the tin at this point gives no information as to the state of oxidation of the tin in the original material. If it is desired to know if stannous tin is a constituent of the sample, proceed as follows:

Boil 10 ml of HCl in a small flask (covered with a watch glass) for 3 min. Quickly introduce 0.5 g of the sample into the flask, cover it, and again boil for 3 min. (if H_2S is evolved, continue the boiling until it is expelled). Add in small portions 0.2 g of $NaHCO_3$ and cool the mixture to room temperature with running tap water, holding the watch glass tightly in place. Pour the cold solution into 10 ml of a saturated solution of $HgCl_2$ (if a residue is present, pass the solution through a rapid-filtering paper filter and collect the filtrate in the $HgCl_2$ solution). (White precipitate, presence of stannous tin.)

The HCl solution is first boiled and then treated with $NaHCO_3$ to prevent the oxidation of stannous chloride by the oxygen of the air. Upon adding a solution of stannous tin in hydrochloric acid (in which the tin is present largely as the ion $SnCl_4^-$) to a mercuric chloride solution, a precipitate of mercurous chloride is formed; the reaction taking place can be represented as follows:

$$SnCl_4^- + 2HgCl_2 = SnCl_6^- + Hg_2Cl_{2(s)}.$$

The stannous chloride solution is cooled and added to a large excess of the mercuric chloride in order that the finely divided, crystalline precipitate characteristic of mercurous chloride will be produced; if the solutions were hot or an excess of stannous tin were present, the reduction would proceed to the formation of a dark precipitate of finely divided mercury.

P. 49. Estimation of Tin

Discussion. This method for the estimation of tin, which has been studied by Hallett,[9] is based upon obtaining complete reduction of the stannic salt to the stannous state by means of metallic nickel, and then oxidizing the reduced solution with a standard solution of iodine. Experiments have shown that the time necessary for complete reduction of the tin is reduced from about 30 min. to about 10 min. by the addition of an antimony salt to the solution.

[9] Hallett, *J. Soc. Chem. Ind.*, **35**, 1087 (1916). This reference should be consulted for a discussion of this and various other methods for the volumetric estimation of tin.

This is probably because the metallic antimony produced reacts more rapidly with the stannic tin than does the nickel foil. This metallic antimony usually adheres to the nickel foil and is removed from the solution. It may, especially if the mixture is vigorously boiled, become detached and remain in the solution. This does not introduce an error if the solution is kept cold during the titration, as neither the iodine nor the oxidized tin is reduced at an appreciable rate. An experimental study[10] has shown that, unless the hydrochloric acid is at least 3 n., a longer time is required for the reduction, and that the acid concentration can be raised to 6 n. without any harmful results being noticed. By diluting the solution before the titration, the acidity is reduced so that starch can be more suitably used as the indicator; also, the color of the dissolved nickel is decreased and the end-point is made more distinct.

Complete reduction having been obtained, the precision of this estimation is determined largely by the effectiveness of the precautions taken to prevent the oxidation of the stannous chloride by the oxygen of the air.

Other methods for the reduction of the tin have been investigated. Thus Ibbotson and Brearly[11] have proposed the use of finely divided metallic antimony in a boiling hydrochloric acid solution. After the mixture is cooled, the stannous tin is titrated with iodine without removal of the antimony, the assumption being that in the cold solution the rate of reduction of the stannic tin by the antimony becomes so slow as to be negligible, so that a permanent starch-iodine end-point can be obtained. A careful study of this method[12] has shown that the reduction of even large amounts of tin can be made complete in 2 to 3 min. and that very consistent results can be obtained by one familiar with the method. It was found, however, that the method was quite dependent upon the fineness of the antimony, material passing a 150- to 200-mesh screen being necessary. If the antimony was finer than this, it remained suspended when the mixture was cooled and apparently reacted with the iodine so that permanent end-points were not obtained; coarser material caused slower reduction. It was also necessary to heat the mixture in such a way as to cause the antimony to remain uniformly suspended, or reduction was incomplete. Finally, practical use showed

[10] Unpublished experiments by G. S. Schull.
[11] Ibbotson and Brearly, *Chem. News*, **84**, 167 (1901).
[12] Unpublished experiments by Robley D. Evans.

that persons unfamiliar with the method found it difficult to detect the starch-iodine end-point in the presence of antimony, and for these reasons the method was not adopted, even though under strictly controlled conditions it is much shorter and as precise as the method given below.

The use of metallic zinc, in a modified method developed by Milon and Fouret,[13] was also investigated. In this method the stannic tin is reduced more or less completely to the metal by the zinc in a hydrochloric acid solution. When the solution is then heated, the excess of zinc is rapidly dissolved and the precipitated tin dissolves as stannous chloride. It was found, however, that under certain conditions the tin dissolved slowly and particles remained undetected in the solution. Other reducing agents, such as "test-lead" pellets,[14] metallic iron (usually with an antimony salt), and aluminum, have been suggested but were found to be not so rapid or so generally satisfactory as the method of this procedure.

Procedure 49: ESTIMATION OF TIN. Add to the precipitate in the flask 10 ml of HCl and heat the mixture until the precipitate dissolves. Pour the hot solution slowly through the precipitate on the filter, catching the filtrate in a 400-ml flask (Note 1). Wash the filter with 10 ml of hot HCl, collecting the washings with the filtrate. Discard any residue.

If the amount of tin present is estimated to be less than 150 to 200 mg, treat the solution by the last paragraph of this procedure.

If the amount of tin present is estimated to be more than 150 to 200 mg, cool the solution to room temperature, pour it into a 100-ml volumetric flask, dilute it to the mark, and thoroughly mix the contents. Pipet 25 ml of this solution into a 400-ml flask and treat it by the next paragraph.

Add to the solution 5 ml of 0.1 f. $SbCl_3$ solution and 30 ml of 12 n. HCl (Note 2), and dilute the solution to a volume of 100 ml. Cut a thin sheet of nickel foil about 3 cm by 30 cm, having a tab about 12 cm long extending perpendicularly from one end (Note 3). Roll the nickel into a loose spiral

[13] Milon and Fouret, *Rept. 8th Int. Cong. App. Chem.*, **1**, 373 (1912).

[14] Powell, *J. Soc. Chem. Ind.*, **37**, 287 T (1918). Lundell and Scherrer, *J. Ind. Eng. Chem.*, **14**, 426 (1922). Patrick and Wilsnack, *J. Am. Chem. Soc.*, **4**, 597 (1882).

and introduce it into the solution by means of the tab. Heat the solution to boiling and keep it boiling for at least 10 min. (Note 4). Remove the flame and just as the solution stops boiling drop into the flask a marble chip about 1 cc in size (Note 5). The marble should be free from iron and should be boiled vigorously in distilled water for 2 to 3 min. just before being used. Cool the flask at once with tap water. If the marble chip is dissolved during this cooling, another should be added. Cool the flask at such a rate that the CO_2 evolved prevents air from being sucked into it. Remove the nickel, washing it with cold, recently boiled water as it is withdrawn. Add rapidly to the cool solution 100 ml of cold, freshly boiled water containing 5 ml of starch indicator solution and titrate it immediately and rapidly with 0.1 n. iodine solution until the appearance of the starch blue color (Note 6). The mouth of the flask should be covered with a card, and the tip of the buret should be introduced into it through a small hole. From the volume of iodine used, calculate the amount of tin present.

Notes:

1. If a large amount of the precipitate has been carried onto the filter, it may not dissolve readily. In this case transfer the precipitate and filter to a small casserole and heat with the HCl until the precipitate dissolves. Filter out the disintegrated paper upon another small paper filter, wash the residue with 10 to 20 ml of HCl, discard it, and treat the solution as directed in the next paragraph of this procedure.

2. The concentration of the HCl should be at least 3 n. during this reduction.

3. The nickel spiral should be of *at least* the size recommended; the more surface exposed the more rapid the reduction. If used previously, the spiral should be cleaned, by immersion in warm 6 n. HCl to which a little 16 n. HNO_3 has been added, until any adhering antimony has been removed and a bright surface has been obtained.

4. It is necessary that the solution be boiled steadily so that it is continuously stirred and all parts are brought into contact with the nickel. Very vigorous boiling may detach the precipitated antimony from the nickel, but, if the solution is cooled to room temperature before making the titration, this antimony then reacts so slowly with both the stannic tin and the iodine that it does not introduce an appreciable error. By applying the heat directly under the nickel spiral, a continuous flow of solution is maintained; if the solution does not cover the spiral, clamp the flask in an inclined position. If the solution does not cover the nickel foil, if the nickel foil has not the surface recommended, or if the solution is not effectively stirred, it is recommended that the boiling be continued for 20 min.

5. If a carbon dioxide generator (or tank) is available, it is preferable to keep a flow of the gas passing continuously through the solution during the boiling as well as during the subsequent cooling and titration.

6. It is essential that the sequence of operations following the stopping of the boiling of the solution be carried out as rapidly as possible. Accordingly, the freshly boiled marble and the freshly boiled water with the starch added to it should be prepared previously. The solution should then be titrated rapidly with a minimum amount of shaking. If a slight excess of iodine is added, it can be back-titrated with standard thiosulfate solution.

TABULAR OUTLINE VI

PRECIPITATION OF THE AMMONIUM SULFIDE GROUP; SEPARATION OF IRON; REMOVAL OF PHOSPHATE; AND SEPARATION OF THE ALUMINUM AND ZINC GROUPS

Filtrate from the Precipitation of the Hydrogen Sulfide Group:
Elements of the Ammonium Sulfide, Alkaline Earth, and Alkali Groups; H^+, NH_4^+, Cl^-, NO_3^-, H_2S

Boil out the H_2S. Neutralize with NH_4OH.
Precipitate: $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, Alkaline Earth phosphates
Treat with H_2S, add excess of NH_4OH. (P. 51)

Precipitate: $Al(OH)_3$, $Cr(OH)_3$, FeS, Fe_2S_3, ZnS, NiS, CoS, MnS, Alkaline Earth Phosphates *Dissolve in 6 n. HCl, adding Br_2. Boil out excess Br_2.* *(Test small portion for Fe with KSCN.)* *Shake with ether. Separate ether from aqueous layer.* (P. 52)	Filtrate: Alkaline Earth and Alkali Group Elements

Ether solution: $FeCl_3$ *Evaporate the ether.* *Add HCl, KI.* (Fe^{++}, I_3^-) *Titrate with $Na_2S_2O_3$.* (Fe^{++}, I^-, $S_4O_6^-$) (P. 53)	Aqueous solution: Al^{+++}, Cr^{+++}, Zn^{++}, Ni^{++}, Co^{++}, Mn^{++}, (Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}), H_3PO_4, H^+Cl^- Phosphate Absent: *Treat by P. 55.* Phosphate present: *Evaporate, add 16 n. HNO_3. Evaporate.* *Make 0.5 n. in HNO_3.* *Add $Bi(NO_3)_3$ reagent.* (P. 54) Precipitate: $BiPO_4$ *Heat.* *Weigh.* Solution: Positive ions listed above and Bi^{+++}, $H^+NO_3^-$. *Saturate with H_2S.* Precipitate: Bi_2S_3 *Discard.* Solution: Positive ions listed above, $H^+NO_3^-$ *Treat by P. 51.*

P. 55. *Neutralize with NH_4OH, make just acid with HCl.*
Add $(NH_4)_2C_2O_4$, $NaHCO_3$.
Treat with H_2S.

Precipitate: ZnS, NiS, CoS, (FeS) The Zinc Group (P. 61–P. 66)	Filtrate: $Al(C_2O_4)_3^{=}$, $Cr(C_2O_4)_3^{=}$, $Mn(C_2O_4)_2^{-}$ The Aluminum Group (P. 71–P. 75)

Precipitation of the Ammonium Sulfide Group; Separation of Iron; Removal of Phosphate; and Separation of the Aluminum and Zinc Groups

P. 51. Precipitation of the Ammonium Sulfide Group

Discussion. Those elements whose sulfides are insoluble in 0.3 n. acid having been precipitated, it is now desirable to find some means of separating another group of elements from the solution. As several methods are available, a study of their relative merits should be made.

Hydroxide Separations. Methods for separating the elements which depend upon their behavior in solutions of various hydrogen ion concentrations are, after the sulfide methods, most extensively used in qualitative and quantitative analysis; because of this there have been collected in Tables XII, p. 212, and XVIII data showing the behavior of the common elements in solutions of various hydrogen ion concentrations.

Surveying the elements remaining after the Hydrogen Sulfide Group is separated, it is seen that, if the solution is made approximately neutral, only the hydroxides of the elements present in the tripositive state—aluminum, chromium, and iron—are precipitated. The isolation of these tripositive elements as their hydroxides would make an ideal group separation, both pedagogically and analytically, and is sometimes attempted (any ferrous iron being first oxidized) by neutralizing the solution and adding a slight excess of ammonium hydroxide, which results in making what is known as an "ammonia precipitation." As this precipitation with ammonia is so extensively used for various separations in qualitative systems and in quantitative work, an experimental study of it was made; a discussion of the results obtained is given below.[1]

The Precipitation by Ammonium Hydroxide. The precipitation by ammonium hydroxide can well be termed one of the classical analytical separations and is, as stated by Hillebrand and Lundell,[2]

[1] The following discussion is taken in part from a study of this method by Swift and Barton, *J. Am. Chem. Soc.*, **54**, 2219 (1932).

[2] Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929, p. 69.

TABLE XVIII

THE BEHAVIOR OF THE AMMONIUM SULFIDE AND ALKALINE EARTH GROUP ELEMENTS IN SOLUTIONS OF VARIOUS HYDROXYL (AND HYDROGEN) ION CONCENTRATIONS

(See Table XII, p. 212, for the behavior of the Hydrogen Sulfide Group elements.)

Element and Oxidation State	Precipitates, Compounds, or Ions Formed		
	I $[OH^-]$ 2 to 4 m.	II $[H^+]$ 10^{-6} to 10^{-7} m.	III $[H^+]$ 10^{-4} to 10^{-6} m.
Al^{III}	$Al(OH)_4^-$	$Al(OH)_3$	$Al(OH)_3$
Cr^{III}	$Cr(OH)_4^-$ [a, d]	$Cr(OH)_3$	$Cr(OH)_3$ [c]
Fe^{III}	$Fe(OH)_3$	$Fe(OH)_3$	$Fe(OH)_3$
Fe^{II}	$Fe(OH)_2$ [e]	(Fe^{++})	(Fe^{++})
Mn^{II}	$Mn(OH)_2$ [e]	(Mn^{++})	(Mn^{++})
Ni^{II}	$Ni(OH)_2$	(Ni^{++}) [f]	(Ni^{++})
Co^{II}	$Co(OH)_2$	(Co^{++}) [g]	(Co^{++})
Zn^{II}	$Zn(OH)_4^-$	(Zn^{++}) [f]	(Zn^{++})
Ba^{II}	$Ba(OH)_2$ [b]	(Ba^{++})	(Ba^{++})
Sr^{II}	$Sr(OH)_2$ [b]	(Sr^{++})	(Sr^{++})
Ca^{II}	$Ca(OH)_2$ [b]	(Ca^{++})	(Ca^{++})
Mg^{II}	$Mg(OH)_2$	(Mg^{++})	(Mg^{++})

Separations which are dependent upon having the hydroxyl ion concentration from 2 to 4 m. (column I) are usually made by the use of solutions of sodium or potassium hydroxide; by the addition of an oxidizing agent (usually Na_2O_2), chromium is oxidized to chromate, ferrous hydroxide to ferric, manganese to manganese dioxide, and cobalt to cobaltic oxide. Separations depending upon maintaining the solution approximately neutral (column II) are obtained (1) by the use of ammonia in the presence of a large excess of ammonium salts, whereby the specific effect of the formation of complex ammino compounds is also obtained; (2) by using an excess of solid barium carbonate in a cold solution; (3) by using a solution containing an excess of iodate and iodide; or (4) by boiling the solution with sodium thiosulfate. The conditions of column III are most commonly obtained by the use of a boiling solution containing acetic acid and a soluble acetate—the so-called "basic acetate method" (see P. 63); other organic acids and their salts which have been similarly used are formic, succinic,* and benzoic.†

See General Note to Table XII in regard to the composition of the hydroxides and the formulas of the ions formed by the amphoteric elements.

[a] $Cr(OH)_3$ dissolves in dilute hydroxide solutions, owing to formation of a stable colloidal system; with more concentrated solutions $Cr(OH)_4^-$ is formed.

[b] Moderately soluble.

[c] Incompletely precipitated.

[d] Oxidized to CrO_4^- by Na_2O_2, NaClO, and so forth.

[e] Oxidized upon exposure to air.

[f] Forms complex ammino ions with ammonia.

[g] With presence of ammonia, is oxidized in air and forms complex ammino ions.

* Treadwell-Hall, *Analytical Chemistry*, Vol. II, Quantitative, 8th Ed., p. 160.

† Kolthoff, Stenger, and Moskovitz, *J. Am. Chem. Soc.*, **56**, 812 (1934).

"one of the commonest operations the analyst has to perform . . . , with the object either of weighing the precipitated compound or of effecting a joint separation of two or more metals from others." That it may be inadequate even as a qualitative separation in certain cases is shown by the experiments of Noyes and Bray[3] in which, with large amounts of aluminum or ferric iron (100 to 200 mg) and with amounts of cobalt, zinc, or nickel up to 20 mg, from 75 to 99 per cent of the latter elements were found to be carried down in the precipitate. Noyes, Bray, and Spear[4] also state that "a large quantity of zinc may be quantitatively precipitated by ammonium hydroxide when a larger proportion of chromium is present; and manganese will in any case be partially precipitated by that reagent owing to its oxidation by the air." However, the somewhat contradictory results which have been obtained in various investigations[5] of the quantitative use of the method have indicated that the effectiveness of the separations which can be obtained are highly dependent upon the exact conditions under which the method is carried out, especially with respect to the excess of ammonia added in making the precipitation. The effects caused by an excess of ammonia depend upon whether the bipositive elements remain in solution because of the solubility of their hydroxides (as is most probable with manganese) or because of the formation of the soluble ammonia complexes, and also upon the relative tendency of these two molecular types to be carried down with the precipitate. The effect of the hydrogen ion concentration of the solution upon the physical nature, and, therefore, the adsorbing tendency of the precipitate, must also be considered. An experimental study of the method, with especial reference to these points, was made,[6] and the data obtained are tabulated in Table XIX and are discussed below.

An inspection of the data in Table XIX seems to lead to two general conclusions: First, in about half of the separations studied the separation is quite unsatisfactory even under the most favorable conditions. Second, in every case studied the separation is more effective when an *excess of ammonia is avoided* and, in most cases, unless this excess is avoided, the separation is so imperfect that little is gained by reprecipitations; thus, under the conditions studied,

[3] Noyes and Bray, *A System of Qualitative Analysis for the Rare Elements*, Macmillan, 1927, pp. 153–155.

[4] Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, **30**, 482 (1908).

[5] Blum, *J. Am. Chem. Soc.*, **38**, 1291 (1916); Lundell and Knowles, *ibid.*, **45**, 676 (1923).

[6] Swift and Barton, *loc. cit.*

TABLE XIX

Separation of Chromium, Aluminum, and Iron from Manganese, Nickel, Cobalt, and Zinc by Precipitation with Ammonia

In these experiments 250 mg of one of the elements in the first column were precipitated from a solution containing 250 mg of one of the elements listed at the top of the four major columns. In each of the four major columns is shown the experiment number, the procedure used (described in the notes below), and the amount (mg) of the soluble element found in the precipitate.

Element Precipitated	Manganese			Nickel			Cobalt			Zinc		
	Expt.	Procedure	Mn in Ppt. (mg)	Expt.	Procedure	Ni in Ppt. (mg)	Expt.	Procedure	Co in Ppt. (mg)	Expt.	Procedure	Zn in Ppt. (mg)
Chromium	1	I	55.	6	I	114	12	I	160	16	I	212
	2	II	0.8	7	I[c]	163	13	II	34	17	II	41
	3	II[a]	0.4	8	I[d]	150	14	II[e]	61	18	III	165
	4	II[b]	0.5	9	II	28	15	III	90			
	5	III[b]	18.	10	II	26–28						
				11	III	35						
Aluminum	19	I	4.0	23	I	230	26	I	230	31	I	214
	20	II	0.2	24	II	10	27	I	216	32	II	75
	21	II	0.3	25	III	190	28	II	8	33	III	121
	22	III	2.5				29	III	166	34	II[g]	68
							30	I, II[f]	23			
Ferric iron	35	I	2.0	39	I	16	42	I	16	45	I	106
	36	II	1.5	40	II	3–4	43	II	4	46	II	11
	37	II	0.8	41	III	8–10	44	III	8	47	III	27
	38	III	2.7	48	III	13				50	III	21
				49	III[h]	13				51	III[h]	19

The separations shown in this table were carried out according to three general procedures. The first of these, designated Procedure I, was designed to conform to usual qualitative technique, and, except where explained by notes, was as follows:

Procedure I: To a boiling solution containing the elements to be separated and 60 milli-equivalents of hydrochloric acid in a volume of 100 to 125 ml, 6 n. ammonium hydroxide was slowly added until red litmus paper just turned a distinct blue color. The mixture was then boiled for 1 to 3 min. and filtered; it was kept hot during the filtration. The precipitate was washed with hot water until the washings were colorless or had no perceptible effect on red litmus.

The second procedure conformed more closely to the procedure outlined by Blum* in his study of the precipitation of aluminum and was as follows:

Procedure II: To a boiling solution which contained 10 g of ammonium chloride and 6 to 12 milli-equivalents of HCl in a volume of approximately 250 ml, 6 n. NH_4OH was added dropwise until a color change was noted, with methyl red, or in a few cases with rosolic acid, as the indicator. Where the color of the solution prevented the use of the internal indicator, litmus test papers were used and the ammonia was added until the color of the litmus matched that obtained from a similar solution of ammonium chloride and hydrochloric acid, to which ammonium hydroxide had been added until the methyl red (or rosolic acid) color transition occurred. Extreme care was taken in these neutralizations; if the color transition was overrun, the mixture was made acid and the process was repeated. The mixture was boiled for 1 or 2 min. and filtered; it was kept hot until the filtration was completed. To expedite filtering and washing, two separate filters were used in most cases. The precipitate was washed with a hot 2 per cent solution of ammonium chloride until the washings gave no appreciable precipitate when tested with ammonium sulfide solution.

Procedure II differs from Procedure I in that the solution was diluted to a larger volume, a larger quantity of ammonium chloride was present, and *extreme care was taken to avoid an excess of ammonium hydroxide*. In order to compare more exactly the effect of an excess of ammonium hydroxide, the experiments labeled III were carried out as follows:

Procedure III: This was performed exactly as was Procedure II, except that, after the solution was carefully neutralized with ammonia, an excess of 2 ml of 6 n. NH_4OH was added.

Observations and variations from the procedures outlined above are contained in the specific notes to the table. The precipitate was analyzed in order to determine the amount of the soluble element carried down.

[a] The chromium hydroxide precipitate obtained in Experiment 3 required about 100 ml of wash solution; the precipitate in Experiment 5 required about 500 ml. The washings were tested for manganese by addition of ammonia and hydrogen peroxide.

[b] In this neutralization a slight excess of ammonia was added; therefore 6 n. HCl was added until the methyl red was distinctly pink, and the neutralization was repeated.

[c] A slightly larger excess of ammonia was added in Experiments 7 and 8 than in Experiment 6.

[d] Five grams of NH_4Cl were used in addition to that formed by neutralization of the hydrochloric acid.

[e] The solution was made just neutral to litmus without using a reference solution with an internal indicator. Probably slightly more ammonia was added than in Experiment 13.

[f] The volume and other conditions were as in Procedure I. Neutralization was made, and an excess of ammonia was avoided, as in Procedure II.

[g] Only 160 mg of zinc were taken.

[h] In Experiments 49 and 51 an excess of 5 ml of 15 n. NH_4OH was added; otherwise Experiments 48 and 49 and Experiments 50 and 51 were carried out in exact duplicate to note the effect of the larger excess of ammonia.

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* Blum, *J. Am. Chem. Soc.*, **38**, 1291 (1916).

when an excess of ammonia is added, more than 50 per cent of the nickel, cobalt, or zinc is carried out by either chromium or aluminum. This would seem to indicate that the ammonia separation is more effectively carried out, at least in dilute solutions, as a process of selective hydrolysis and not as one depending on the formation of the soluble complex ammino ions. In support of this, it is to be noted that manganese, where the tendency toward this complex formation is least, is much less coprecipitated than nickel, cobalt, or zinc.

Also, the *p*H values at which these bipositive elements are precipitated from solution are given by Britton[7] as follows: zinc, 5.2; nickel, 6.7; cobalt, 6.8; and manganese, 8.5 to 8.8. It is seen that the coprecipitation in the experiments carried out by Procedure II in every case varies in amount in the same order—zinc, the least soluble hydroxide, showing the greatest tendency to be carried with the precipitate. The same order, in general, holds for the experiments by Procedures I and III, which is somewhat surprising, as, with an excess of ammonia present, it would be expected that the formation of the soluble ammonia complexes would be a more deciding factor; for the same reason it would have been predicted that the large excess of ammonia added in Experiments 49 and 51 would have decreased markedly the amount of coprecipitation; however, the difference is within the experimental variations. That the effect is due to an adsorption process and not to mechanical inclusion or local precipitation is indicated by experiments which have been made by Ibbotson and Brearly[8] and Noyes and Bray.[9] These show that, when an ammoniacal solution of the bipositive element is added to a suspension of the freshly precipitated hydroxide, the coprecipitation approaches in amount that obtained by precipitation in the presence of the bipositive element. That the complex ammonia compounds are not extensively carried down was shown by the fact that relatively little ammonia was found upon analysis of an aluminum precipitate, produced by Procedure III, which had coprecipitated with it about 200 mg of nickel.

Specifically, in addition to confirming the conclusions of Lundell and Knowles[10] that, by proper methods of neutralization, a satisfactory separation of manganese from aluminum and from iron is

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[7] Britton, *Hydrogen Ions*, Van Nostrand, 1929, pp. 254, 278.

[8] Ibbotson and Brearly, *Chem. News*, **81**, 193 (1900).

[9] Noyes and Bray, *A System of Qualitative Analysis for the Rare Elements*, Macmillan, 1927, p. 154.

[10] Lundell and Knowles, *J. Am. Chem. Soc.*, **45**, 676 (1923).

obtained, it is shown that under these same conditions manganese can be separated from chromium. However, it is to be noted that the coprecipitation of manganese is increased much more by an excess of ammonia in the separation from chromium than it is in the separation from either aluminum or iron. The separations of nickel from aluminum and chromium show from 50 to 90 per cent of this element brought down when an excess of ammonia is added, demonstrating the futility of reprecipitations; the same general behavior is obtained with these elements and cobalt. Even under the most favorable conditions, these separations are hardly adequate for quantitative work. The separations of nickel and cobalt from iron, made from carefully neutralized solutions, show about 2 per cent coprecipitation, so that a reprecipitation would probably reduce this to satisfactory limits. The separation of zinc under these conditions is unsatisfactory regardless of the method of neutralization. It is to be noted that the coprecipitation in Procedure I is usually greater than that in Procedure III, showing the favorable effect of an increased volume and the thereby decreased concentration of the coprecipitated substance. It is perhaps worthy of note that, although it is almost universal in textbooks of qualitative analysis, the procedure which directs that a *slight excess* of ammonia be added to a relatively small volume of solution produces conditions which are apparently the *least* favorable of those studied for the separations desired.

Because the separation of the tripositive elements, as a group, from the solution by an ammonia precipitation is so unsatisfactory, under even the most closely regulated conditions, it is not used in this system of analysis.

Other Possible Group Separations. If one considers the further use of sulfide separations, an inspection of Table XI, p. 200, suggests several possibilities. First, if the hydrogen ion concentration is reduced from 0.3 m. to 0.01 m., of the elements remaining in the solution zinc alone is precipitated. This method is not used, however, because it is not expedient to employ a procedure which may take considerable time in order to detect and separate a single element from the original solution. This element will often be absent, and any system which generally used single separations would require a large expenditure of time even when very few elements were present.

If the hydrogen ion concentration is reduced to approximately 10^{-6} m., nickel and cobalt sulfides are included with zinc; and by the use of acetic acid and an acetate this hydrogen ion value can be very

effectively maintained. The formation of this group, including zinc, nickel, and cobalt, would offer several advantages if it could be quickly done and if clean separations could be obtained. However, the complete precipitation of nickel and cobalt under these conditions is slow, and, as is indicated in Table XI, p. 200, iron is likely to be coprecipitated, while aluminum and chromium tend to hydrolyze and precipitate under these same conditions.

The Precipitation by Ammonium Sulfide and Ammonium Hydroxide. Finally, if the hydrogen ion concentration is reduced until the solution is alkaline, the hydroxyl ion concentration being approximately 10^{-5}, practically complete precipitation of zinc, cobalt, nickel, iron, and manganese as their sulfides, and of aluminum and chromium as their hydroxides is obtained. The alkalinity of the solution is usually adjusted by the use of ammonium hydroxide and ammonium salts; hydrogen sulfide is then passed into the solution in a limited amount, forming ammonium sulfide, or a solution of the latter may be added. This method effects a satisfactory separation of the above-mentioned elements from those of the Alkaline Earth and Alkali Groups, except when phosphate is present; then the alkaline earth elements may be precipitated as their phosphates and their presence has to be provided for in the subsequent group analysis (the absence of carbonate from the reagents has to be assured, as it also causes precipitation of the Alkaline Earth elements). This separation is very commonly used and has been adopted in this system. Other sulfide separations in more alkaline solutions are not practical, as the solubility of aluminum hydroxide is increased and as magnesium hydroxide, which is not amphoteric, will be precipitated.

In the procedure which has been adopted, the filtrate from the hydrogen sulfide precipitation is boiled until the hydrogen sulfide is expelled, in order that the effect of adding ammonium hydroxide alone may be noted. For, upon just neutralizing the solution, which contains a considerable amount of ammonium salts, the formation of a precipitate will indicate the presence of aluminum, chromium, and iron (the latter upon heating the solution so that any ferrous iron is partially oxidized to ferric). If phosphate and alkaline earth elements are present, a precipitate of an alkaline earth phosphate may also be obtained; manganese and cobalt may also be precipitated as phosphates. Thus if no precipitate is obtained, the absence of aluminum, chromium, and iron can be assumed and the analysis of the Ammonium Sulfide Group is simplified.

The neutralized solution is then treated with hydrogen sulfide, as zinc, nickel, and cobalt will be precipitated almost completely from the neutral solution, and the precipitate will be much more readily coagulated and filtered than if it were produced in an alkaline solution. Possible information as the presence of these elements is also obtained. The solution is finally made distinctly alkaline in order to cause the complete precipitation of the sulfides of manganese and iron.

Procedure 51: PRECIPITATION OF THE AMMONIUM SULFIDE GROUP. Transfer the filtrate from the H_2S precipitation (P. 11) to a 500-ml conical flask and boil it until the H_2S is completely expelled (Note 1). While keeping the solution just boiling, slowly add NH_4OH until it is neutral to litmus (Note 2), and then boil the mixture for 2 to 3 min. (No precipitate, absence of aluminum, chromium, and of alkaline earth elements as phosphates, probable absence of iron. Note 3.)

Saturate the neutral solution with H_2S. (If considerable precipitate forms, add 1 ml of NH_4OH to the solution and resaturate it with H_2S. Note 4.) Finally make the solution just alkaline with NH_4OH, add 2 ml in excess, and pass in a moderate stream of H_2S (2 or 3 bubbles a second) for 15 sec. at a time until, after the contents of the flask are thoroughly mixed, the gas above the solution rapidly darkens a strip of filter paper which has been moistened with $Pb(C_2H_3O_2)_2$ solution. Cover the flask with a watch glass (or loosely stopper it, Note 5), heat the mixture nearly to boiling, shake it vigorously as long as the precipitate seems to be coagulating, and allow the precipitate to settle. If the solution is not alkaline to litmus, add NH_4OH (0.5 ml at a time) until it is, and again test for the presence of H_2S above the solution (Note 6). (No precipitate, absence of Ammonium Sulfide Group elements.)

Filter the hot solution through a paper filter, using suction if the precipitate is large, and wash the precipitate with two to five 5-ml portions of a solution made by passing H_2S for 10 sec. through a solution containing 0.5 ml of NH_4OH and 0.5 g of NH_4Cl in 25 ml of water. Add these washings to the filtrate. Keep the solution hot during the filtration; cover the funnel with a watch glass and collect the filtrate

in a 400-ml flask provided with a two-hole rubber stopper, inserting the stem of the funnel through one hole. Wash the precipitate with three 5-ml portions of hot water, discarding the washings (Notes 7, 8). Treat the precipitate by P. 52 (Note 9). Immediately acidify the filtrate with HCl, boil out the H_2S (Note 10), and treat it by P. 81.

Notes:

1. To determine when the H_2S has been completely expelled, smell the escaping vapors or test them with strips of paper moistened with $Pb(C_2H_3O_2)_2$; as long as H_2S is present, PbS will be formed and the strips will darken.

2. The solution is kept boiling and an excess of NH_4OH is avoided in order to prevent the precipitation of manganese. In an alkaline solution manganous salts are oxidized by air, and a brown precipitate (of hydrous Mn_2O_3) is obtained. The ammonia should be added until litmus paper is turned to an intermediate purplish color—not to a distinct blue. If any of the test papers mentioned in P. 3, Note 6, are available, they can be advantageously used for this neutralization and the solution can be adjusted to a *p*H of 6.

3. Unless there is considerable iron present, ferrous hydroxide is not precipitated under these conditions. However, there is such a pronounced tendency for ferrous iron to be oxidized (partly because of the very slight solubility of $Fe(OH)_3$) that upon boiling the solution, even with small amounts of iron present, a precipitate of ferric hydroxide will be obtained; a black precipitate, consisting of a mixture of ferric and ferrous hydroxides, may also result.

If only a small precipitate is obtained, and if phosphate is absent (see Note 1, P. 54), considerable time may be saved by separating the tripositive elements at this point. This can be done as follows:

Add HCl, 1 ml at a time and heating after each addition, until the precipitate is dissolved. To the hot solution add saturated bromine water, 1 ml at a time, until an excess is present (indicated by its odor above the solution or color in the solution). Boil the solution vigorously (*under a hood*) until the excess of bromine is expelled and then for 2 min. longer. Keep the mixture just boiling and neutralize with NH_4OH as directed in the procedure above. Filter while keeping the mixture hot and wash the precipitate with hot water.

Treat the precipitate by the procedure given in paragraphs 2 to 8 of Note 3, P. 55, for the separation and detection of small amounts of iron, aluminum, and chromium. Treat the filtrate as directed in the second and third paragraphs of the procedure above in order to detect and precipitate the bipositive elements.

4. If, when the neutral solution is saturated with H_2S, a white precipitate is obtained, the presence of zinc is indicated; a black precipitate will indicate nickel or cobalt. If the color of the solution has indicated the presence of

nickel, it is advisable to avoid admitting air to the flask (by keeping a constant flow of H_2S) and separately to filter and wash the precipitate obtained from the neutral solution. This is done because nickel sulfide, when precipitated from an alkaline solution containing disulfide (usually formed by oxidation of the sulfide by the air), tends to form a dark brownish colloidal solution which is exceedingly difficult to coagulate. The precipitation of the remaining elements is then made in an alkaline solution as directed, and the two precipitates are united for treatment by P. 52.

5. The solution and precipitate are protected from exposure to air during the precipitation and filtration in order to avoid oxidation of the sulfide with formation of disulfide. This not only causes nickel sulfide to become colloidal but increases the amount of sulfate which is later formed; the latter may cause the premature precipitation of barium and strontium.

6. The solution should be distinctly alkaline, but a large excess of ammonia should be avoided; the solubility of aluminum hydroxide becomes appreciable under such conditions, and, unless the ammonium hydroxide solution has recently been distilled, it is likely to contain carbonate (by absorption of carbon dioxide), which may cause the partial precipitation of alkaline earth elements as carbonates.

7. The precipitate is finally washed with hot water in order to remove ammonium salts, which are likely to precipitate as NH_4Cl in the HCl-ether treatment of P. 52.

8. If nickel is present and a brownish colloidal filtrate is obtained, this can usually be coagulated by making the filtrate just acid with HCl, heating it almost to boiling, again making it just neutral with NH_4OH, and saturating it with H_2S. This precipitate is filtered separately and combined with the first one.

9. If phosphate has not been present and the tripositive elements have been precipitated and removed by ammonium hydroxide as suggested in Note 3, this precipitate (which contains the bipositive elements of this group) should be dissolved as directed in the first paragraph of P. 52, and the solution should then be treated as directed in P. 55.

10. The filtrate is at once made acid and the H_2S is expelled in order to avoid oxidation of the sulfide by air, with final formation of sulfate. This takes place to a considerable extent if the alkaline solution is allowed to stand for any length of time. If a white precipitate of sulfur forms, it should be coagulated, filtered out, and discarded.

P. 52. Detection and Separation of Iron

Discussion. The Ammonium Sulfide Group precipitate having been obtained, it would be logical next to separate this large group of elements into two smaller groups. However, iron is detected and separated singly, as this can be done with so little loss of time and so effectively from the small volume of solution which is here obtained. When the ammonium sulfide precipitate is dissolved in hydrochloric acid, the presence of iron is indicated by the yellow

color which it imparts to the solution. If the color of other elements masks this effect, a simple test with thiocyanate is made on a portion of the solution and this portion is then combined with the main solution.

The separation of iron which is used here is based upon experiments[11] which have shown that when a solution which contains 125 to 250 mg of iron and which is 5.5 to 9.0 n. in hydrochloric acid is shaken with an equal volume of isopropyl ether, over 90 per cent (99 per cent at 6.5 to 8.5 n. hydrochloric acid) of the ferric iron passes into the ether. From the data collected in Table XX it is seen that of the elements of the Ammonium Sulfide Group none passes into the ether in appreciable quantity (more than 0.01 per cent).

TABLE XX

BEHAVIOR OF THE AMMONIUM SULFIDE GROUP ELEMENTS ON SHAKING A 7.75 N. HYDROCHLORIC ACID SOLUTION WITH AN EQUAL VOLUME OF ISOPROPYL ETHER

Element	Amount Taken (mg)	Amount Extracted (mg)	Per Cent Extracted
Co^{II}	500	0.0	
Mn^{II}	500	0.00	
Ni^{II}	500	0.00	
Al^{III}	500	0.00	
Cr^{III}	500	<0.03	<.01
Zn^{II}	500	0.0	
P (as H_3PO_4)	125	0.1	0.1
P (as H_3PO_4)	62.5	39	62
Fe^{III}	250		
Fe^{II}	250	0.0	
Fe^{III}	248.8	248.6	99.9

It has long been known that ferric iron could be extracted with ethyl ether from solutions approximately 6 n. in hydrochloric acid, and thus could be separated from all the elements of the Ammonium Sulfide, Alkaline Earth, and Alkali Groups.[12] Although such an

[11] Dodson, Forney, and Swift, *J. Am. Chem. Soc.*, **58**, 2573 (1936).

[12] For discussions of this separation with ethyl ether, see Rothe, *Stahl u. Eisen*, **12**, 1052 (1892); Ledebur, *ibid.*, **13**, 333 (1893); Langmuir, *J. Am. Chem. Soc.*, **22**, 102 (1900); Kern, *ibid.*, **23**, 689 (1901); Speller, *Chem. News*, **83**, 124 (1901). For a table showing the behavior of the chlorides of the less common metallic elements in this treatment, see Swift, *J. Am. Chem. Soc.*, **46**, 2378 (1924).

extraction process offers obvious advantages over precipitation methods, this separation has not been used as widely in general qualitative and quantitative procedures as would seem justified. This has been due to several factors: The efficiency of the extraction process is critically dependent on the hydrochloric acid concentration; the solubility of ether in the acid is so large that the volume of the aqueous phase is increased by as much as 25 per cent, making

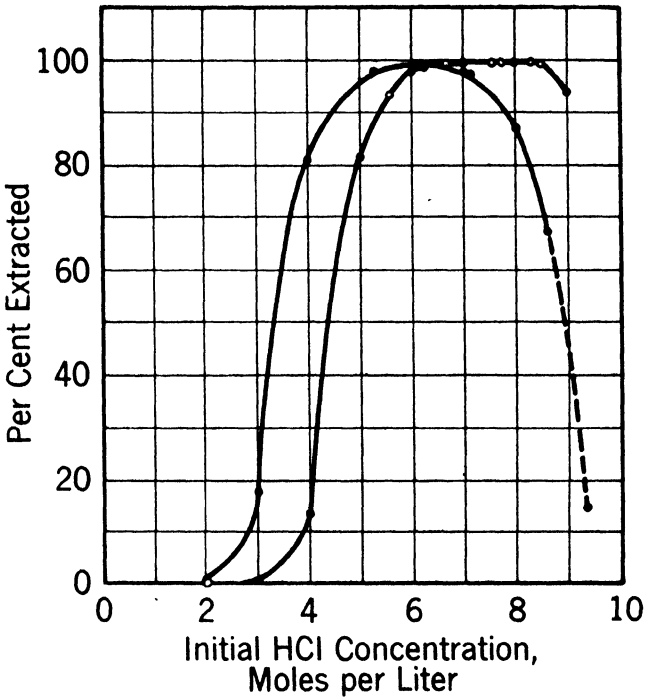

Fig. 30. Extraction of Ferric Chloride from Aqueous Hydrochloric Acid Solutions by an Equal Volume of Ethyl and of Isopropyl Ether. -●-, ethyl ether; -○-, isopropyl ether.

the concentration of the acid after an extraction uncertain or requiring the use of acid previously saturated with the ether; it has been feared that peroxide or alcohol, which are frequently present in ether, would reduce the iron to the ferrous state, in which form it is not extracted; and, finally, the volatility of ethyl ether makes the quantitative technique of the extraction somewhat difficult at room temperatures and involves a serious fire hazard, especially for student use.

Because of these facts the behavior of isopropyl ether was investi-

gated,[13] and it was found that more complete extractions could be made over a wider range of acid concentrations than could be made with ethyl ether. Curves showing the percentage of iron extracted by these two ethers at various acid concentrations are shown in Fig. 30. It is seen that an equal volume of isopropyl ether extracts more than 99 per cent of the ferric iron from solutions which are from 6.5 to 8.5 n. in hydrochloric acid. With ethyl ether 99 per cent is extracted only when the acid is approximately 6.2 n., and the efficiency of extraction diminishes rapidly at higher concentrations, owing in part to the more rapid increase in the solubility of the latter ether in the more concentrated acid.

Because of the above facts and also because isopropyl ether is less volatile and therefore can be used with less danger of mechanical loss in separating funnels and with less fire hazard, it is recommended for use in the procedure below.[14] Should it not be available, provision is made in Note 8 of this procedure for the substitution of ethyl ether. This extraction separation is most advantageously used when a large amount of iron is present, as it entirely avoids the coprecipitation errors inherent in a precipitation method and, if properly carried out, is quite precise. However, the operations involved have to be carefully performed, or loss of the solutions may result; it is also necessary that the concentration of the hydrochloric acid be closely controlled. The time required is usually less than that required to filter and wash an iron hydroxide precipitate. If only a small amount of iron is present, it is recommended that the ether extraction be omitted and the iron be separated in the optional procedure provided in P. 55, Note 3, or allowed to precipitate with the other Zinc Group sulfides. It will remain in the solution when the zinc is precipitated as sulfide in P. 62 and can be precipitated as directed in the notes to P. 63.

Procedure 52: DETECTION AND SEPARATION OF IRON. Transfer, by means of a stirring rod, as much as possible of the ammonium sulfide precipitate (P. 51) from the filter to a 100-ml flask. Transfer any precipitate remaining in the original flask to this flask with the aid of 10 to 25 ml of warm HCl, heat the mixture as long as the residue seems to be

[13] Dodson, Forney, and Swift, *loc. cit.*

[14] The technical grade of isopropyl ether has been found to be satisfactory for this separation; it is less expensive than a comparable grade of ethyl ether.

dissolving, and pour this solution through any precipitate left on the filter. Finally, add liquid Br_2 to the solution, a drop at a time, until the residue becomes light colored and an excess is present (Note 1); also pour this solution through any residue left on the filter. Wash the filter and residue with 2 to 5 ml of HCl. Filter out any residue on a small filter and wash it with HCl (Note 2). Add to the filtrate 2 ml of 12 n. HCl, evaporate the solution to a volume of approximately 10 ml (or until the excess Br_2 is expelled), and cool it (Note 3).

If the solution is colorless, treat it by P. 54 (Note 4).

If the solution is colored, remove with a dropper 0.5 ml to a small test tube and add 0.1 ml (3 drops) of 1 n. KSCN. (Pink or red color, presence of iron Note 5.) Pour this solution back into the main filtrate and wash the dropper and test tube with 2 ml of 6 n. HCl.

If iron is not present, treat the solution by P. 54.

If iron is present, treat the solution by the next paragraph (Note 6).

Pour the cold HCl solution into a 50-ml separating funnel (Note 7), wash out the flask with two 2-ml portions of 12 n. HCl, and add to the solution an equal volume of isopropyl ether (Note 8). Use the ether to wash out the flask further. (*Caution: Ether is very inflammable. Do not carry out these operations near a flame.*) Cool the mixture (Note 9), shake it vigorously for 5 to 10 sec., and then allow the layers to separate completely (Note 13). Again cool the mixture and draw off all the water layer into a second separating funnel (Note 10). Add 1 ml of 7.5 n. HCl (made by mixing equal volumes of 6 n. and 9 n. acids) to the ether in the first funnel, rinsing the stopper as it is added, again shake the mixture, let the layers separate, and add this water layer to the first. Draw off the ether layer into a flask, washing out the funnel with two to five 1-ml portions of 1 n. HCl. Repeat these operations with the water layer in the second funnel, using only 5 ml of ether each time, until the ether layer remains colorless (Note 11). Draw off the final water layer into a 200-ml flask and treat it by P. 54 if phosphate is present, or by P. 55 if phosphate is absent. Return the previous ether extracts to the funnel containing the final one and treat these by P. 53 (Note 12).

Notes:

1. When the precipitate from P. 51 is treated with HCl, the sulfides of manganese, iron, and zinc are readily dissolved with evolution of H_2S; however, the sulfides of nickel and cobalt dissolve so slowly that an oxidizing agent is required to bring them into solution. The Br_2 is not added at first because its action would cause the formation of considerable sulfate; this is undesirable, as barium or strontium might be present. It is also necessary for the iron to be in the ferric form for it to be extracted by the ether, and, as it would have been reduced by the H_2S first set free, Br_2 is added until an excess is present, thus insuring that the iron is oxidized.

2. If there are any sulfides present, there is usually a small residue of sulfur left after this treatment. If the mixture is heated until this is light colored, it will contain only insignificant amounts of the metallic elements and can be filtered out and discarded.

3. It is necessary that the Br_2 be completely expelled, as it would oxidize the thiocyanate which is later added according to the reaction:

$$SCN^- + 3Br_2 + 4H_2O = HCN + HSO_4^- + 6H^+ + 6Br^-.$$

It is necessary that the volume be approximately 10 ml, as the adjustment of the acid concentration for the ether extraction is based upon this volume. Upon evaporation of the solution, the acid approaches 6 n.—the constant-boiling solution. There are added 2 ml of 6 n. and 6 ml of 12 n. acid, giving a solution of approximately 8 n. HCl. Ferric bromide solutions are orange-yellow, and therefore the complete expulsion of the Br_2 can best be determined by smelling the vapors above the boiling solution.

4. Even 1 mg of iron will impart a distinct yellow color to this volume of 6 n. HCl; if this distinctive yellow color is obtained, it is not necessary to make the thiocyanate test. If any chromium is present, it may make the detection of iron uncertain because of the green color which it causes. One mg of chromium will also cause an easily perceptible color, so that, if the solution is colorless, chromium need not be further tested for.

5. The presence of 0.5 mg of iron in the original solution will cause a distinct pink color in the solution being tested. The color change is noticeable even when a large quantity of chromium is present.

6. As mentioned in the discussion, if it is not desired to use the ether separation, especially if only a small amount of iron (less than 10 mg) is thought to be present, this solution can be carried directly to P. 54 (or to P. 55 if phosphate is absent) and the iron present can be separated and detected as indicated in Note 3 of P. 55, or it may be later separated as $Fe(OH)_3$ and $Fe(OH)_2C_2H_3O_2$ in P. 63.

7. A separating funnel with the stem cut off as close to the stopcock as possible is desirable because of the difficulty in removing the solution from a long stem.

8. As mentioned in the discussion, it is possible to substitute ethyl ether for the isopropyl ether when the latter is not available. In this case only 1 ml of 12 n. and 4 ml of 6 n. HCl should be used for washing out the flask: otherwise the procedure remains the same.

When working with ethyl ether, *extreme care* should be taken to extinguish

all flames in the vicinity; also, the operations should be carried out near a hood so that the ether vapor does not accumulate where it may be subsequently ignited.

9. Unless the mixture is kept cold, the ether develops a pressure in the funnel and tends to force the solution out around the stopper and stopcock. For this reason, the funnel should be cooled under running tap water or, preferably, with ice water. Since the volume of solution is small, great care should be taken to avoid loss during this operation.

10. The successive shaking with ether can be more easily carried out by drawing the water layer directly into a second separating funnel, thus avoiding additional transfers of the solution.

11. The color of the iron in the ether layer is so distinctive that when this layer is colorless there remains so little iron (less than 0.5 mg) in the water layer that it will not interfere with any of the subsequent separations; the aqueous layer may be colored by other constituents, thus, titanium (often present in ores) forms a yellow compound with peroxide (present in the ether) very similar in color to that of ferric chloride solutions.

12. No information as to the state of oxidation of the iron in the original material is obtained from its detection in the above procedure. In case this information is desired, proceed as follows:

> Boil 10 ml of 6 n. H_2SO_4 for 2 to 3 min. in a flask which is covered with a watch glass; then quickly introduce 0.1 g of the original sample and again boil for 5 min. Add, in small portions, 0.2 g of $NaHCO_3$ and cool the flask, with running tap water, to room temperature. Filter the mixture through a rapid-filtering paper filter and collect the solution in a flask to which has been added 0.1 g of $NaHCO_3$.
>
> Pour half of the solution into a small flask (or test tube) and add to it, 0.1 ml at a time and as long as a precipitate forms, $K_3Fe(CN)_6$ solution. (Blue precipitate, presence of ferrous iron.)
>
> Pour the other half of the solution into a test tube containing 5 ml of KSCN solution. (Red color, presence of ferric iron.)

The H_2SO_4 solution is first boiled in a covered flask, and the $NaHCO_3$ is added to insure that any ferrous iron present is not oxidized by oxygen in the solution or in the air above it. For a discussion of the precipitates formed by ferrous and ferric iron with ferro- and ferricyanide, see P. 133. If silver or copper were present, they would give orange and green precipitates, respectively; the blue compound formed with ferrous iron is so very insoluble and intensely colored that even small amounts can be recognized in the presence of these other precipitates, especially if the ferricyanide is added gradually so that the blue precipitate is formed first. The red-colored compound formed by thiocyanate with ferric iron is a very distinctive test and has been used in the above procedure; a large excess is added to increase the sensitivity of the test and to provide an excess in case any oxidizing agents (which might oxidize thiocyanate to sulfate and cyanide) are present.

13. When isopropyl ether is used and large amounts of iron are present, two ether layers may form; both of these layers should be retained in the funnel.

P. 53. Iodometric Estimation of Iron

Discussion. The ferric chloride is recovered from the ether solution by shaking it with water. As is seen from the curves shown in Fig. 30, under these conditions the iron will pass quantitatively into the aqueous layer, and the ether can be recovered and reserved for future use. The method for estimating iron which is recommended for use here depends upon the fact that ferric chloride in a hydrochloric acid solution oxidizes iodide to free iodine and is itself reduced to the ferrous state; the iodine can then be titrated with a standard thiosulfate solution. The principal reaction can be represented by the equation

$$2Fe^{+++} + 3I^- = 2Fe^{++} + I_3^-,$$

and from the potentials involved it can be calculated that the reaction would reach an equilibrium with a considerable amount of ferric iron present if iodide were added in only an equivalent amount. However, it can be shown that the equilibrium would be so shifted by the addition of an excess of iodide that less than 0.2 per cent of the iron would remain in the ferric form; this amount should be greatly reduced as the iodine is removed during the titration with the thiosulfate. Several factors not shown by the above equation have to be considered: First, the rate of the reaction is somewhat slow, and therefore it is necessary to allow the iodide and ferric iron to react in a small volume for an appreciable length of time before beginning the titration. Second, although it is not evident from the equation given above, an experimental study of the reaction has shown that the accuracy of the method is dependent upon the hydrochloric acid concentration. With insufficient acid the reaction becomes slow and incomplete, because of the hydrolysis of the ferric iron; with the hydrochloric acid concentration too high the reaction is also incomplete, probably because of the formation of complex molecules of the type $HFeCl_4$ (such salts as $KFeCl_4$ having been prepared). In addition to these effects, oxidation of the iodide by the oxygen of the air becomes appreciable as the acid concentration is increased. It is thus indicated that the accuracy of the process is very dependent upon the conditions obtaining and to a certain extent upon a compensation of errors. It has been found experimentally that, if the reaction is allowed to proceed under the conditions given in the procedure below, results accurate to 0.2 to 0.3

per cent can be obtained.[15] If sulfates are present, higher concentrations of acid and of iodide are required; the reaction can be reversed by the addition of phosphoric acid. The reaction of phosphoric acid with ferric iron is discussed in P. 53*A*.

Iron is more commonly determined by titration with an oxidizing agent, most frequently standard permanganate solution. This requires that the iron be in the ferrous state, and various reagents and methods are used for this preliminary reduction (see the discussion of P. 53*A*). These methods are often time-consuming, and special precautions have to be taken to prevent oxidation of the ferrous salt after the reducing agent has been removed. Also, the titration of ferrous iron with permanganate in the presence of chloride has to be carried out under very closely controlled conditions, or appreciable reduction of permanganate by the chloride may occur.

As in this procedure the iron is already in the ferric form and in a hydrochloric acid solution, and as the iodometric method is so very rapidly carried out, its use is recommended. However, as the titration with permanganate in a hydrochloric acid solution is so frequently used for the analysis of iron ores, it is possible that the special reagents required may be available and that this method may be preferred; therefore a procedure for this method is given in P. 53*A*.

Procedure 53: IODOMETRIC ESTIMATION OF IRON. Add an equal volume of water to the ether extracts, cool, shake, allow the layers to separate, and draw the water layer into a 200-ml flask. Repeat this process with two 5-ml portions of water. Reserve the ether solution for future extractions.

Evaporate the aqueous extracts on a steam bath (*Caution:* Note 1) until all dissolved ether is expelled, and then evaporate over a flame until just 15 ml of the solution remain. Estimate this volume by comparing the solution left in the flask with a measured 15-ml volume of water in a similar flask. Cool the flask with tap water and add to it 4 ml of HCl.

If less than 75 to 100 mg of iron are thought to be present, treat the solution as directed in the last paragraph of this procedure.

If more than 75 to 100 mg of iron are thought to be present, transfer the cold solution to a 100-ml volumetric flask,

[15] Swift, *J. Am. Chem. Soc.*, **51**, 2682 (1929).

dilute it to the mark, and thoroughly mix the solutions. Pipet 25 ml of this solution into a 200-ml flask, preferably one with a ground-glass stopper, add to it 4 ml of HCl, and treat it as directed in the next paragraph.

Add to the solution 3 g of solid KI, close the flask, gently swirl the mixture until the KI is dissolved, and allow it to stand for 5 min. (Note 2). Dilute the solution to 100 to 125 ml with cold water, and rapidly titrate with 0.1 n. $Na_2S_2O_3$ solution as long as the iodine color is apparent. When the iodine color becomes indistinct, add 5 ml of starch indicator solution and carefully titrate until the blue color just disappears (Note 3). From the volume of thiosulfate solution used, calculate the amount of iron present.

Notes:

1. As some ether may remain in these solutions and as its vapors are very inflammable, the first part of this evaporation should be performed under a well-ventilated hood or on a steam bath heated with an electric heater (it is usually sufficient to heat a large beaker of water to boiling and then extinguish the flame before beginning to evaporate the ether). See Note 8, P. 52.

2. The results obtained by this method are dependent upon the amount of HCl in the solution, upon the volume during the reaction between the ferric iron and the iodide, upon the amount of potassium iodide added, and upon the length of time for which the solution is allowed to stand. The effect of the acid is mentioned in the discussion. Increasing the volume of the solution decreases the concentration of acid, ferric iron, and iodide, and slows the rate of reaction. With insufficient iodide the reaction is again slow; with too much the oxidation of the iodide by air is increased. If insufficient time is allowed, the reaction may not be complete when the end-point is taken; if the solution is allowed to stand too long, oxidation of the iodide by the air takes place.

3. Both ferrous chloride and ferrous iodide are oxidized by air in a HCl solution, and the rate is dependent upon the concentration of the HCl; for this reason the solution is diluted before making the titration. The titration should be carried out as rapidly as possible, and after reaching an end-point it is advisable to stopper the flask and allow it to stand for 2 to 3 min. If a blue color reappears, it can usually be permanently removed with less than a full drop of the thiosulfate.

P. 53A. Optional Method for the Estimation of Iron by Titration with Permanganate

Discussion. This method is based upon the oxidation of ferrous iron, in a hydrochloric acid solution, with a standard permanganate solution.

The Reduction of Ferric Salt Solutions. In the procedure below, the iron is obtained in solution in the ferric state (as is usually the case in the analysis of iron ores) and must be reduced before the titration. This reduction can be accomplished by (1) metals (such as zinc, cadmium, or aluminum), (2) reducing gases (such as hydrogen sulfide or sulfur dioxide), or (3) solutions of a reducing agent (usually stannous chloride). After such a reduction the excess of the reducing agent must be removed. In the case of metals this may involve a filtration or the use of a special reduction apparatus,[16] and the gases have to be expelled by long boiling or swept out with an inert gas. If the iron is in a hydrochloric acid solution (as is frequently the case because of the effectiveness of this acid in dissolving iron ores), the reduction can be very quickly carried out with a stannous chloride solution and the excess stannous tin can be removed by oxidation with mercuric chloride. This reagent is uniquely fitted for the purpose, as (1) mercuric chloride does not oxidize ferrous iron, and as (2) the reduction product (mercurous chloride) is so insoluble that, especially if it is caused to precipitate in a crystalline form, it is not appreciably oxidized by either ferric iron or permanganate during the course of the titration.

The Titration of Ferrous Salts in Hydrochloric Acid Solutions. As was mentioned in the general discussion of permanganate methods, it would be calculated from the potentials involved that, in a strongly acid solution, permanganate, even in the small concentration necessary to give an end-point, would be reduced by chloride. Fortunately, the rate at which this reaction takes place is so slow under most conditions that such titrations can be carried out; thus oxalate (P. 85 and P. 87) and ferrocyanide (P. 133) are titrated in the presence of relatively high concentrations of hydrochloric acid. However, it was realized quite early in the history of this titration[17] that, when ferrous salts in hydrochloric solutions are titrated with permanganate, there is oxidation of the chloride.

Investigations have shown that this effect is due to the reaction between permanganate and ferrous iron inducing the oxidation of chloride; ferric ions do not catalyze the reaction between permanga-

[16] This is usually the "Jones Reductor," which is a vertical glass tube filled with amalgamated zinc. The solution to be reduced is passed through this tube, the rate of flow being controlled by a stopcock at the bottom end.

[17] The ferrous iron-permanganate titration appears to be the first permanganate method to have been used (Marguerite, *Ann. Chem. Phys.*, **18**, 244 (1846)). The first mention of the effect of chloride was made bv Lowenthal and Lenssen, *Z. anal. Chem.*, **1**, 329 (1862).

nate and chloride. Experimental evidence has been obtained[18] that this induction is caused by the permanganate first oxidizing the ferrous iron to an unstable higher oxidation state, probably ferrate ($FeO_4^=$), as follows:

$$MnO_4^- + Fe^{++} = FeO_4^= + Mn^{+++}.$$

The ferrate then oxidizes chloride ion to hypochlorous acid, it having been shown that the oxidized chlorine is largely present as this compound.[19] It was also observed quite early[20] that this effect was decreased by the presence of a relatively high concentration of manganous salts. The mechanism of the inhibiting effect of the manganous ion has not been clearly established. In partial explanation the suggestion has been advanced that raising the concentration of the manganous ion decreases the oxidizing potential of the permanganate—manganous ion half-cell. However, the change in potential which can be thus produced is so limited that the validity of this explanation is doubtful. It is more probable that the effect is one in which the mechanism of the reaction is changed by the presence of the manganous ion. Thus the manganous ion, by reacting rapidly with the permanganate to give an intermediate oxidation state or states (as is the case in the permanganate-oxalate catalysis), may eliminate the formation of the higher oxidation states of iron; or, alternatively, the ferrate (or the hypochlorous acid which it forms) may react very rapidly with manganous ion to give tri- or quadripositive manganese, which then rapidly oxidizes ferrous iron to the ferric state. Zimmermann[21] appears to have been the first to have made practical use of this phenomenon by the addition of large amounts of manganous salts to the solution to be titrated.

Ferric iron in hydrochloric acid solutions causes an intense yellowish color (due to complex compounds of the type $HFeCl_4$) which obscures the permanganate color and necessitates the addition to such solutions of a higher concentration of permanganate in order to obtain an end-point. This yellow color can be bleached by the addition of phosphoric acid, which forms more stable (but colorless) complex compounds with ferric iron;[22] sulfuric acid forms similar

[18] Manchot, *Ann. Chem. Pharm.*, **325**, 105 (1902); Bohnson and Robertson, *J. Am. Chem. Soc.*, **45**, 2493 (1923); Hale, *J. Phys. Chem.*, **33**, 1633 (1929).

[19] Baxter and Frevert, *Am. Chem. J.*, **34**, 109 (1905).

[20] Kessler, *Ann. J. Chem.*, **118**, 17 (1863).

[21] Zimmermann, *Ann. d. Chem.*, **213**, 305 (1882).

[22] These were thought by Weinland and Ensgraber, *Z. anorg. Chem.*, **84**, 340 (1913), to be complex acids of the type $H_3Fe(PO_4)_2$. However, the experi-

but less stable compounds. Thus, by the addition of these acids a colorless solution and a much sharper end-point are obtained. The addition of phosphoric acid may decrease the tendency toward chloride oxidation, as, by decreasing the ferric ion concentration, it facilitates the oxidation of ferrous iron and, by bleaching the solution, decreases the concentration of the permanganate required for recognition of the end-point. It has been found experimentally possible, under rather closely controlled conditions, practically to eliminate the chloride oxidation by the use of large amounts of phosphoric acid or of phosphates.[23] Reinhardt[24] suggested that manganous sulfate, phosphoric acid, and sulfuric acid be combined in one reagent, and this solution is still quite universally used and known as the Zimmermann-Reinhardt "preventative" solution.

By the use of this solution, by avoidance of an excess of stannous chloride and therefore of mercurous chloride precipitate, and by slow titration in a cold dilute solution, the method can be made to give quite precise results, and, because of the rapidity with which it can be carried out, it is very extensively employed, especially for the analysis of iron ores.

Procedure 53A: ESTIMATION OF IRON BY TITRATION WITH PERMANGANATE. Treat the ether extracts as directed in the first paragraph of P. 53.

Evaporate the aqueous extracts on a steam bath (*Caution:* Note 1, P. 53) until any ether is expelled, add 0.2 f. $KMnO_4$ until a distinct reddish-pink color is obtained, and then add 2 or 3 drops in excess (Notes 1, 2).

Evaporate the solution to a volume of about 15 ml and, while keeping it hot, add 1 n. $SnCl_2$ drop by drop, swirling the solution, until the yellow color disappears and the solution is colorless (or only a very slight greenish tinge remains), and then add 1 drop of $SnCl_2$ in excess.

Cool the solution to at least room temperature and add rapidly 10 ml of a saturated mercuric chloride solution (Note 3). Allow the mixture to stand 2 min. (Note 4), transfer it to a 600-ml beaker containing 400 ml of water and 25 ml of Zimmermann-Reinhardt solution (Note 5),

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ments of Bonner and Romeyn, *J. Ind. Eng. Chem., Anal. Ed.*, **3**, 85 (1931), do not confirm this but indicate that an un-ionized molecule of the type $Fe(H_2PO_4)_3$ is formed.

[23] Hough, *J. Am. Chem. Soc.*, **32**, 539 (1910); Barneby, *ibid.*, **36**, 1429 (1914).

[24] Reinhardt, *Chem. Zeit.*, **13**, 323 (1889).

and titrate immediately with standard $KMnO_4$. Do not add the $KMnO_4$ rapidly at any time. Stir the solution continuously and approach the end-point drop by drop. Take the end-point when the first perceptible pink tinge spreads uniformly throughout the solution and persists for at least 15 sec. (Note 6). Use a white background for viewing the solution and avoid overrunning the end-point. Make an end-point correction (Note 7). From the corrected volume of standard permanganate used, calculate the amount of iron present.

Notes:

1. The $KMnO_4$ is added to oxidize any reducing materials (organic compounds or peroxide) which may have been introduced into the solution by the ether separation. The excess permanganate is reduced by the chloride, and the chlorine thus formed is expelled during the subsequent boiling or is reduced by the $SnCl_2$ next added.

2. Many iron ores can be brought into solution by treatment with HCl and the iron can be determined by directly treating the resulting solution by the procedure given above; elements which would cause errors in the titration (vanadium, molybdenum, tungsten, and platinum) are not commonly present in the iron ores. Proceed as follows:

Weigh out an amount of the ore which will require from 25 to 35 ml of the standard permanganate, add to it in a 150-ml beaker 20 ml of 6 n. HCl and 1 ml of $SnCl_2$, cover the beaker, and heat the mixture almost to boiling until only a white residue remains (if the solution becomes yellow, add $SnCl_2$ in 0.1-ml portions until it is decolorized). When solution is complete, add 0.2 f. $KMnO_4$ until the first yellow color is obtained and treat the solution by the second and subsequent paragraphs of the procedure above.

The presence of an excess of $SnCl_2$ greatly increases the rate at which iron ores are dissolved by HCl, probably by causing a surface reduction of the iron.

3. The solution is cooled and the $HgCl_2$ solution is added all at once in order to prevent the formation of metallic mercury. If a large excess of $SnCl_2$ is added, or if the solution is warm, this may occur and will cause a black precipitate. In this case the analysis must be discarded, as metallic mercury rapidly reduces both permanganate and ferric iron.

4. The mixture is allowed to stand for 2 min. in order that complete precipitation of the mercurous chloride may occur and so that it may change from the finely divided, often colloidal, form in which it first separates to a more compact crystalline form. In this state it is oxidized much more slowly by ferric iron or permanganate.

The solution should not stand much longer than this time, or oxidation of the ferrous iron by the oxygen of the air will become appreciable. For the same reason the solution should be titrated immediately after adding the Zimmermann-Reinhardt solution.

5. The Zimmermann-Reinhardt solution is approximately 0.3 f. in $MnSO_4$, 3 f. in H_3PO_4, and 4.6 f. in H_2SO_4. See the Appendix for directions for its preparation.

6. The end-point will slowly fade because of the oxidation of the mercurous chloride, but, if the above conditions have been adhered to, it will persist for at least 15 sec. and usually considerably longer.

7. The end-point correction should be made by taking the volume of hydrochloric acid and of stannous chloride originally used, oxidizing the stannous chloride with the 0.2 f. $KMnO_4$, then decolorizing this solution with stannous chloride, and carrying out the remainder of the operations as in the procedure above. This correction will usually vary between 0.03 and 0.05 ml of 0.1 n. $KMnO_4$.

P. 54. Removal of Phosphate

Discussion. If phosphate has been found (in P. 164, or by the test given in Note 1 below) to be one of the constituents of the material being analyzed, and if a precipitate was obtained on adding ammonium hydroxide to the filtrate from the hydrogen sulfide precipitate, this may have been due to the precipitation of one or more of the alkaline earth elements as phosphate. In order to recover the alkaline earth elements, and because phosphate might cause the precipitation of manganese with the Zinc Group, a supplementary procedure is necessary to remove phosphate before separating the Zinc and Aluminum Groups.

The method used here depends upon the fact that bismuth phosphate is the only phosphate of the common elements which is only slightly soluble in 0.5 n. nitric acid. Therefore, upon the addition of bismuth nitrate to such a solution, the phosphate is precipitated and the other basic elements remain in solution. The solubility of bismuth phosphate is much greater in hydrochloric acid because of the formation of compounds such as $HBiCl_4$; therefore, because of this fact and because of the slight solubility of BiOCl, chloride must be removed before the precipitation is made; this is done by evaporating the hydrochloric acid solution with nitric acid. If it is desired to estimate the amount of phosphate present, the precipitate of bismuth phosphate can be collected on a previously heated and weighed Gooch-type crucible, and the precipitate can be dried at 400° to 500°C. and weighed as $BiPO_4$. Confirmatory experiments[25] have shown that, of the basic elements which may be present in this solution, less than 1 mg of iron, aluminum, cobalt, nickel, or zinc is carried out with the precipitate when 500 mg of phosphate are

[25] Unpublished experiments by Dr. R. C. Barton.

present with 250 mg of any one of these elements. However, with the same quantity of chromium, the normally white $BiPO_4$ precipitate is greenish in color and may contain as much as 12 to 15 mg of chromium.

The excess of bismuth is removed by precipitating it as sulfide from the solution, which is 0.5 n. in nitric acid. After filtering out the sulfide precipitate, the Ammonium Sulfide Group elements can be precipitated (by P. 51) and the Alkaline Earth Group elements are left in the filtrate.

Procedure 54: REMOVAL OF PHOSPHATE. If either (a) phosphate has not been found present (Note 1) or (b) if no precipitate was obtained on adding NH_4OH to the filtrate from the H_2S precipitation (P. 51), treat the HCl solution from P. 52 by P. 55. If phosphate has been found present and if a precipitate was also obtained on adding NH_4OH to the filtrate from the H_2S precipitation, treat the HCl solution as directed in the next paragraph (Note 2).

Evaporate the HCl solution from P. 52 (*Caution*: It contains ether. See Note 1, P. 53) to 1 to 2 ml (colorless solution, absence of chromium, cobalt, and nickel. Note 3.) Add 5 ml of 16 n. HNO_3 and evaporate the solution to 1 to 2 ml. Add 5 ml of 16 n. HNO_3 and again evaporate the solution to 1 to 2 ml (Note 4). Dilute the solution to 50 ml and add 3 n. Na_2CO_3 solution, 0.5 ml at a time, until the solution is neutral (Note 5) or slightly alkaline to litmus. (White precipitate, presence of aluminum, manganese, zinc, or alkaline earth elements. Colored precipitate, presence of chromium, cobalt, or nickel. Note 6.) Add 4 ml of 6 n. HNO_3, heat the solution nearly to boiling, and, while keeping it hot, add dropwise to it 0.5 ml portions of 0.1 f. bismuth nitrate reagent until a precipitate no longer forms (Note 7). Boil the mixture for a minute or two, keeping the flask in motion to prevent bumping, and then let it stand until the precipitate has settled. Filter the mixture by decantation through an asbestos filter (Note 8) and wash the precipitate with three 5-ml portions of hot 0.3 n. HNO_3, collecting the washings with the filtrate. Saturate the warm filtrate with H_2S and filter the mixture. Wash the precipitate with three 5-ml portions of hot water, collecting the washings with the filtrate. Discard the precipitate (Note 9). Treat the solution by P. 51 (Note 10).

Notes:

1. If the analysis for the acidic constituents has not been made and a quick qualitative test for phosphate is desired, it can be made on a portion of the original material as follows:

Take approximately 0.1 g of the original sample in a casserole (if arsenic has been found present, add 5 ml of 12 n. HCl, 2 ml of 9 n. HBr, and 2 drops of liquid bromine and evaporate the mixture just to dryness under a hood), add to it 5 ml of 16 n. HNO_3, and evaporate the mixture almost to dryness. Add to the residue 5 ml of 6 n. HNO_3 and filter out the residue on a small paper filter. Collect the filtrate in a small flask in which has been mixed 5 ml of HNO_3 and 5 ml of $(NH_4)_2MoO_4$ reagent. Warm the mixture to 40° to 60°C. and let it stand for 10 min. (Canary yellow precipitate, presence of phosphate.)

This method for the precipitation of phosphate—which, because it can be made from an acid solution, is extensively used for the separation of phosphate from the basic constituents with which it is associated—depends upon the formation of the tri-ammonium salt of a complex molybdophosphoric acid. The reaction can be represented as follows:

$$3NH_4^+ + 12\ MoO_4^- + H_3PO_4 + 21H^+ = (NH_4)_3PO_4 \cdot 12MoO_{3(s)} + 12H_2O.$$

As is indicated by the equation, the sensitivity of this test is dependent upon (1) a large excess of molybdic acid, required to insure the formation of the complex molybdophosphoric acid; (2) a high concentration of ammonium ion, to reduce the solubility of the tri-ammonium salt of this acid; and (3) an acid solution, to convert the molybdate ion to the acidic form.

If the solution is made too acid or is heated much above 70°C., white or pale yellow molybdic acid, $MoO_3 \cdot H_2O$, may precipitate. In this case the precipitate should be dissolved in NH_4OH and the solution should be reacidified with HNO_3. The yellow precipitate is of too uncertain composition and is too unstable for it to be used as the basis of a precise gravimetric or volumetric determination. Accordingly, when a gravimetric determination is desired, the yellow precipitate is dissolved in ammonium hydroxide and the phosphate is reprecipitated as magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$) from the ammoniacal solution.

If arsenic is present, the sample is evaporated with HCl and HBr in order to volatilize it as arsenic trichloride. Bromine is added to insure the solution of arsenic sulfides, and bromide to insure that all the arsenic is reduced to the tripositive state. The removal of arsenic is necessary because arsenic acid, as would be predicted from the periodic relationships, forms a yellow precipitate, $(NH_4)_3AsO_4 \cdot 12MoO_3$, analogous in its properties to the phosphorous compound.

2. It is possible that the precipitate obtained on adding ammonia to the H_2S filtrate (in P. 51) may have been due to iron phosphate alone, and in that case the removal of phosphate is not necessary. Also, if alkaline earth elements have not been brought into this group and if manganese is not present in considerable amount, the presence of phosphate is permissible. Therefore, one may add a slight excess of NH_4OH to the HCl solution above, and, if no precipitate is obtained, no alkaline

earth phosphates are present; also, if no brownish precipitate results upon adding to this slightly ammoniacal solution a few drops of 3 per cent H_2O_2, the absence of manganese is shown and the removal of phosphate is unnecessary. If a brownish precipitate is obtained, the mixture should be made acid with HCl, boiled until the precipitate dissolves, and treated as directed.

3. This volume of HCl solution is colored a distinct blue by 0.5 mg of cobalt and green by the same quantity of chromium, while 1 mg of nickel imparts a pale yellowish-green color. However, it should be remembered that the presence of as little as 0.1 mg of ferric iron would give a distinct yellow color to this small volume of HCl, and this may vitiate the color detection of traces of cobalt, chromium, and nickel.

4. The solution is evaporated repeatedly with 16 n. HNO_3 to remove chloride ion, which interferes with the precipitation of $BiPO_4$ because of the tendency of bismuth to form such complex compounds as $HBiCl_4$. The formation of these complexes reduces the concentration of bismuth ion and requires the addition of a large excess of bismuth nitrate reagent to precipitate completely the phosphate present.

5. This neutralization is conveniently followed by the effervescence produced upon the addition of Na_2CO_3. The neutralization of the acid is complete when the addition of 0.5 ml of the Na_2CO_3 solution gives no evolution of CO_2. Avoid an excess of Na_2CO_3, because the acidity of the solution is to be adjusted for the removal of phosphate.

6. A white precipitate is produced upon neutralizing with Na_2CO_3 an acid solution containing phosphate and aluminum, manganese, zinc, or alkaline earth elements. Under the same conditions cobalt gives a purplish-blue, chromium a bluish-green, and nickel a light green precipitate.

7. The reagent is added dropwise because a more easily filtered precipitate is obtained if the precipitation takes place slowly. The precipitate should be allowed to settle before each addition of the bismuth nitrate reagent. This enables the completeness of the precipitation to be followed closely and prevents the use of too large an excess of the reagent.

The bismuth nitrate reagent is 0.1 f. in bismuth nitrate and 0.5 f. in HNO_3. The reagent is made acid with HNO_3 to prevent the precipitation of oxy-salts of bismuth. About 65 ml of the reagent are required to precipitate 500 mg of phosphate.

8. If it is desired to estimate the amount of phosphate present, a filter of the Gooch type should be used. In this case, after the precipitate has been washed thoroughly, it should be heated to constant weight at 300° to 500°C. The crucible should have been heated to constant weight at this temperature before being used.

9. If the $BiPO_4$ precipitate is greenish, it indicates that chromium has been coprecipitated (see the discussion). If desired, this chromium can be determined as follows:

> Transfer as much as possible of the precipitate from the filter to a 300-ml flask. Dissolve the precipitate remaining on the filter with 1 to 5 ml of HCl and wash the filter with two 5-ml portions of 2 n. HCl, collecting the solution and washings in the flask. Shake the flask until the precipitate dissolves and dilute the solution until the acid concentration is about 0.3 n. Saturate the solution with H_2S and filter it, collecting the filtrate in a 300-ml

flask. Wash the precipitate with three 5-ml portions of hot water and combine the washings with the solution. Add 6 n. NaOH to the solution until it is definitely alkaline, cool it, and treat the cold mixture with 1 to 2 g of Na_2O_2. Boil the solution until the excess peroxide has decomposed and the volume of the solution has been reduced to about 80 ml. Cool the flask and treat the solution by the last paragraph of P. 75.

10. The solution, which may contain alkaline earth elements, is treated by P. 51 in order to again precipitate any Ammonium Sulfide Group elements. This precipitate should then be dissolved in HCl as directed in the first paragraph of P. 52, and the solution should be treated by P. 55. The filtrate, containing any alkaline earth elements, can be combined with the original filtrate from the ammonium sulfide precipitation if the alkali elements are not to be tested for or can be treated separately by P. 81.

P. 55. Separation of the Zinc and Aluminum Groups

Discussion of general methods for separating the Ammonium Sulfide Group elements into two groups. After the iron has been removed from the group of elements obtained by the ammonium sulfide precipitation, it would be advantageous to separate the remaining elements into two smaller groups. An obvious method would be the precipitation of the tripositive hydroxides of aluminum and chromium by suitably adjusting the hydrogen ion concentration of the solution. The unsatisfactory results obtained when this is done by the "ammonia precipitation" have been shown in the discussion of P. 51. Similar conditions of acidity are obtained by treating an acid solution of these elements with an excess of solid barium carbonate; however, this introduces barium into both the precipitate and the solution, and the presence of the excess of barium carbonate makes it difficult to detect small precipitates of aluminum or chromium hydroxides. Various other methods of obtaining this desired hydrogen ion concentration are used in quantitative separations, but these are in general not suitable for use in qualitative systems, owing to the wide variations in the quantities and combinations of elements which may be encountered.[26] Other methods of separating these elements into two groups are discussed below.

The Separation by Sodium Hydroxide and Peroxide. As is shown in Table XVIII, p. 282, if a high concentration of hydroxyl ion is used, the amphoteric nature of aluminum, chromium, and zinc is taken

[26] Descriptions and discussion of these methods will be found in Hillebrand and Lundell, *Applied Inorganic Analysis*, pp. 68–76, and in Treadwell-Hall, *Analytical Chemistry*, Vol. II, Quantitative, 8th Ed., pp. 155–162.

advantage of and these elements are dissolved (chromium hydroxide dissolves in dilute hydroxide solutions largely because of its tendency to form a stable colloid; in concentrated hydroxide solutions chromite is formed), while manganese, nickel, and cobalt are precipitated as hydroxides or hydrated oxides. Owing to the tendency of chromium to be carried down with the precipitate and to the appreciable solubility of cobalt in high concentrations of alkali, this method is nearly always modified by adding an oxidizing agent (usually sodium peroxide), which oxidizes the chromium to chromate, the manganese to manganese dioxide, and the cobalt to cobaltic oxide. The process is used extensively in qualitative systems, and in quantitative methods for the separation of the individual elements.[27]

Statements in the literature as to the effectiveness of these individual separations are somewhat incomplete and often not definite. Noyes, Bray, and Spear[28] state: "The separation of the two groups by this process is entirely satisfactory, at any rate, from the standpoint of qualitative analysis, with the single exception that when 5 or 10 mg. of zinc are present this may be carried down completely when elements of the Iron Group (especially manganese) are present in large quantity." However, there appears to be a certain amount of distrust of the method; this is perhaps explained by the statement of Hillebrand and Lundell:[29] "The use of sodium hydroxide for precipitations has not been in good repute among analysts because of the uncertain quality of the reagent and the slimy character of the solution and precipitate." It is explained, however, that the first objection is not as well founded today as in the past, that the difficulty in filtering about 5 per cent solutions is not serious, and that "in the hands of one of us (L.) the method has proved very satisfactory."

The confirmatory experiments and test analyses of Noyes, Bray, and Spear give quite complete information as to the qualitative value of the separation, as they perform it, in the detection of small amounts of an element in the presence of even large amounts of another; additional data showing the completeness of the individual separations, when considerable amounts of each element are present, have been collected[30] and are presented in Table XXI.

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[27] Frequently in quantitative methods other oxidizing agents, such as bromine, chlorine, or peroxysulfate, are substituted for the peroxide, but these are not as convenient as the peroxide, and, in qualitative systems, may introduce objectionable ions into the analysis.

[28] Noyes, Bray, and Spear, *J. Am. Chem. Soc.*, **30**, 484 (1908).

[29] Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929, p. 76.

[30] Swift and Barton, *J. Am. Chem. Soc.*, **54**, 4155 (1932).

In Procedure II of this table (see p. 312) the slightly acid solution containing the hydrogen peroxide was poured into the hot hydroxide solution, as there is agreement that a better separation results from this order of mixing. Qualitative experiments also indicated that a more rapid and complete oxidation of chromium was obtained when hydrogen peroxide was present in the acid solution; when sodium peroxide was added to an alkaline solution, as in Procedure I, or an acid solution was added without peroxide to a hot sodium hydroxide solution, a precipitate which oxidized slowly was obtained. The acid solution could be added to a cold sodium peroxide solution; however, the preparation of a solution of sodium peroxide, even when it is kept cold, results in excessive loss of peroxide by decomposition. Furthermore, the precipitate produced upon addition of the acid solution to the hot hydroxide seemed more readily handled than that formed by precipitating in the cold and then heating.

The data in the table show that the separation of aluminum from manganese and iron can be made sufficiently complete for qualitative and for most quantitative work; with 250 mg of each element, from 4 to 5 per cent of the aluminum is left with the cobalt precipitate and from 12 to 14 per cent with the nickel precipitate.

The separation of chromium, beginning with chromic ion and with sodium peroxide as the oxidizing agent, is unsatisfactory in every case regardless of method. That this is due to incomplete oxidation of the chromium by the peroxide was shown by analysis of the precipitates;[31] only tripositive chromium was found to be present. This is also shown by Experiments 20 to 23, where, beginning with the chromium as chromate, satisfactory separations were obtained, except in the case of manganese, in which the coprecipitation is reduced from 20 per cent to about 3 per cent.

The separation of zinc from the elements precipitated by sodium hydroxide is unsatisfactory, from 10 to 50 per cent of the zinc remaining in the precipitate. Because of these difficulties, this method has not been used in this system of analysis.

Separations Obtained by Controlling the Sulfide Concentration and also Adding a Complex-Forming Anion. Aluminum (and chromium) are often quantitatively separated from iron by treating the solution with tartaric acid or a tartrate—which in alkaline solutions forms soluble complex ions with both aluminum and chromium—and then adding ammonium sulfide, which precipitates the iron as sulfide. Experiments have shown that this method provides ex-

[31] Experiments by Harrison Backus.

TABLE XXI

The Separation of Manganese, Iron, Cobalt, and Nickel from Aluminum, Chromium, and Zinc by Precipitation with Sodium Hydroxide and Peroxide

In these experiments 250 mg of one of the elements in the first column were precipitated from a solution containing 250 mg of one of the elements listed at the top of the three major columns. In each of the three major columns are shown the experiment number, the procedure used, and the amount in milligrams of the soluble element found in the precipitate.

Element Precipitated	Aluminum			Chromium			Zinc		
	Expt.	Procedure	Al in Ppt. (mg)	Expt.	Procedure	Cr in Ppt. (mg)	Expt.	Procedure	Zn in Ppt. (mg)
Manganese	1	I[a]	12 to 15	3	I	50 to 70	29	I[d]	65
	2	II	2 to 3	4	II[b,c]	51	5	II[d]	60
				25	I[e]	7			
Iron (ferric)	6	I[a]	1 to 2				9	I	103
	7	II	1 to 2	8	II	56	10	II[d]	37
				24	I	37	32	II	47
				24	I[e]	0.2	33	II	46
							34	[f]	67
							35	[f]	62
Cobalt	28	I	20 to 25	12	I	65 to 80	30	I[d]	50
	11	II	12 to 15	13	I	65	16	II[d]	88
				14	I	87			
				15	II	21			
				23	II[e]	1			
Nickel	17	I	30 to 35	27	I	44	31	I[d]	30
	18	II	30 to 40	19	II	42	21	II	25
				22	II	0.5 to 1			

The separations were carried out according to two general procedures. The first of these, called Procedure I, conforms closely to that given by A. A. Noyes* and by Noyes and Bray,† and more nearly represents the usual qualitative technique. It was as follows:

Procedure I: To a solution of the elements to be separated, containing 1 to 2 ml of 6 n. hydrochloric acid and having a volume of 30 to 40 ml was added 6 n. sodium hydroxide until the solution was alkaline to litmus, and then 5 g of sodium peroxide. The sodium peroxide was sprinkled in very gradually, and the mixture was kept cold during the addition. Then the mixture was boiled until the sodium peroxide was decomposed, diluted to 60 ml, and filtered through hardened filters; in order to facilitate washing, two separate filters

* Noyes, *Qualitative Chemical Analysis*, Macmillan, 1922, 9th Ed., p. 95.

† Noyes and Bray, *A System of Qualitative Analysis for the Rare Elements*, Macmillan, 1927, pp. 164, 168.

were used if the precipitate was bulky. The precipitate was washed with hot water until the washings no longer turned red litmus blue.

In Procedure II certain modifications were used which are recommended as giving more quantitative separations. It was as follows:

Procedure II: To a solution of the elements to be separated, containing 1 to 2 ml of 6 n. hydrochloric acid and having a volume of 15 to 20 ml, 6 n. sodium hydroxide was added dropwise until the first permanent turbidity was produced. To this was added 20 ml of 3 per cent hydrogen peroxide, and the resulting solution was poured dropwise into 100 ml of 5 per cent sodium hydroxide which was kept just boiling during this addition. The mixture was then cooled and kept cool during the slow addition of 5 g of sodium peroxide. Finally, the mixture was boiled until the peroxide was decomposed, and it was then filtered, two separate papers being used in most cases. Hardened filters were not necessary in filtering these solutions. The precipitate was washed with 50 ml of hot 5 per cent sodium hydroxide and then with a hot 1 per cent solution until no test for the soluble element being separated was obtained. Observations and variations from the procedures outlined are contained in the notes to the table.

[a] Only 125 mg of aluminum were taken.

[b] The color of the solution indicated that the chromium was completely oxidized when the acid solution containing hydrogen peroxide was poured into the sodium hydroxide.

[c] Difficulty was experienced in washing the precipitate free of chromate.

[d] Only 160 mg of zinc were taken.

[e] The chromium was taken as potassium chromate; and no hydrogen peroxide was added to the acid solution.

[f] Duplicates of Experiments 32 and 33, except that the sodium hydroxide was added to the acid solution instead of the reverse order.

ceptionally fine separations of iron and zinc from aluminum and chromium, and that the separation of cobalt from either aluminum or chromium was equally satisfactory, although these separations are surprisingly imperfect by either the ammonium hydroxide or sodium hydroxide-peroxide methods.[32] However, there was some uncertainty as to the complete precipitation of manganese and nickel; and, in addition, the removal of the tartrate from the filtrate by fuming with sulfuric and nitric acids (and the re-solution of the chromic sulfate, apparently $Cr_4H_2(SO_4)_7$, which formed) proved so tedious and time-consuming that the method was considered as undesirable.

It is known that oxalate tends to form complex compounds with all of these elements, and many of these compounds have been prepared. Very stable ions of the type $M(C_2O_4)_3^{=}$ are formed with aluminum and chromium (as well as with ferric iron), and ions, apparently somewhat less stable, of the type $M(C_2O_4)_2^{=}$ are formed with manganese, zinc, nickel, and cobalt. As oxalate can be much

[32] Unpublished experiments by F. N. Laird.

more easily oxidized and removed from a solution, its use as a substitute for tartrate was investigated.

It was found that moderate amounts of aluminum or chromium could be held in an ammoniacal solution if sufficient oxalate was present, but that the precipitation of manganese as sulfide from such solutions was quite incomplete, as much as 50 mg of manganese being present before a precipitate was obtained, and that in slightly acid solutions a precipitate of manganese oxalate was obtained. However, upon neutralization of the solution with sodium hydrocarbonate, no precipitate of manganous oxalate formed when an excess of oxalate was present, and it was found possible to have even large amounts of manganese present without formation of a precipitate upon saturation of the solution with hydrogen sulfide.

A detailed study of the behavior of manganese and of the other elements of the Ammonium Sulfide Group in solutions containing sodium hydrocarbonate and an excess of oxalate was therefore made.[33] These experiments showed that the manganese remains in solution largely because of the formation of a supersaturated solution, but that this state of supersaturation can be maintained for a considerable length of time even when another precipitate is present. They also showed that, by properly adjusting the amount of sodium hydrocarbonate added, the volume of the solution, and the time for which the hydrogen sulfide is passed, even 500 mg of aluminum, chromium, and manganese (hereafter designated as the Aluminum Group) can be held in solution, while 1 mg of zinc, nickel, and cobalt (hereafter designated as the Zinc Group) are precipitated. Iron, if present, is likewise precipitated. Furthermore, it was shown that 1 mg of any one element of the group can be detected in the presence of 500 mg of any element of the other group, and that with 250 mg of any element of the Zinc Group and 250 mg of any element of the Aluminum Group not over 1 mg of the Aluminum Group element will be carried into the precipitate. These results were so satisfactory that this method has been adopted for use in this procedure when a precise separation of considerable amounts of these elements is desired.

Optional Method for Separating the Aluminum Group. As the sulfide-oxalate procedure requires a fairly close adjustment of conditions and is somewhat time-consuming, and as the destruction of the oxalate in P. 71 is also time-consuming, an operation is provided whereby an indication of the amount of the Aluminum Group ele-

[33] Swift, Barton, and Backus, *J. Am. Chem. Soc.*, **54**, 4161 (1932).

ments present is obtained. For the case that these are present in small amounts, an optional and much shorter, though less exact, method is provided in Note 3 of this procedure for their separation and detection. By this method aluminum and chromium (and iron, if it is present) are precipitated by ammonium hydroxide and separated from manganese, zinc, nickel, and cobalt. Manganese is then separated from these elements by the addition of bromine, which oxidizes and precipitates it as hydrated manganese dioxide. The filtrate is then carried to the Zinc Group for analysis. The ammonia precipitate is subjected to a "sodium hydroxide-peroxide" treatment, which precipitates any iron, leaving aluminate and chromate in the solution. The aluminum is precipitated as hydroxide by acidifying the solution and then neutralizing with ammonium hydroxide; chromate remains in the filtrate.

Procedure 55: SEPARATION OF THE ZINC AND ALUMINUM GROUPS. Transfer the HCl solution (from P. 52) to a 200-ml flask and evaporate it to 4 to 5 ml (Note 1). Dilute the solution to 50 ml, heat it to boiling, and carefully make it just alkaline with NH_4OH, avoiding an excess (Note 2). (White or greenish precipitate, presence of aluminum or chromium; reddish precipitate, presence of iron. See Note 3 in regard to optional method of analysis.)

Slowly add HCl to the hot mixture until any precipitate is dissolved (avoiding an excess), dilute the mixture to 100 ml, add 2 to 10 g of solid $(NH_4)_2C_2O_4$, and heat the mixture until this dissolves (Notes 4, 5). Cool the solution and carefully add 1 f. $NaHCO_3$, in 1-ml portions, until it is neutral to litmus—that is, until it turns both blue and red litmus to an intermediate purplish color (Note 6). Saturate the cold solution with H_2S under pressure, first sweeping the air from above the solution with the gas, and then bubble a rapid stream through the solution for 10 to 15 sec. and a slow stream (2 or 3 bubbles a second) for 5 min. (Note 7); avoid exposing the solution to the air insofar as is possible (Note 8). Test the solution (which should be slightly alkaline) with litmus, and, if it is neutral or at all acid, add 10 ml of the $NaHCO_3$ (taking care to avoid loss due to effervescence), and again saturate it; repeat this process until the solution remains slightly alkaline (Note 9). Finally, while continuing the slow stream of H_2S, heat the

mixture just to boiling and keep it at that temperature until the precipitate settles rapidly. (White precipitate, presence of zinc; black precipitate, presence of cobalt or nickel. Note 10.) If the precipitate does not settle rapidly, tightly close the flask with a clean rubber stopper, cool the mixture to 60° to 70°C., and, holding the stopper firmly in place, vigorously shake the mixture for a few minutes. Immediately filter the hot mixture through a paper filter, decanting as much as possible, and wash the precipitate with a hot wash solution which has been prepared by adding 1 ml of $NaHCO_3$ and 1 g of $(NH_4)_2C_2O_4$ to 100 ml of hot water and passing a stream of H_2S through it for 30 sec. Add the first 10 to 15 ml of the wash solution to the filtrate and treat it by P. 71 (Note 11). Treat the precipitate by P. 61.

Notes:

1. If iron has been present, this solution will contain a considerable amount of ether dissolved in it. In this case the first part of the evaporation, which should be carried out under a hood, can be effectively done by heating a beaker of water to boiling, extinguishing the flame, and immersing the flask in the water. After the ether is expelled, the flask may be heated directly with a flame.

The solution is evaporated to a small volume in order that less NH_4OH be required for the neutralization. A high concentration of ammonium ion might later cause ammonium oxalate to crystallize from the solution. See Note 3, P. 54, as to the information concerning the elements present which may be obtained from the color of the HCl solution.

2. The neutralization should be carefully made and an excess of ammonia should be avoided; if an excess is added, the solution should be acidified and the neutralization should be repeated. If the solution is colorless, methyl red may be used as an indicator and ammonia may be added until the transition from pink to yellow is obtained; if the solution is colored, litmus paper can be used and an intermediate purplish color can be taken as the neutralization point, or, if they are available, use one of the indicator test papers mentioned in P. 3, Note 6, and adjust the solution to a *p*H of 6. The first perceptible smell of ammonia from the boiling solution is also a sensitive indication of when the proper amount has been added; the NH_4OH should be added with a dropper and care should be taken not to spill it on the sides of the flask.

If the solution is made too alkaline, manganese may be oxidized and may appear as a brown precipitate (hydrous Mn_2O_3). If present in large amounts (300 mg or more), zinc may precipitate as the white hydroxide; therefore, if a white precipitate is obtained (and zinc may be present in large amounts), add HCl until the precipitate is dissolved and then 1 ml in excess. Repeat the neutralization with ammonia, taking extreme care to avoid an excess.

By providing a higher concentration of ammonium salts and of chloride, the precipitation of zinc is prevented.

3. Under these conditions less than a milligram of aluminum or chromium will cause a precipitate; therefore, if no precipitate is obtained, the absence of these elements is proved. If no precipitate is obtained here and no color was present in the HCl solution when it was evaporated to a small volume, the absence of cobalt and nickel is also proved; and only magganese and zinc can be present. In this case treat the solution at once by P. 61 (second paragraph), beginning with the addition of 5 ml of 36 n. H_2SO_4. By this procedure (P. 61) the zinc is precipitated as sulfide, the manganese remaining in solution; by then expelling the H_2S and making the solution alkaline with sodium peroxide, the manganese will be precipitated as hydrous manganese dioxide. Each of these precipitates can then be treated directly by the procedures provided for their estimation.

If only a small precipitate of aluminum, chromium, or iron is obtained (one corresponding to 25 to 50 mg, depending upon the exactness which is desired in the separation and estimation of these elements), it may be filtered out and analyzed as follows:

While keeping the solution hot, filter out the precipitate on a small paper filter. Wash the precipitate with hot water, collecting only the first 5 ml of wash water with the filtrate. Stopper and reserve the filtrate.

Dissolve the precipitate by pouring 5 to 10 ml of hot HCl dropwise through the filter; wash the filter with 2 to 3 ml of water. Evaporate the solution to 3 to 5 ml, cool, and dilute to 10 ml. Make the solution alkaline by sprinkling in small portions of Na_2O_2, add about 0.5 ml of the solid in excess, and then boil until small bubbles are no longer evolved. (Brownish-red precipitate, presence of iron; yellow solution, presence of chromium.) Filter out the precipitate and treat it by Note 6, P. 63.

(The solution should be cold before adding the Na_2O_2, as otherwise this substance may decompose explosively. A porcelain spatula or spoon should be used—not paper. The solution is boiled until no more oxygen bubbles are evolved, as the excess peroxide must be decomposed or it would reduce any chromate present when the solution is subsequently acidified.)

Make the filtrate from the Na_2O_2 treatment just acid with HCl, then just alkaline with NH_4OH, avoiding an excess, and heat it to boiling. (White precipitate, presence of aluminum.) Estimate the amount by comparison with known amounts of aluminum precipitated under similar conditions. Filter out the precipitate and treat it as directed in Notes 1 and 2, P. 73.

If chromium is present, estimate the amount by adding a standard chromate solution to the same volume of a solution made just alkaline with NH_4OH. To confirm the presence of chromium, make the solution just acid with $HC_2H_3O_2$ and add 1 ml of 1 n. $Pb(NO_3)_2$. (Yellow precipitate, presence of chromium.) Discard the mixture.

As has been pointed out, the "ammonia precipitation" and the "sodium hydroxide-peroxide" separation cannot be used when large amounts of the

above elements are to be separated or when quantitative separations are desired; however, their use as indicated above effects a considerable saving of time for separating and detecting smaller amounts. This is especially advantageous in detecting and removing small amounts of aluminum, as this element is often introduced into the analysis in small amounts as impurities in the reagents, especially by alkaline solutions which have stood in glass containers. In such cases it is an advantage to remove it as expeditiously as possible.

Aluminum and chromium (and iron) having been removed from the solution, the reserved filtrate can now also be tested for manganese, which, if present in small amounts, can be separated at this point. This is desirable, as the necessity for carrying out P. 55 and P. 71, both long and troublesome procedures, is thus eliminated. Proceed as follows:

> Add to the filtrate (from the ammonia precipitation) 2 ml of NH_4OH and 1 ml of bromine water. (Brownish precipitate, presence of manganese.) If a large precipitate is produced and a precise separation is desired, make the mixture acid with HCl and, without dissolving the precipitate (Note 4), treat it by the second paragraph of P. 55 above. If only a small precipitate is produced, add 2 ml more of bromine water and of NH_4OH, warm the mixture, filter out the precipitate, and treat it as directed in Note 1, P. 72. Treat the filtrate by P. 61, beginning with the addition of 5 ml of 36 n. H_2SO_4.

By the addition of Br_2 to an ammoniacal solution, manganese is precipitated as hydrated manganese dioxide. Zinc, nickel, and cobalt remain in solution as complex ammino ions. Complete precipitation of the manganese requires that the solution be alkaline whan filtered and that an excess of bromine be added. As bromine and hydroxyl ion are used by the precipitation reaction

$$Mn^{++} + Br_2 + 4OH^- = MnO(OH)_2 + 2Br^- + H_2O,$$

and as bromine and ammonia react and are removed by the reaction

$$3Br_2 + 2NH_3 + 6OH^- = 6Br^- + N_2 + 6H_2O,$$

more of each is added in case manganese is found present.

4. If the solution has been made too alkaline or has been allowed to stand exposed to the air for a considerable time, the manganese may be partially oxidized and a brownish precipitate may appear. This precipitate may not rapidly dissolve in the dilute HCl; and, because the addition of a large excess of acid is undesirable, it is left in the solution, as it will be reduced and dissolved by the oxalate next added.

5. Ammonium oxalate dissolves slowly in a cold solution; for this reason the solution is heated until it is dissolved. If too much acid is present, and if large quantities of cobalt, nickel, or zinc are present, the oxalates of these elements may precipitate; it is not necessary to dissolve them, as they will be completely metathesized by the subsequent H_2S treatment.

6. If methyl red has been used in the first neutralization, it may also be used here, a distinct yellow color being obtained.

7. This flow is preferably regulated by passing the gas into the solution at the pressure of the generator or tank, and then connecting a short piece of rubber tubing to the outlet tube with a screw clamp. By adjusting the screw the flow of gas is evenly controlled. This arrangement causes the H_2S to bubble *through* the solution at the generator pressure, thus expediting the complete precipitation of nickel; unless the directions of this procedure are followed *exactly*, large amounts of nickel may not be completely precipitated.

8. Repeated experiments have shown that, when nickel is present, exposure to the air causes the precipitate to become colloidal, apparently because of the formation of disulfide; for this reason the air is swept from the flask.[34] When the neutrality of the solution is subsequently being tested, the flow of gas should be continued, the stopper being raised just sufficiently to permit removing a drop of the solution on a stirring rod.

9. In order to secure rapid and complete precipitation of nickel (or of iron, if it is present), the solution should be distinctly alkaline to litmus *after* precipitation is complete. For this reason it is advisable to test the solution again with litmus just before stopping the flow of H_2S and beginning the filtration.

10. If a white precipitate is obtained, the presence of zinc alone is indicated; and, as even 1 mg of nickel or cobalt will cause a large precipitate of zinc to be discolored, these elements are absent. In this case the precipitate should be treated directly by P. 62. A black precipitate indicates the presence of cobalt or nickel, but a smaller amount of zinc may also be present.

11. If the filtrate is dark colored, this is probably due to colloidal nickel sulfide, which often partly coagulates after passing through the filter. In this case test the neutrality of the solution, making sure that it is slightly alkaline, again saturate it with H_2S, slowly add to it 5 ml of 6 n. HNO_3 (which should make the solution distinctly acid), heat it almost to boiling for 2 to 3 min., cool it to 60° to 70°C., and again vigorously shake it. Filter out the precipitate through a separate smaller paper, wash it, and combine it with the first one. Treat the filtrate by P. 71. Although it causes an intensely dark solution and is voluminous in appearance, this second precipitate usually contains not over 1 to 2 mg of nickel.

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[34] It should be mentioned that a black colloidal solution has been obtained by various investigators in ammonium sulfide solutions supposedly free of disulfide; for a discussion of the phenomenon, see Weiser, *The Colloidal Salts*, McGraw-Hill, 1928, p. 103.

TABULAR OUTLINE VII

THE ANALYSIS OF THE ZINC GROUP

H_2S precipitate from P. 55: ZnS, NiS, CoS, [FeS][a]
Dissolve the precipitate in HCl and HNO_3.
Add 5 ml of 36 n. H_2SO_4. Fume. Cool. Dilute.
Neutralize with NaOH. Add 3 ml of 6 n. H_2SO_4.
Treat with H_2S. (P. 61).

Precipitate: ZnS
Add to excess of $Fe_2(SO_4)_3$, heat, add H_2SO_4.

Filtrate: Ni^{++}, Co^{++}, [Fe^{++}], HSO_4^-, $SO_4^=$
Boil out H_2S.
Add excess NaOH.
Precipitate: $Ni(OH)_2$, $Co(OH)_2$, [$Fe(OH)_2$]

Precipitate: S
Solution:
Zn^{++}, Fe^{++}, excess Fe^{+++}
Titrate with $KMnO_4$.
(Fe^{+++}, Mn^{++})
(P. 62)

[If iron is present:
Dissolve with HCl, add Br_2, boil out excess Br_2.
Solution: Ni^{++}, Co^{++}, Fe^{+++}

Neutralize, add $HC_2H_3O_2$ and $NaC_2H_3O_2$. Boil.
Precipitate: $Fe(OH)_3$, $FeOC_2H_3O_2$
Filter and treat by P. 53.]

Add excess Na_2O_2. (P. 63)

Precipitate: $Ni(OH)_2$, Co_2O_3
Dissolve in HCl.
Evaporate. Add ethyl ether.
Saturate with HCl gas. (P. 64)

Filtrate:
Discard.

Precipitate: $NiCl_2$
Dissolve in H_2O.
Add NH_4Cl, NH_4OH.
Add $AgNO_3$, KI.
(AgI; $Ni(NH_3)_4^{++}$)
Titrate with KCN.
($Ni(CN)_4^=$, $Ag(CN)_2^-$)
(P. 65)

Filtrate: H_2CoCl_4
Neutralize, add $NaBO_3$.
Precipitate: Co_2O_3
Boil to decompose $NaBO_3$.
Add HCl, KI.
(Co^{++}, I_3^-)
Titrate with $Na_2S_2O_3$.
(Co^{++}, I^-, $S_4O_6^=$)
(P. 66)

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[a] If iron has not been separated by the ether treatment (P. 52), it will be precipitated with this group. Its subsequent behavior and separation is indicated in brackets.

The Analysis of the Zinc Group

P. 61. The Precipitation and Separation of Zinc as Sulfide

Discussion of Methods for Separating the Elements of the Zinc Group. After the sulfides of zinc, cobalt, and nickel have been obtained, several methods might be used for the separation of these elements. A method commonly used in qualitative systems consists of treating the mixed sulfides with cold 1 n. hydrochloric acid in an effort to dissolve the zinc sulfide and leave undissolved the nickel and cobalt sulfides. This method appears inconsistent with the fact that nickel and cobalt do not precipitate with the Hydrogen Sulfide Group elements and with the fact that zinc can be precipitated as sulfide from a solution with a higher hydrogen ion concentration than can either nickel or cobalt. The phenomenon is attributed to the existence of two or more allotropic forms of nickel and cobalt sulfides of differing solubilities; only the more soluble modification can be formed in solution, but, once formed, it is changed into a less soluble form or forms (which may be polymers of the soluble form). This transformation seems to be favored by heat and by acid; in general, the longer the sulfides have stood, the less readily soluble they become. It is also possible that the phenomenon may be at least partly explained by a slow rate of solution; many compounds which dissolve readily when recently precipitated dissolve only slowly after they have been allowed to stand for a considerable time. This method was not used here because it has been found that the zinc sulfide also dissolves slowly when it is present with large amounts of nickel or cobalt, and that appreciable amounts of nickel and cobalt may be dissolved if the treatment is prolonged or if considerable amounts of other sulfides are present.

It would be expected that nickel and cobalt could be separated from zinc by precipitating them from a strongly alkaline solution, the zinc remaining in solution as the zincate ion; however, as is shown in Table XXI, large amounts of zinc are carried down with the nickel and cobalt and small amounts were found to be so completely coprecipitated that zinc could not be detected in the filtrate. This method was tried under many different conditions, such as varying the order of mixing the reagents, using powerful oxidizing agents (for example, peroxysulfate, which would oxidize both cobalt and nickel), and adding an excess of sodium hydroxide to an am-

moniacal solution and then boiling off the ammonia; but in no case were the results satisfactory.

As is shown in Table XI, zinc is precipitated as sulfide from a solution in which the hydrogen ion concentration is approximately 10^{-2}, while nickel and cobalt are not. The precipitation of zinc sulfide has been the subject of many investigations, and it has been realized for over half a century that there are advantages in precipitating zinc sulfide from an acid solution rather than from one which is neutral or alkaline. Specifically, certain separations can be made by proper adjustment of the hydrogen ion concentration, and the precipitate usually separates in a form which is more readily handled. Because of these effects, many early workers[1] recommend the use of various organic acids for acidifying the solution and thereby obtained, somewhat uncertainly, the effect of a buffered solution prior to the development of the modern theory and use of such solutions.

Somewhat more recently the use of sulfuric acid solutions was studied by Weiss,[2] who recommended that the precipitation be made from a solution 0.01 n. in sulfuric acid by means of a very rapid stream of hydrogen sulfide, but apparently provided no means for controlling the increase in hydrogen ion concentration taking place during the precipitation; by Waring,[3] who once more recommended the use of formic acid; by Funk,[4] who studied the effect of various organic acids on the precipitation and on the separation of zinc from various other elements; and by Glixelli,[5] who made a comprehensive study of the effect of the nature of the solution on the forms and apparent solubility of the precipitate, and also on the time factor which enters into the establishment of the precipitation equilibrium.

In the excellent study of Fales and Ware,[6] the limits of the hydrogen ion concentration between which quantitative precipitation could be effectively made were first precisely determined, and means were provided for controlling the acidity within these limits. They used formic acid–formate buffered solutions and found that for such solutions the hydrogen ion concentration most favorable for

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[1] Deeffs, *Chem. News*, **41**, 279 (1880); Bragard, *Dissertation*, Berlin, 1887; *Z. anal. Chem.*, **27**, 209 (1888); Beilstein, *Ber.*, **11**, 1715 (1885); Mühlhäuser, *Z. angew. Chem.*, **15**, 731 (1902); Berg, *Z. anal. Chem.*, **25**, 512 (1886); Dohler, *Chem. Ztg.*, **23**, 399 (1899); Neumann, *Z. anal. Chem.*, **28**, 57 (1889).

[2] Weiss, *Dissertation*, München, 1906.

[3] Waring, *J. Am. Chem. Soc.*, **26**, 26 (1904).

[4] Funk, *Z. anal. Chem.*, **46**, 93 (1907).

[5] Glixelli, *Z. anorg. Chem.*, **55**, 306 (1907).

[6] Fales and Ware, *J. Am. Chem. Soc.*, **41**, 487 (1919).

quantitative precipitation of zinc sulfide was between 10^{-2} to 10^{-3}. Lundell, Hoffman, and Bright[7] recommended the precipitation of zinc sulfide from a 0.01 n. sulfuric acid solution and stated that the best precipitation is obtained from a sulfuric acid-sulfate solution. They did not present any discussion or experimental data in support of this recommendation. As there are certain advantages in using sulfate-hydrosulfate buffered solutions for this precipitation, a study of this method was made,[8] and a discussion of the results obtained is given below.

As the value of the second ionization constant of sulfuric acid has been determined[9] to be 1.15×10^{-2}, and as the optimum hydrogen ion concentration for the precipitation of zinc sulfide from sulfate solutions has been found to be about 10^{-2}, it would seem that the required ratio of sulfate to hydrosulfate should be about one—the most favorable ratio for effective buffer action. As compared with this, Fales and Ware had to use an acid-to-salt ratio of 84 to 1, with the formic acid concentration 4.7 f., in order to obtain an initial *p*H of 1.86, a value at which, in sulfate solutions, quantitative precipitation was obtained. This *p*H was experimentally obtained in the sulfate-hydrosulfate solution by using an acid-to-salt ratio of 20.7 to 66, with the total concentration of sulfate and hydrosulfate 0.347 f. In addition, Fales and Ware recommended the use of considerable ammonium citrate and 6.25 g of ammonium sulfate in 200 ml of solution. They state that "ammonium citrate is used for the purpose of forming complexes with interfering metals," thus assisting in holding in solution such elements as iron and manganese. It was found that from a sulfate-hydrosulfate solution of the proper *p*H such an agent was not needed. The ammonium sulfate was added as a "salting-out agent." In the sulfate solutions the need of adding an additional salting-out agent was not apparent; quantitative precipitation was obtained, and the form of the precipitate left nothing to be desired as to ease of filtration and washing; furthermore, it seemed that the hydrogen ion concentration was the predominant factor governing the form as well as the solubility of the precipitate. It should also be mentioned that, when the precipitation of zinc

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[7] Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*, Wiley, 1931, p. 388.

[8] Jeffreys and Swift, *J. Am. Chem. Soc.*, **54**, 3220 (1932).

[9] Sherrill and Noyes, *J. Am. Chem. Soc.*, **48**, 1873 (1926); as the result of more recent measurements, Hamer, *J. Am. Chem. Soc.*, **56**, 860 (1934), gives the value 1.2×10^{-2} at 25°C.

sulfide is used as a means of effecting a qualitative separation, it is a decided advantage not to have to add organic matter to the solution, for, especially in a group analysis, material such as citrates may cause difficulties in subsequent operations. The solubility of zinc sulfide in solutions with varying ratios of hydrosulfate to sulfate, and therefore of hydrogen ion concentration, is shown in Table XXII.

TABLE XXII

THE SOLUBILITY OF ZINC SULFIDE IN SULFATE-HYDROSULFATE SOLUTIONS OF VARIOUS HYDROGEN ION CONCENTRATIONS

(Volume, 250 ml; zinc taken, 257 mg.)

Expt.	Initial Ratio $NaHSO_4$/ Na_2SO_4 (millimoles)	Initial *p*H	Final *p*H	Zinc Found in Filtrate (mg)
1	8.3/66	2.18	1.83	0.0
2	12.4/66	2.08	1.78	Trace
3	20.7/66	1.86	1.66	0.20
4	22.8/66	1.78	1.62	Trace[a]
5	24.9/66	1.77	1.62	0.1 to 0.2
6	27.0/66	1.72	1.57	0.3 to 0.5
7	27.0/66	1.72	1.56	0.3 to 0.5
8	27.0/66	1.72	1.58	0.3 to 0.5[a]
9	27.0/66	1.72	1.58	0.3 to 0.5[b]
10	31.0/66	1.67	1.47	0.3 to 0.5[b]
11	37.3/66	1.57	1.46	0.5
12	45.0/66	1.49	1.39	0.8 to 1.0
13	58.0/66	1.38	1.29	1.5
14	70.5/66	1.31	1.22	4.0
15	87.2/66	1.19	1.14	6.0

[a] Filtered after standing for 3 hr.
[b] Filtered after standing overnight.

From the above data it may be concluded that from these solutions precipitation will be complete to less than 0.25 mg at a *p*H of 1.6 or at a hydrogen ion concentration as high as 2.5×10^{-2}. Less than 1 mg remains in solution at a *p*H of 1.54 or a hydrogen ion concentration of 2.9×10^{-2}. It would seem that the conditions of Experiment 4, in which the ratio of $NaHSO_4$ to Na_2SO_4 is about 1 to 3 and the initial *p*H is 1.78, are best adapted for securing the desired completeness of precipitation of zinc and for holding other elements in solution. If desired, the buffer action could be made considerably more effective and the change in hydrogen ion concentration during precipitation could be made much smaller by increasing the concentrations of sulfate and hydrosulfate. It was considered desirable, in

order to minimize the difficulty in washing the precipitate and avoid the use of excessive quantities of buffer material, to keep the buffer concentrations at the lowest values which would adequately control the acidity. It should be pointed out that, because of the high concentration of electrolyte in these solutions, the evaluation of the activities of the various ions is subject to considerable uncertainty, and a simple calculation of the hydrogen ion concentration from the formal salt-acid ratios may lead to results considerably divergent from the experimental values. This is evident from a series of experiments made to show the effect of dilution on the *p*H of such a solution. The results are given in Table XXIII.

TABLE XXIII

THE EFFECT OF DILUTION ON THE *p*H OF SULFATE-HYDROSULFATE SOLUTIONS

Expt.	$NaHSO_4$ (moles/liter)	Na_2SO_4 (moles/liter)	*p*H
1	0.1	0.5	1.99
2	0.05	0.25	1.48
3	0.025	0.125	2.17
4	0.01	0.05	2.43
5	0.0025	0.0125	2.82

The decrease in acidity in the more dilute solutions is due to the fact that there is not adequate buffering material to keep the ratio of hydrosulfate to sulfate constant, the fraction of the hydrosulfate ionized into hydrogen and sulfate ions becoming large at these concentrations; the increase in the more concentrated solutions is due to the effect of the high salt concentrations on the activities of the various ions. It is therefore seen that, if, in order to control more closely the acidity, a higher concentration of the buffer is used, the initial ratio of hydrosulfate to sulfate should be adjusted accordingly. Thus, with the sodium sulfate concentration 0.25 f., a ratio of $NaHSO_4$ to Na_2SO_4 of 1 to 3 is required to produce an initial *p*H of 1.78 (Table XXII, Experiment 4); with the sodium sulfate concentration 0.5 f., this ratio has to be reduced to 1 to 5 (Table XXIII, Experiment 1). As it was desired to keep the volume small in the procedure below, the sulfate concentration is approximately 1 f. and the ratio is 1 to 7.

It was found that the presence of a high concentration of chloride ion lengthens the induction period in the beginning of precipitation, apparently slows down the precipitation, and, with the same *p*H, increases the solubility of zinc sulfide by three or four times. This is shown by comparing the results in Table XXIV with those obtained at corresponding *p*H values in Table XXII.

TABLE XXIV

THE EFFECT OF CHLORIDE ION ON THE SOLUBILITY OF ZINC SULFIDE

(Potassium chloride added, 132 milli-equivalents; zinc taken, 257 mg; volume, 250 ml.)

Expt.	Initial Ratio $NaHSO_4$/ Na_2SO_4 (millimoles)	Initial *p*H	Final *p*H	Zinc Found in Filtrate (mg)
16	20.7/66	1.73	1.51	1.5
17	27.0/66	1.62	1.46	2.0
18	37.3/66	1.43	1.37	2.0

The Precipitation of Zinc Sulfide in the Presence of Other Elements. The separation of zinc from cobalt and nickel and also from the other elements of the Ammonium Sulfide Group was also studied, and Table XXV shows the results obtained.

TABLE XXV

THE SEPARATION OF ZINC FROM OTHER METALS BY PRECIPITATION AS SULFIDE

(Volume, 250 ml; initial ratio $NaHSO_4/Na_2SO_4$ in millimoles, 20.7/66, except in Experiment 20; 257 mg of zinc and 250 mg of other metal taken unless otherwise stated under remarks.)

Expt.	Other Metal	Initial *p*H	Final *p*H	Other Metal in ZnS Ppt. (mg)	Remarks
19	Co	1.82	1.64	7	200 mg Co.
20	Co	1.35		Trace	200 mg Co; initial ratio $NaHSO_4/Na_2SO_4$ = 58/66.
21	Co	1.82		Large quantity	100 mg Zn, 400 mg Co.
22	Co	1.82		No ppt.	No Zn, 600 mg Co; solution stood 3 days.
23	Ni	1.82	1.66	0.3 to 0.4	
24	Ni			0.3 to 0.4	
25	Mn	1.81	1.65	0.1	
26	Mn			0.1	
27	Fe	1.82	1.65	0.5 to 0.6	
28	Fe			0.5 to 0.6	
29	Al			<0.25	
30	Cr			0	

From the results shown in Table XXV it is seen that the separations are satisfactory in all cases except with cobalt. Even in a solution whose initial *p*H was 1.35, too high in acid for complete precipitation of zinc, cobalt is still coprecipitated. In Experiment

21, where 100 mg of zinc were precipitated from a solution containing 400 mg of cobalt, the zinc sulfide precipitate came down quite white for several minutes, then darkened rapidly, and finally was almost black in color.

This effect appears to be similar to the induced precipitation of zinc sulfide in more concentrated acid solutions, which has been studied by Kolthoff and Pearson.[10] This effect they designate "post-precipitation" and attribute to an induced precipitation of the zinc sulfide from a supersaturated solution, the induction being caused in their experiments by adsorption of hydrogen sulfide on the copper sulfide. Under the conditions of certain of their experiments, this adsorption became effective in promoting the precipitation of the zinc sulfide only after quantitative precipitation of the copper sulfide had taken place. That the effect obtained here is a case of either promoted precipitation or coprecipitation is shown by Experiment 22. In this experiment the solution, which was identical with that in Experiment 21, but contained 500 mg of cobalt alone, was saturated with hydrogen sulfide in the usual way, except that the gas was bubbled through for more than an hour; then the flask was closed and allowed to stand for 3 days. No cobalt sulfide precipitated. Fales and Ware also report that cobalt cannot be separated from zinc by a hydrogen sulfide precipitation from formic acid-formate solutions. It is of interest to note that when a few milligrams of cobalt are coprecipitated with zinc sulfide, as in Experiment 19, the resulting precipitate is green. This phenomenon was noted in a large number of experiments.[11]

Experiments have shown that the amount of cobalt which is carried down with the zinc can be very much reduced if the solution is not heated to boiling; thus a zinc sulfide precipitate which had been formed at 60°C. in the presence of cobalt became only slightly greenish in color even after standing 24 hr., but turned quite dark when the mixture was heated to boiling. It is not practicable to make the precipitation at room temperature, as under these conditions zinc sulfide forms very slowly and complete precipitation would require many hours.

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[10] Kolthoff and Pearson, *J. Phys. Chem.*, **36**, 549 (1932).

[11] Caldwell and Mayer, *J. Am. Chem. Soc.*, **57**, 2375 (1935), have found that the addition of a small amount of acrolein to the solution greatly reduced the amount of cobalt precipitated with the zinc sulfide, and, *ibid.*, **57**, 2372 (1935), that a very small amount of gelatin or agar-agar causes much more rapid coagulation of the zinc sulfide precipitate. The original articles should be consulted for a discussion of the phenomena.

The hydrogen ion concentrations at which cobalt and nickel can be quantitatively precipitated are shown in Table XXVI. The data for this table are taken from studies[12] which were made in solutions in which the hydrogen ion concentration was controlled by means of acetic acid and ammonium acetate.

TABLE XXVI

THE PRECIPITATION OF COBALT AND NICKEL AS SULFIDES IN SOLUTIONS OF VARIOUS HYDROGEN ION CONCENTRATIONS

Known amounts of cobalt and nickel were taken. The cobalt in the precipitate was weighed after reduction to the metal; the nickel sulfide precipitate was converted to the oxide and weighed. More complete and exact data are given in the original articles.

(Volume, 100 ml; Ni or Co taken, about 0.2 g.)

*p*H	Error in the Determination	
	Cobalt (mg)	Nickel (mg)
4.9		+0.2
4.7		−0.1
4.4	−0.2	−0.2
4.2	−0.3	−0.3
4.0	−0.1	−0.4
3.9	−0.1	−0.8
3.7	−0.2	−0.6
3.4	−1.4	−1.6
3.3	−1.3	−9.9
3.1	−13.5	

Procedure 61: PRECIPITATION OF ZINC. If the hydrogen sulfide precipitate from P. 55 is white, treat it by P. 62 (Note 1).

If the precipitate is discolored (Note 2), transfer as much as possible of it from the filter to the flask. Dissolve that remaining on the filter by pouring repeatedly through it 5 ml of hot HCl to which has been added 1 ml of 16 n. HNO_3 (Note 3). Add the solution to the precipitate in the flask, together with 1 to 5 ml of 12 n. HCl and 2 to 10 ml of 16 n. HNO_3. Evaporate the mixture slowly until the sulfides are dissolved (Note 4). Slowly (*Caution*) add just 5 ml of 36 n. H_2SO_4 and heat the solution until it begins to fume (Note 5). Cool the solution to room temperature (P. 24,

[12] Haring and Heatherman, *J. Am. Chem. Soc.*, **52**, 5135 (1930); Haring and Westfall, *ibid.*, **52**, 5141 (1930).

Note 3) and, while continuously cooling the flask with running water, pour slowly into it, in 1-ml portions, 20 ml of water, and then dilute the solution to about 70 ml. Add carefully 6 n. NaOH until the solution is just neutral to litmus or until a faint permanent turbidity is obtained, and then add exactly 2 ml of 6 n. H_2SO_4 (Notes 6, 7). Heat the solution to about 60°C. and pass in a moderately rapid stream of H_2S for about 10 min. (White precipitate, presence of zinc. Notes 8, 9.)

Filter the mixture, retaining as much as possible of the precipitate in the flask. Wash the precipitate by decantation with three 5-ml portions of a hot wash solution which has been prepared by adding 2.5 g of Na_2SO_4 and 15 drops of H_2SO_4 to 100 ml of water (Note 10). Collect these washings with the filtrate (after combining with it any cobalt or nickel recovered in Note 12). Again wash the precipitate with the wash solution until it is free of sulfide (Note 11). Treat the precipitate by P. 62 (Note 12). Treat the filtrate by P. 63.

Notes:

1. Since even 1 mg of nickel or cobalt will distinctly discolor the precipitate, it should be treated directly by P. 62 if it is quite white.

2. Small amounts of cobalt or nickel may not make the precipitate dark or merely gray, as would be expected. Thus a precipitate containing 500 mg of zinc and 5 mg each of cobalt and nickel was greenish-gray in color.

3. Cobalt and nickel sulfides do not dissolve readily in even hot 6 n. HCl; therefore an oxidizing agent, such as HNO_3 or $KClO_3$, must be used to facilitate the solution.

4. A small dark residue consisting of sulfur and some enclosed sulfide may remain when this mixture is evaporated. When this becomes light in color, the residue may be removed with a stirring rod and discarded. If the analyst wishes to be sure that no nickel or cobalt remains in this residue, it should be placed in a small porcelain crucible and gently heated with a burner until the sulfur is burned. If a black residue remains, it should be dissolved in HCl and added to the main solution.

5. The fuming must be stopped at the first escape of dense white fumes from the mouth of the flask, in order to prevent excessive loss of sulfuric acid. The quantity of acid present must be known closely in order that the solution may be buffered effectively for the separation of zinc.

6. This neutralization of the acid must be done precisely, as the ratio of HSO_4^- to $SO_4^=$, and therefore of the H^+ concentration, will depend upon this and upon the amount of H_2SO_4 added. If a large precipitate is produced, it should be dissolved in the smallest possible volume of H_2SO_4 and the neutralization should be repeated.

This neutralization can be carried out more exactly and the formation of a precipitate can be avoided by the use of "Nitrazine" indicator test papers. The sodium hydroxide should be added until the color given by the paper corresponds to a *p*H of 5 to 5.5 on the chart provided with the indicator papers. (See Note 1, P. 161; see also Note 6, P. 3, in regard to the use of other indicator test papers.)

7. If iron has not been separated by the ether treatment (or as suggested in P. 55, Note 3), it will be in the ferric form here, having been oxidized by the HNO_3, and will cause a precipitate upon treatment of the solution with H_2S, because of the reaction

$$2Fe^{+++} + H_2S = 2Fe^{++} + S_{(s)} + 2H^+.$$

As this precipitate may be mistaken for ZnS, the iron should be reduced by passing an excess of SO_2 into the solution. As SO_2 and H_2S also react,

$$SO_2 + 2H_2S = 3S_{(s)} + 2H_2O,$$

the solution should be boiled until the SO_2 is completely expelled. The water lost by evaporation should be replaced.

8. When a small quantity of zinc, 1 mg or less is present, only a faint turbidity may be observed after the solution has been treated with H_2S for 10 min. at 60°C. In this case, heat the solution slowly to 80°C. while passing in a slow stream of H_2S, then stopper the flask, and let it stand 5 min. before filtering. The coagulation of the precipitate is hastened by this treatment.

If a large precipitate is obtained after 10 min., it is advisable to continue the passage of H_2S for 10 min. more at 60°C. Do not heat the solution to boiling, because a large amount of cobalt may precipitate at the boiling temperature when large quantities of both cobalt and zinc are present.

9. When much cobalt is present with zinc, the ZnS which first forms is pure white, but on prolonged treatment with H_2S it may turn a greenish color, owing to the coprecipitation of cobalt. With 250 mg each of cobalt and zinc present, 4 to 8 mg of cobalt may coprecipitate.

10. As the precipitation of zinc may be incomplete because of slow precipitation or improper adjustment of the acid, the filtrate should be tested by being heated to 60°C. and again saturated with H_2S while the precipitate is being washed.

11. The washing should be continued until the wash solution gives no test for sulfide; this is necessary, as any sulfide left in the precipitate will cause an error in the estimation of zinc by P. 62. The test may be made conveniently by adding a drop of copper nitrate to the solution.

12. If the precipitate is dark colored, indicating that cobalt (or nickel, if the acidity of the solution has not been properly adjusted) has been carried out with it, it may be treated as follows:

> Dissolve the precipitate in 20 ml of hot 6 n. H_2SO_4, adding Br_2 water to the solution if it is needed. Boil out the excess of Br_2, neutralize the solution with NaOH as directed in the above procedure, dilute it to 50 ml, add 1 ml of 6 n. H_2SO_4, saturate it with H_2S, and heat the mixture to 60° to 80°C., keeping the gas flowing. Finally, close the flask and allow it to stand for 10 min., filter out the precipi-

tate, wash it, and treat it as directed in the last paragraph of the procedure above. Combine the filtrate with the original filtrate.

P. 62. Estimation of Zinc

Discussion. This estimation is based upon the same principle as was involved in the estimation of cadmium. As there, the method consists in treating the sulfide precipitate with an excess of an acidified ferric sulfate solution and thereby causing the formation of an equivalent amount of ferrous iron as a result of its reduction by the sulfide; the ferrous iron is then titrated with permanganate. Sulfur is precipitated but does not react sufficiently rapidly with either the ferric iron or the permanganate to introduce serious error. Experiments[13] have shown that this method is more rapid and requires less experienced technique than the titration of a zinc solution with standard ferrocyanide solution,[14] but that the results are usually from 1 to 2 per cent high.

Procedure 62: ESTIMATION OF ZINC. Prepare a ferric sulfate solution by dissolving 3 to 4 g of solid $Fe_2(SO_4)_3$ (Note 4, P. 30) in 50 ml of boiling water in a 400-ml beaker. Transfer the washed ZnS precipitate to the solution (Note 1), and heat the mixture (almost to boiling) until only a coagulated residue of sulfur remains (usually 2 to 3 min.); cover the beaker with a clock glass during this heating. Add to the mixture 2 ml of H_2SO_4 and again heat it for 1 min. Quickly cool the mixture with tap water, dilute it to 150 to 200 ml, and add to it 10 ml of H_2SO_4 and 5 ml of 15 f. H_3PO_4. Titrate the solution at once with standard $KMnO_4$ until a faint pink color persists throughout the solution for 10 sec. Stir the solution continuously during the titration. From the volume of standard permanganate solution used. calculate the amount of zinc present.

Notes:

1. If a very large precipitate is obtained, it is suggested that it be dissolved and an aliquot portion be used for the following analysis. By this means, check titrations can be made and a better estimate can be obtained. This can be done as follows:

Dissolve the precipitate as directed in Note 12, P. 61, boiling out the Br_2 and cooling the solution. Transfer the cold solution to

[13] Unpublished experiments by F. N. Laird.

[14] Treadwell-Hall, *Analytical Chemistry*, Vol. II, Quantitative, 8th Ed., p. 672; Hillebrand and Lundell, *Applied Inorganic Analysis*, p. 335.

a 100-ml volumetric flask, dilute it to the mark, mix the solution thoroughly, and pipet 25 ml of it into a 200-ml conical flask. Neutralize this solution and treat it further as directed in Note 12, P. 61. Treat the precipitate obtained there by the above procedure; discard the filtrate.

P. 63. Precipitation of Nickel and Cobalt (and Iron), and the Separation of Iron from Nickel and Cobalt

Discussion. The filtrate from the zinc sulfide precipitation is boiled to expel the hydrogen sulfide, and the nickel and cobalt are then detected by the addition of an excess of sodium peroxide. The nickel is precipitated as pale greenish nickelous hydroxide, while cobalt is oxidized to the tripositive form and appears as the black hydrous oxide. If the precipitate is not darkened, the absence of cobalt is shown. The elements could be precipitated as their sulfides, but this method is more rapid and furnishes more information, and the precipitate is more easily handled and redissolved.

The Basic Acetate Separation. If iron has not been separated by the ether treatment or removed as suggested in Note 3, P. 55, it would precipitate with the Zinc Group sulfides (in P. 55) and appear as ferric hydroxide when the solution is neutralized with sodium peroxide. The separation of iron from the cobalt and nickel can be effectively made at this place by redissolving the precipitate and carrying out what is known as a "basic acetate" precipitation. In this method the solution is so buffered by adding acetic acid and an acetate in the proper ratio that, upon heating the solution, the ferric salt hydrolyzes and precipitates. The precipitate is a mixture of ferric hydroxide and basic ferric acetate ($FeOC_2H_3O_2$) in which the molal ratio of iron to acetate is usually approximately 2 to 1.

This process is extensively used in quantitative work for separating ferric iron (and aluminum) from the bipositive elements of the Ammonium Sulfide Group, and, by the addition of an excess of iron, it affords a means of separating phosphate from the alkaline earth elements. As this method is extensively used in both quantitative and qualitative work, the results of a series of experiments[15] made to investigate the effects of various factors on the precipitation and separation of certain elements are shown in Table XXVII.

It is seen from the data of this table that the proper ratio of acetic acid to acetate is dependent upon the separations desired. Iron can be precipitated from solutions in which this ratio is greater than

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[15] Experiments by the author. For a much more complete study of the basic acetate method, especially in regard to its application to the rarer elements, see Noyes and Bray, *Qualitative Analysis for the Rare Elements*, Macmillan, 1927, pp. 396–410.

TABLE XXVII

THE BEHAVIOR OF VARIOUS ELEMENTS IN THE BASIC ACETATE SEPARATION

In these experiments, 100 ml of a solution containing the elements listed, NH_4Cl, $NH_4C_2H_3O_2$, and $HC_2H_3O_2$, in the amounts shown, were heated just to boiling in a covered flask for the time indicated, and filtered. The composition of the precipitate and filtrate was determined by analysis.

Expt.	Elements Taken (mg)	Milli-equivalents Present			Time Boiled (min.)	Amount Found (mg) In	
		$HC_2H_3O_2$	$NH_4C_2H_3O_2$	NH_4Cl		Precipitate	Filtrate
1	Fe 1	6	39	6	2	1	0
2	Fe 10	36	9	36	2	10	0
3	Fe 10	42	3	42	2	2 to 3[a]	7 to 8
4	Fe 10	42	3	42	4	10	0
5	Fe 10	48	0	48	5	1 to 2	8 to 9
6	Fe 10	42	3	0	3	No ppt.	10
7	Fe 10	42	3	30	3	2 to 3	7 to 8
8	Fe 10	42	6	30	3	10	0
9	Fe 10 Al 10	24	21	24	5	No ppt.	10 Fe 10 Al
10	Fe 10 Al 10	18	27	18	2	Ppt.	Trace Fe 3 to 5 Al
11	Fe 300	18	27	18	2	300	0
12	Fe 300	24	21	24	2	Large ppt.	1 to 2
13	Fe 300	30	15	30	2	Large ppt.[a]	15 to 20
14	Fe 200 Ce^{III} 100	6	39	30	2	No ppt.[b]	
15	Al 1	6	39	6	2	Turbidity	
16	Al 2	6	39	6	2	Small ppt.	0
17	Al 10	6	39	6	2		1
18	Al 300	6	39	6	2	15 to 30[a]	
19	Cr 300	12	33	30	5	2 to 3	
20	Fe 300 Cr 300	12	33	30	2	Large ppt.	3 to 5 Fe 15 to 20 Cr
21	Zn 500	6	39	30	5	No ppt.	
22	Fe 300 Zn 300	6	39	30	2	300 Fe 15 to 25 Zn	0
23	Mn 200	14	31	30	5	No ppt.	
24	Fe 300 Mn 200	14	31	30	2	1	0
25	Fe 300 Mn 1	6	39	30	2	Large ppt.	0 Fe 0.6 Mn
26	Fe 300 Ni 1	6	39	30	2	Large ppt.	0 Fe 0.5 Ni
27	Fe 300 Ni 200	6	39	30	2	20	0 Fe
28	Fe 300 Co 1	6	39	30	2	Large ppt.	0.8 to 1.0 Co
29	Fe 300 Co 200	6	39	30	2	20	0 Fe

[a] The precipitate was colloidal and difficult to filter.

[b] No precipitation was observed until the solution was neutralized with NH_4OH.

10 to 1, while with aluminum a much lower ratio is required; also, if aluminum is present, a lower ratio is required for the precipitation of the iron. Chromium is very incompletely precipitated and so inhibits the precipitation of iron and aluminum that its presence precludes the use of the method. The inhibiting effect of certain elements is strikingly shown in Experiment 14, where the precipitation of iron is completely prevented by the presence of a cerous salt; this is probably due to stabilization of the precipitate in a colloidal system by adsorption of the tripositive cerium. By comparison with Table XIX, p. 284, it is seen that the separation of iron from nickel and cobalt by this method is not so satisfactory as that which could be obtained by an ammonia precipitation. However, only a small amount of iron should be present here, and the presence of ammonia in the solution is undesirable, since the nickel and cobalt would have to be precipitated as their sulfides rather than as their hydroxides, and, as stated above, the sulfide precipitates are much more difficult to handle.

Other organic acids and their salts have been used for buffering systems to approximately the *p*H used in the basic acetate method. Included in this group are formic acid ($K_A = 2 \times 10^{-4}$), succinic acid (K_A, first hydrogen $= 6.6 \times 10^{-5}$), and benzoic acid ($K_A = 6.6 \times 10^{-5}$). The benzoic acid system has been shown to give unusually complete separations.[16]

Procedure 63: PRECIPITATION OF NICKEL AND COBALT AND THEIR SEPARATION FROM IRON. Boil the filtrate from the zinc sulfide precipitation until the H_2S is completely expelled (Note 1), and then add NaOH to the hot solution until it is alkaline to litmus. (Light green precipitate, presence of nickel; blue precipitate, turning pink, presence of cobalt; greenish-gray precipitate, presence of iron. Note 2.)

If iron has been previously separated, treat the mixture as directed in the last paragraph of this procedure.

If iron has not been previously separated, proceed as follows: Make the mixture acid with 12 n. HCl, add 1 ml in excess, and boil the mixture until the precipitate dissolves. Cool the solution somewhat and add liquid bromine, 1 drop at a time until an excess is present, and then boil it again until the excess of bromine is expelled (Note 3). Cool the

[16] Kolthoff, Stenger, and Moskovitz, *J. Am. Chem. Soc.*, **56**, 812 (1934).

solution and add NaOH until the first permanent precipitate is obtained. Dissolve this in HCl (avoiding an excess), add 1 ml of $HC_2H_3O_2$ and 10 ml of 3 n. $NaC_2H_3O_2$ (Note 4), and boil the solution for 2 min. (Reddish precipitate, presence of iron.) If a large precipitate forms, add 5 ml more of the $NaC_2H_3O_2$ and again boil for 1 min. Filter the mixture through a paper filter and wash the precipitate with hot water (Note 5). Treat the precipitate as directed in Note 6. Treat the filtrate as directed in the next paragraph.

Cool the solution and add in 0.1-g portions, shaking after each addition, Na_2O_2 until the solution is alkaline, then 1 to 2 g in excess. (Light green precipitate, presence of nickel; black precipitate, presence of cobalt. Note 7.) Filter the precipitate on a paper filter, wash it with hot water, and treat it by P. 64 (Note 8). Discard the filtrate.

Notes:

1. The H_2S must be completely expelled, or the black sulfides will be precipitated when the solution is made alkaline.

2. Information as to the elements present may be obtained from the color of the precipitate. Nickelous hydroxide is pale green. Cobaltous hydroxide, when first precipitated, is blue but turns pink on standing. This effect is usually attributed to the formation of a blue basic salt which is converted by excess of alkali to the normal hydroxide,[17] while according to Hantzsch[18] the precipitate which first forms has the formula $CoO \cdot H_2O$ and the pink form has the formula $Co(OH)_2$. In contradiction to these theories, X-ray studies show no difference in the crystal structure of the two forms; and from these and other studies Stillwell[19] has concluded that the difference in color is due to the difference in degree of dispersion of the precipitate. If iron is present, it will be mostly in the ferrous form. Pure ferrous hydroxide is white, but it nearly always contains some ferric hydroxide and appears gray-green; on standing exposed to the air, it is rapidly oxidized and becomes reddish brown. If a solution containing ferrous and ferric iron is made alkaline, the precipitate may be black, corresponding to the oxide Fe_3O_4.

3. Ferrous salts are not precipitated by the basic acetate process. Ferrous hydroxide is a stronger base than ferric hydroxide, and therefore ferrous salts are not so easily hydrolyzed; also, ferrous hydroxide is considerably more soluble.

The excess of bromine must be expelled, as, in a solution containing

[17] Treadwell-Hall, *Analytical Chemistry*, Vol. I, Qualitative, 9th Ed., 1937, p. 239.

[18] Hantzsch, *Z. anorg. Chem.*, **73**, 305 (1912).

[19] Stillwell, *J. Phys. Chem.*, **33**, 1256 (1929).

$HC_2H_3O_2$ and $NaC_2H_3O_2$, cobalt may be oxidized by it and precipitated as Co_2O_3.

4. $NaC_2H_3O_2$, rather than $NH_4C_2H_3O_2$, is used, since the presence of ammonium salts would prevent the subsequent precipitation of nickel and cobalt by NaOH and Na_2O_2.

5. If the precipitate tends to become colloidal and pass through the filter, use a wash solution prepared by adding 1 ml of 3 n. $NaC_2H_3O_2$ and 0.1 ml of $HC_2H_3O_2$ to 100 ml of hot water.

6. If only a small precipitate is obtained, the presence of iron should be confirmed by dissolving it in 5 ml of HCl, adding 1 ml of 1 n. KSCN, and noting if a red color is produced. The amount present can be estimated by adding the ferric iron test solution to 5 ml of 6 n. HCl and 1 ml of KSCN until a color match is obtained, or by precipitating with NH_4OH and comparing the precipitate with known amounts of iron precipitated under similar conditions.

If iron has not been separated by the ether treatment and a considerable precipitate is obtained, proceed as follows:

> Pour 10 ml of warm 6 n. NH_4OH repeatedly through the precipitate and discard the solution. Dissolve the precipitate with 10 to 20 ml of HCl, evaporate the solution to 4 to 5 ml, dilute to 25 ml and treat as directed in P. 53, beginning with the third paragraph.

The precipitate is treated with NH_4OH in order to metathesize most of the basic acetate to hydroxide and thus remove the acetate. The presence of acetic acid would tend to inhibit the reaction between ferric iron and iodide in P. 53.

7. By the addition of Na_2O_2 the nickel hydroxide precipitate is not appreciably changed in appearance, although it may be partly converted into a nickelous peroxide; when the mixture is heated, the peroxide is decomposed. More powerful oxidizing agents, such as hypochlorite or peroxysulfate, convert the nickel to a black oxide of approximately the composition Ni_2O_3. The cobaltous hydroxide rapidly darkens because of the formation of Co_2O_3, which appears as a brown or a black precipitate, depending upon the alkalinity and temperature of the solution. When cobalt is being precipitated, the cobaltous solutions should not be treated with a high concentration of alkali in the absence of an oxidizing agent, as cobaltous hydroxide dissolves slightly under these conditions, forming a blue solution which supposedly contains the ion $CoO_2^=$.

8. If the precipitate is light green in color and not at all darkened, the absence of cobalt can be assumed. In that case the precipitate can be dissolved in 3 to 10 ml of HCl, and the solution can be evaporated to 2 to 3 ml and treated directly by P. 65; or, if the precipitate is small, it can be treated as suggested in Note 2 of P. 64.

P. 64. Separation of Nickel and Cobalt

Discussion. The separation of nickel and cobalt which is used here when large amounts of the two elements are present and a quantitative separation is desired depends upon the difference in the solubilities of the chlorides of the two elements in an ether

solution saturated with hydrochloric acid gas. Under these conditions, nickel chloride is precipitated, and cobalt remains in solution because of the formation of a complex ion. This compound is so intensely colored that even 1 mg of cobalt will impart to the ether solution a distinct blue color, which serves as the detection of this element. This method for separating nickel and cobalt, developed by Havens,[20] is usually considered inadequate for quantitative work because of the inclusion of cobalt in the precipitate. Experiments[21] have shown that, when, under the conditions of this procedure, 250 mg of nickel are precipitated in the presence of 250 mg of cobalt, not over 2 mg of cobalt are coprecipitated; it was also shown that 1 mg of nickel causes a precipitate and 1 mg of cobalt causes a blue color, each of which is easily perceptible.

Coördination Compounds of Cobalt. The color changes which cobalt solutions undergo upon treatment with various reagents, such as an alkaline cyanide, ammonia, or ammonia plus an oxidizing agent, or upon evaporation of its solutions with concentrated solutions of the halogen acids are due to the formation of complex, or coördination, compounds of the type mentioned in the discussion of P. 11. Thus, in dilute aqueous solutions there is evidence that the cobaltous ion surrounds itself with six water molecules, forming the ion $Co(H_2O)_6^{++}$, which is pink colored. This behavior is characteristic of many other ions: thus, the blue color of aqueous cupric solutions is due to the hydrated ion $Cu(H_2O)_4^{++}$; on dehydration by heating with concentrated sulfuric or perchloric acid, the solution becomes colorless. If an excess of a soluble cyanide is added to a cobaltous solution, there is first formed the complex cobaltocyanide ion, $Co(CN)_6^{\equiv}$; if an oxidizing agent is present (even the oxygen of the air), the much more stable cobalticyanide ion, $Co(CN)_6^{\equiv}$, is formed. These ions are analogous to the ferro- and ferricyanide ions, $Fe(CN)_6^{\equiv}$ and $Fe(CN)_6^{\equiv}$, respectively.

Cobaltous ion does not readily form ammonia complexes, but, as was mentioned in P. 11, the tendency toward complex formation increases as the positive charge on a given ion increases, so that, if an oxidizing agent is added to an ammoniacal cobaltous solution, an intense dark red to brown solution results. This is due to the formation of various ions and compounds which vary according to the concentration of the ammonia and of the other anions in the

[20] Havens, *Am. J. Sci.* (4), VI, 396.

[21] Unpublished experiments by Edwin McMillan and Carter Gregory.

solution. Examples of such compounds are as follows: $Co(NH_3)_6^{+++}$, $Co(NH_3)_5Cl^{++}$, $Co(NH_3)_4Cl_2^-$, $Co(NH_3)_3(NO_2)_3$ (un-ionized), $Co(NH_3)_2(NO_2)_4^-$, and so forth. It is to be noted that in all cases a total of six negative or neutral groups are attached, cobalt having a coördination number of six in these compounds.

The cause of the change in color from pink to blue as a cobaltous chloride solution is evaporated or treated with concentrated hydrochloric acid has been the object of much study, with two general theories being advanced: first, that the color change was due to a change in the degree of hydration of the ion, this being represented by an equation of the type

$$Co(H_2O)_6^{++} + 2Cl^- = CoCl_2 \cdot 2H_2O + 4H_2O,$$

and, second, that the change was due to the transformation from a hydrated complex compound to one containing halogen ion, probably as follows:

$$Co(H_2O)_6^{++} + 4Cl^- = CoCl_4^= + 6H_2O.$$

However, it has been shown by Donnan and Bassett[22] that in the blue solution the cobalt migrates to the anode, while in the pink solutions it migrates toward the cathode. Further work by Bassett and Croucher[23] has demonstrated that the blue hydrochloric acid solutions contain the negative ions $CoCl_4^=$ and $Co(Cl_3H_2O)^-$. In the ether solution saturated with hydrochloric acid, the cobalt probably exists as H_2CoCl_4.

Procedure 64: SEPARATION OF NICKEL AND COBALT. *Method for the More Exact Separation of Large Amounts of Nickel and Cobalt.* Dissolve the hydroxide precipitate (from P. 63) on the filter by pouring repeatedly over it 10 to 20 ml of hot HCl (Note 1). If it dissolves slowly, pour 1 ml of 3 per cent H_2O_2 over the precipitate, again treat it with the HCl, and then evaporate the solution to a volume of 4 to 5 ml (Note 2).

Transfer the HCl solution to a large test tube (15 mm by 200 mm; Note 3), using 3 to 5 ml of HCl to wash out the flask, and again evaporate the solution to 4 to 8 ml (Notes 4, 5). Cool the solution, immerse the test tube in a beaker

[22] Donnan and Bassett, *J. Chem. Soc.*, **81**, 939 (1902).
[23] Bassett and Croucher, *J. Chem. Soc.*, **1930**, 1784.

containing a mixture of ice and water, add 15 to 25 ml of ethyl ether, and (*working under a hood and with no flames in the vicinity*) pass a fairly rapid stream, 2 or 3 bubbles a second, of dry HCl gas (Note 1, P. 94) through the solution until it is saturated, as shown by the gas being no longer absorbed (Note 6). (Yellow precipitate, presence of nickel; blue solution, presence of cobalt.)

If nickel is present, cork the tube and let it stand; in a similar test tube saturate another 15- to 30-ml portion of ether with HCl gas. Filter the mixture by decantation through an asbestos or, preferably, a sintered-glass filter (which has been sucked dry of water and then washed with 2 to 3 ml of the ether-HCl solution), and wash the precipitate by decantation with 2- to 5-ml portions of the ether-HCl solution. Collect the washings with the filtrate in a 400-ml flask. Treat the precipitate by P. 65.

If the filtrate has a detectable blue color, treat it by P. 66; if it is colorless, discard it.

Notes:

1. If the precipitate is large, it can be more advantageously dissolved by transferring most of it, using a stirring rod, to the vessel in which it was precipitated, and heating it there with the HCl.

2. If the precipitate is small, or if it is of moderate size (containing not over 200 mg of the two elements) and an exact separation and estimation is not required, the two elements may be detected and the amount of each more rapidly estimated by treating the HCl solution by Optional Procedure 64A.

3. If a test tube of this size is not available, a small flask may be used, although it is not as efficient a vessel in which to saturate the solution with HCl gas.

4. The volume of solution remaining should be adjusted to the amount of the two elements thought to be present. The precipitation of nickel is more complete, and the color of the cobalt is more pronounced, when only the minimum volume of water is left and the minimum amount of ether is added later. When large amounts of the elements are present, the larger volumes should be used to prevent coprecipitation of cobalt with the nickel chloride.

5. The solution tends to bump during this evaporation so that it has to be kept in continual motion. It is advisable to keep an ebullition tube (Note 3, P. 42) in the solution, or, if one is not available, a light-weight stirring rod (one cut from capillary tubing without rounding the edges is very effective) may be used.

6. Saturation of the solution is also indicated by the aqueous and ether layers becoming miscible.

P. 64A. Optional Method of Detecting Nickel and Cobalt

Discussion. An optional method of detecting and estimating nickel and cobalt is provided for use when the amount of the two elements is small (as judged by the precipitates obtained in P. 63), or where exactness is not required and only a rapid method of detecting and estimating the two is desired. In this method the solution is divided, and the nickel is detected in one portion by precipitating it with dimethylglyoxime (diacetyl dioxime). Dimethylglyoxime, $(CH_3)_2C_2(NOH)_2$, is an organic compound which acts in the nature of a weak acid and forms a salt with nickel, $((CH_3)_2C_2(NOH)NO)_2Ni$, in which only one of the hydrogen atoms is displaced. This compound is so insoluble in alkaline or weakly acid solutions and is so voluminous and intensely red colored that it affords an extremely sensitive test for nickel; thus, in 50 ml of a solution made slightly alkaline with ammonia, 0.05 mg of nickel gave the characteristic precipitate within 1 min., while 0.02 mg could be detected when the solution was allowed to stand for 15 min. When large amounts of cobalt are present, an intense brown color is formed, the precipitation of nickel is inhibited, and an excess of the reagent must be added. These effects are due to the formation by the cobalt of a stable soluble compound with the dimethylglyoxime. They can be partly overcome by making the precipitation from a solution containing acetic acid and acetate; thus, under the conditions of this procedure, 0.05 mg of nickel can be readily detected in the presence of 50 mg of cobalt.

Cobalt is detected in another portion of the solution by precipitating it as potassium cobaltinitrite, $K_3Co(NO_2)_6$. This compound is formed by the addition of potassium nitrite to the cobaltous salt in a slightly acid solution. Under these conditions the dipositive cobalt is oxidized to the tripositive state and forms the nitrite complex, $Co(NO_2)_6^{\equiv}$, the potassium salt of which is insoluble. The oxidation of cobalt to the tripositive state by nitrite, an apparent anomaly, is due to the stability of the complex ion, which reduces the concentration of the simple tripositive ion to an exceedingly small value, and to the concentration of the complex ion being maintained at a small value by its precipitation as the potassium salt. The dipositive nickel is not appreciably oxidized by the nitrite, and, although nickelous nitrite ion, $Ni(NO_2)_6^{\equiv}$, is formed, the salt $K_4Ni(NO_2)_6$ is relatively soluble. If alkaline earth elements are present, the separation is unsatisfactory, as yellow precipitates of the type $BaK_2Ni(NO_2)_6$ are then formed. The proper conditions

for the quantitative precipitation of cobalt require a high concentration of nitrite ion in order to cause the formation of the complex ion at an appreciable rate and a high concentration of potassium ion in order to reduce the solubility of the precipitate. The solution should be only slightly acid, as the precipitate is soluble in strong acids; it should not be basic, as the complex ion is decomposed by hydroxyl ion with precipitation of cobaltic oxide.

Procedure 64A: DETECTION OF NICKEL AND COBALT. *Optional Method for Use with Small Amounts or When Only Qualitative Information Is Desired.* Dissolve the hydroxide precipitate (from P. 63) as directed in the first paragraph of the procedure above.

Cool the solution, transfer it to a 50-ml volumetric flask, dilute it to the mark, mix it thoroughly, and pipet 5 to 25 ml (Note 1) into a 200-ml flask. Add a slight excess of NH_4OH (filter out any precipitate), dilute the solution to 50 ml, and add 5 to 20 ml of a 0.1 n. solution of dimethylglyoxime in ethyl alcohol. (Red precipitate, presence of nickel. Note 2.) Compare the precipitate with that produced under similar conditions by known amounts of nickel, or collect it on a weighed Gooch crucible or, preferably, one of sintered-glass (Note 3), wash it with hot water, dry it at 110°C. for 1 hr., and cool and weigh it.

Transfer 10 to 25 ml of the remainder of the solution to a 100-ml flask and evaporate it to 3 to 5 ml. Neutralize the solution with KOH, make it acid with $HC_2H_3O_2$, and then add 5 ml in excess. Add 5 ml of 6 n. KNO_2, cool the mixture, shake it vigorously, and let it stand, shaking it frequently, for at least 10 min. (Yellow precipitate, presence of cobalt.) If a large precipitate is obtained, add 2 ml more of $HC_2H_3O_2$ and 5 ml of 6 n. KNO_2 (Note 4). Compare the precipitate with that produced under similar conditions by known amounts of cobalt, or, if a more precise estimation is desired, treat another portion of the solution in the volumetric flask by the last paragraph of P. 66 (Note 5).

Notes:

1. Too large a portion of the solution should not be taken, as an excessive volume of the reagent may be required; also, over 10 to 20 mg of nickel produce so voluminous a precipitate that it is difficult to filter and wash.

2. If considerable cobalt is present, the solution may be so dark colored as to prevent determining if a red precipitate is present. In this case make the solution just acid with $HC_2H_3O_2$ and let it stand for 10 min.

3. If a quantitative precipitation is desired, the solution should be allowed to stand for 30 min. to 1 hr. before being filtered. The filtrate should be tested by adding more of the dimethylglyoxime reagent and allowing it to stand.

4. The quantitative precipitation of considerable amounts of cobalt requires from 12 to 24 hr.; smaller amounts are precipitated in a much shorter time. Since 0.1 mg of cobalt can be readily detected, small portions of the original solution should be used if considerable cobalt is present. Completeness of precipitation should be tested for by adding more nitrite to the filtrate and allowing it to stand.

5. If no more of the original solution is available, add cautiously 5 ml of 36 n. H_2SO_4 to the mixture, evaporate it until the acid fumes, cool the solution, dilute it with 25 ml of water, and treat it by the last paragraph of P. 66.

P. 65. Estimation of Nickel

Discussion. In the method for estimating nickel which is used here, the nickel chloride solution is titrated with a standard cyanide solution, the principal reaction being the formation of the nickelous cyanide complex ion, $Ni(CN)_4^{--}$. As this compound is unstable in an acid solution, the nickel chloride precipitate (from P. 64) is dissolved in an ammoniacal solution and is thus largely converted into the tetrammino nickel complex ion, $Ni(NH_3)_4^{++}$. However, upon addition of cyanide, the cyanide complex is rapidly formed, as it is much less dissociated. The tetrammino nickel ion is blue, but this color is not sufficiently intense for its disappearance to be used as the end-point. The end-point is therefore determined by first adding a known volume of standard silver nitrate and then an excess of potassium iodide, which produces a colloidal precipitate of yellowish silver iodide. When this mixture is titrated with the cyanide, the complex nickelous cyanide anion is formed first; after an amount of cyanide equivalent to the nickel has been added, further addition of cyanide forms the $Ag(CN)_2^-$ anion, which causes the precipitate of silver iodide to dissolve. The end-point is taken when the last yellowish opalescence due to the silver iodide precipitate disappears. For a discussion of this end-point, see P. 23.

It is, of course, necessary to correct for the amount of silver which has been added. As cobalt also forms a cyanide complex ion, it should not be present in appreciable amounts. The solution should be cold during the titration. Only a slight excess of ammonia should

be present, as otherwise the conversion of the ammino complex to the cyanide complex takes place more slowly.

Procedure 65: ESTIMATION OF NICKEL. Dissolve the $NiCl_2$ precipitate (from P. 64) from the filter by pouring through it, in small portions, 10 to 20 ml of hot water. Collect the solution in the test tube and dissolve the precipitate remaining there. Transfer the solution to a 200-ml flask, and add 5 ml of 3 n. NH_4Cl and then NH_4OH until a clear blue color is obtained and the solution is alkaline, taking care to avoid an excess of the NH_4OH (Note 1). Cool the solution.

If less than 100 mg of nickel are thought to be present, treat the solution as directed in the last paragraph of this procedure.

If more than 100 mg of nickel are thought to be present, transfer the cold solution to a 100-ml volumetric flask, dilute it to the mark, mix the contents thoroughly, and pipet from it into a 200-ml flask a volume of solution which is thought to contain 50 to 100 mg of nickel.

Dilute the solution to 100 ml, and add to it 1 ml of 1 n. KI and then (from a buret or graduated pipet) 0.10 ml of standard 0.1 n. $AgNO_3$ solution. Add the $AgNO_3$ dropwise while swirling the solution. Titrate the solution with a standard 0.2 f. KCN solution, adding the KCN rapidly as long as the turbidity does not decrease and then slowly, swirling the mixture constantly, until the yellowish precipitate dissolves. If it is thought that the end-point has been overrun, titrate the clear solution with 0.1 n. $AgNO_3$ solution until a permanent precipitate is again produced. From the volumes of standard $AgNO_3$ and KCN used, calculate the amount of nickel present (Note 2).

Notes:

1. If a flocculent precipitate, usually due to aluminum from reagents or vessels, persists after the solution is made alkaline, it can be neglected if it is not sufficient to interfere with the detection of the end-point; however, it is preferable to filter it out.

2. The standard KCN solution is not stable and may be standardized at the completion of the titration by pipeting a known volume of the standard $AgNO_3$ into the solution and again titrating with KCN to the end-point.

P. 66. Estimation of Cobalt

Discussion. This method for the estimation of cobalt, developed by Engle and Gustavson,[24] and studied further by Willard and Hall,[25] is based upon the oxidation of cobalt in an alkaline solution to cobaltic oxide by sodium peroxyborate, $NaBO_3$. Nickel, if present, is not oxidized to the higher oxidation state; it may form a peroxide compound, but this is decomposed by heating. The excess peroxyborate is destroyed by merely boiling the alkaline mixture, with the evolution of oxygen. The precipitate is then reduced by an excess of iodide in an acid solution, an equivalent amount of iodine being liberated; this is titrated with a standard thiosulfate solution. Experiments[26] have shown that the cobaltic oxide dissolves more rapidly if hydrochloric acid is used for acidifying the mixture instead of sulfuric acid, as originally proposed, and also that low results are obtained when large amounts of cobalt (over 50 mg) are present. The article by Willard and Hall contains a discussion of other methods for the volumetric estimation of cobalt.

Procedure 66: ESTIMATION OF COBALT. In case a blue color was obtained in P. 64, evaporate the ether solution (under a hood by immersing the flask in a beaker of water which has been heated to boiling and from which the flame has then been removed) until the ether is expelled; then evaporate the aqueous solution almost to dryness. Dissolve the residue in 25 ml of water.

If less than 50 mg of cobalt are thought to be present, treat the solution as directed in the last paragraph of this procedure.

If more than 50 mg of cobalt are thought to be present, cool the solution and transfer it to a 100-ml volumetric flask, dilute it to the mark, mix the contents, and pipet from it into a 400-ml flask (preferably one with a ground-glass stopper) that volume of the solution which is thought to contain 40 to 60 mg of cobalt.

Make the solution just alkaline with NaOH, gradually sprinkle into it 1 to 2 g of sodium peroxyborate ($NaBO_3$), and then add 10 to 15 ml of NaOH (Note 1). Swirl the mixture until the contents are thoroughly mixed, and then

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[24] Engle and Gustavson, *Ind. Eng. Chem.*, **8**, 90 (1916).
[25] Willard and Hall, *J. Am. Chem. Soc.*, **44**, 2237 (1922).
[26] Unpublished experiments by Dr. Lucas Alden.

boil it vigorously for 10 min. Cool the mixture (Note 2), add to it 2 g of KI dissolved in 10 ml of water, washing down the sides of the flask and mixing the solutions, and then add 50 ml of HCl. Again cool the mixture, close the flask, and let it stand for 5 min., or until the precipitate dissolves. Dilute the solution with 100 ml of water which has been recently boiled and cooled, and then titrate it with 0.1 n. $Na_2S_2O_3$ until the brownish-yellow iodine color becomes indistinct. Add 5 ml of starch indicator solution and again titrate until the starch blue color disappears. From the volume of standard $Na_2S_2O_3$ used, calculate the amount of cobalt present.

Notes:

1. If sodium peroxyborate is not available, substitute for it 2 to 3 ml of solid Na_2O_2. Cool the mixture during the addition of the Na_2O_2.

2. If a carbon dioxide generator (or tank) is available, the flask should be swept with the gas sufficiently to remove all the air from it before adding the KI and acidifying. This minimizes the probability of error due to oxidation of the iodide in the hydrochloric acid solution by the oxygen of the air.

TABULAR OUTLINE VIII

The Analysis of the Aluminum Group

Filtrate from P. 55: $Al(C_2O_4)_3^{=}$, $Cr(C_2O_4)_3^{=}$, $Mn(C_2O_4)_2^{-}$, $C_2O_4^{-}$, HCO_3^{-}, HS^{-}, Na^{+}, NH_4^{+}, H_2S
Make acid with HNO_3, heat. (H_2S and CO_2 expelled.)
Evaporate. Add 16 n. HNO_3, evaporate almost to dryness.
Add HNO_3 and $KClO_3$, heat. (CO_2, ClO_2) (P. 71)

Precipitate: MnO_2 *Dissolve in HCl and KI.* Solution: Mn^{++}, I_3^{-} *Titrate with $Na_2S_2O_3$, starch indicator.* Solution: Mn^{++}, I^{-}, $S_4O_6^{-}$ (P. 72)	Filtrate: Al^{+++}, $Cr_2O_7^{-}$, $H^{+}NO_3^{-}$ *Neutralize with NH_4OH.* (P. 73)	
	Precipitate: $Al(OH)_3$ *Heat and weigh.* (P. 74)	Filtrate: CrO_4^{-}, NH_4^{+}, NO_3^{-}, NH_4OH *Make acid with H_2SO_4.* *Add KI.* Solution: Cr^{+++}, I_3^{-} *Titrate with $Na_2S_2O_3$, starch indicator.* Solution: Cr^{+++}, I^{-}, $S_4O_6^{-}$ (P. 75)

The Analysis of the Aluminum Group

P. 71. Destruction of Oxalate, Precipitation of Manganese, and Detection of Chromium

Discussion. The filtrate from the H_2S precipitation of the Zinc Group contains aluminum, chromium, and manganese in the form of complex oxalates. It is necessary that the oxalate be removed from the solution, as neither aluminum nor chromium can be precipitated in its presence. The procedure adopted for destroying the oxalate consists in evaporating with concentrated nitric acid, which causes partial oxidation of the oxalate, and then completing this process by adding chlorate to the nitric acid solution. Two other desirable results are attained: The manganese is oxidized by the chlorate under these conditions and precipitates as the hydrated dioxide, thus being separated from aluminum and chromium, and the chromium is oxidized to chromate, in which form it can be separated from the aluminum by precipitating the latter with ammonium hydroxide. The oxalate could have been destroyed by fuming the filtrate with sulfuric acid, but this process causes the formation of the difficultly soluble chromic dihydroheptasulfate, $Cr_4H_2(SO_4)_7$, which is so slowly dissolved by ordinary reagents that the process was not adopted; furthermore, manganese dioxide is not readily precipitated by chlorate from solutions containing sulfuric acid, as soluble complex compounds of tripositive manganese are formed.

It was found that the presence of manganese very markedly catalyzed the oxidation of oxalate by nitric acid; for this reason, a simple preliminary test for manganese is made on a portion of the solution, and, if it is absent, a moderate amount is added. A further advantage of having manganese present is that the precipitation of the dioxide is proof that all oxalate has been destroyed and that further addition of chlorate for that purpose is unnecessary; the chromium is also oxidized to chromate before precipitation of the manganese dioxide occurs.

The Precipitation and Separation of Manganese as Dioxide by Chlorate in a Nitric Acid Solution. The precipitation of manganese from a nitric acid solution by chlorate is a very distinctive test for this element and also can be used to separate it from all the other elements of the Ammonium Sulfide Group. The extent to which other elements are carried down with the manganese was determined by

treating 250 mg of manganese and 250 mg of each of the other elements of the Ammonium Sulfide Group in separate solutions by the last paragraph of this procedure. The precipitates were then analyzed to determine the amount of the other element coprecipitated. The amounts found (mg) were as follows: aluminum, 3; chromium, 10; iron, 25; zinc, 3 to 5; nickel, 4; and cobalt, 10. As there has been some question as to how quantitative the precipitation of manganese can be made by this method, the filtrates were also examined; in none of the above experiments was more than 0.1 to 0.2 mg of manganese found in the filtrate, and in repeated experiments 0.3 mg of manganese was detected without difficulty, even in the presence of large amounts of aluminum. When large amounts of chromium were present, the detection of 0.3 mg was uncertain but 0.7 mg gave a readily detected precipitate. Small amounts of manganese such as these often gave first a pink color, which changed into a brownish suspension and then, on heating, into a dark precipitate.

Procedure 71: PRECIPITATION OF MANGANESE AND DETECTION OF CHROMIUM. Make the filtrate from P. 55 (contained in a 500-ml flask) just acid to litmus with HNO_3 and add 5 ml of acid in excess. Evaporate the solution until the H_2S has been expelled and the volume has been reduced to slightly less than 100 ml, and then cool and dilute it to 100 ml (Notes 1 and 11). Pipet 10 ml of the solution into a 100-ml flask and add to it 5 ml of 6 n. KOH (Note 2) and 0.5 ml of solid Na_2O_2. Boil the solution for 1 or 2 min. (Brownish-black precipitate, presence of manganese; yellow solution, presence of chromium. Note 3.)

If there is no precipitate, return this portion to the main body of the solution. Add 2.5 ml of 1 n. manganous nitrate solution (Note 4) and treat the solution according to the last paragraph of this procedure.

If the precipitate is small, 1 mg or less (Note 5), filter the mixture through an asbestos filter and wash the precipitate with two 5-ml portions of hot water. Combine the filtrate and washings with the main body of the solution. Add 2.5 ml of 1 n. manganous nitrate solution (Note 4) and treat the solution according to the last paragraph of this procedure. Treat the precipitate by P. 72.

If the precipitate is large, greater than 1 mg (Note 5), return the mixture to the main body of the solution and treat it by the next paragraph.

Evaporate the solution until salts crystallize or until the volume has been reduced to 3 to 5 ml. Add cautiously (Note 6), in 1-ml portions, 10 ml of 16 n. HNO_3, allow the flask to stand without heating as long as a vigorous reaction continues, and then evaporate the solution slowly to 3 to 5 ml. Repeat the treatment with HNO_3 and again evaporate. Add 20 ml of 16 n. HNO_3, heat the solution to boiling, and add finely powdered $KClO_3$ in 0.1-g portions (*Care*: Note 7) until a precipitate of manganese dioxide has been obtained which does not disappear upon boiling the mixture (Note 8) for 1 min. Boil the solution gently between each addition of chlorate until any greenish-yellow vapors of ClO_2 are expelled from the flask. Continue to add $KClO_3$ (1 to 5 g) in small portions until no more manganese is precipitated and ClO_2 is no longer rapidly evolved. Dilute the mixture to about 30 ml with water and filter it through an asbestos (or sintered-glass) filter, retaining as much as possible of the precipitate in the flask (Notes 9, 10). (Orange-red solution, presence of chromium.) Wash the precipitate by decantation with three 5-ml portions of hot water, combining these washings with the filtrate. Treat the filtrate by P. 73. If manganese was added in the earlier part of this procedure, discard the precipitate; if no manganese was added, wash the precipitate with hot water until it is free of acid and treat it by P. 72.

Notes:

1. A 100-ml graduate is sufficiently precise for this dilution, for the aliquot portion to be used for the detection of manganese is analyzed for that element only when 1 mg or less is present; and the volumetric precision obtained with the use of a graduate is well within the limits of accuracy of the colorimetric method used for the estimation of small quantities of manganese.

2. Because chromium and manganese are present largely as the oxalate complexes, the quantity of KOH added must exceed the amount of ammonium salts (about 17 milli-equivalents) present so that the OH^- concentration will be sufficiently high for the peroxide to oxidize these elements completely. KOH rather than NaOH is used to prevent the precipitation of $Na_2C_2O_4$.

3. Experiments have shown that under these conditions 0.1 mg of manganese and 0.5 mg of chromium are easily detected.

If iron, nickel, or cobalt were incompletely removed from this solution, they would behave as follows: Iron would give a grayish-green precipitate of $Fe(OH)_2$, which upon the addition of Na_2O_2 would be oxidized to reddish-brown gelatinous $Fe(OH)_3$; cobalt would give a purplish-red solution due to

the formation of a complex ion with the ammonia, and this would decompose and precipitate black Co_2O_3 when the alkaline peroxide solution was heated; nickel would remain in solution because of the formation of the bluish tetrammino ion. These effects will be more or less masked when much manganese or chromium is present.

4. The presence of 10 mg or more of manganous ion catalyzes the oxidation of oxalate by concentrated HNO_3 and reduces appreciably the quantity of $KClO_3$ required to complete the oxidation. Furthermore, since MnO_2 is reduced in acid solution by oxalate, no permanent precipitate of MnO_2 will be formed until all the oxalate has been destroyed. Hence the formation of a permanent black precipitate indicates the complete elimination of oxalate.

If a 1 n. manganous nitrate solution is not available, 5 ml of manganese test solution containing 10 mg/ml may be substituted.

5. If there is any doubt as to the size of the precipitate, it should be compared with the precipitate obtained by oxidizing 1 mg of manganese to the dioxide according to the first paragraph of this procedure.

6. Concentrated nitric acid in the presence of manganous salts reacts very vigorously with oxalate, and, unless the acid is added slowly, the solution may foam out of the flask.

7. The action of $KClO_3$ in concentrated HNO_3 is rapid and vigorous, giving as one of its decomposition products unstable ClO_2, an easily identified greenish-yellow gas. The chlorate is added in small quantities, and the solution is boiled between additions to prevent the accumulation of ClO_2; large quantities of this may explode dangerously when overheated. Under the conditions of this procedure, when the chlorate has been added in small quantities, the only evidence of such explosions has been gentle puffs of gas from the mouth of the flask. However, to eliminate the danger of explosions, the addition of large quantities of $KClO_3$ at one time *must be avoided.*

8. With 10 g of $(NH_4)_2C_2O_4$ present, from 5 to 10 g of $KClO_3$, depending upon the quantity of manganous ion present, are required to oxidize the oxalate completely.

9. A paper filter cannot be used, as it would reduce the MnO_2 and be attacked by the concentrated HNO_3.

10. The filtrate should be tested for manganese by adding a small amount of $KClO_3$ and boiling the solution for a few minutes. If any precipitate does form, evaporate the solution to 5 ml, add 10 ml of 16 n. HNO_3, and treat the solution with small portions of $KClO_3$ until no additional precipitate forms.

Very often the oxidation of manganese with $KClO_3$ in HNO_3 solution produces a visible permanganate color; the quantity is usually so small that it does not interfere in the subsequent procedures.

11. If an adequate supply of the sample of the original material is available, a more sensitive test for manganese can be made and the division of the solution described in the remainder of this first paragraph can be avoided by proceeding as follows:

> Transfer 0.2 g of the original sample to a large test tube, add 5 ml of 16 n. HNO_3, heat the mixture almost to boiling until solvent action seems complete, cool, and add 10 ml of cold water. Add 2 to

3 g of solid sodium bismuthate, shake the mixture, and allow any residue to settle. (Purple color, presence of manganese.)

See the discussion and Note 1 of P. 72 in regard to this method of detecting and estimating manganese. Organic matter would in most cases prevent this test by reducing the permanganate; it should be eliminated by P. 4, and the bismuthate should be added to the perchloric acid solution obtained there.

P. 72. Estimation of Manganese

Discussion. After the manganese has been obtained in the form of the dioxide (P. 71), it is conveniently estimated by treating it with an excess of potassium iodide in a hydrochloric acid solution and titrating the iodine liberated with standard thiosulfate solution. The reaction by which the precipitate is dissolved may be represented as follows:

$$MnO_{2(s)} + 3I^- + 4H^+ = Mn^{++} + I_3^- + 2H_2O.$$

Native manganese dioxide (the mineral pyrolusite) is dissolved only slowly by iodide in a cold hydrochloric acid solution, but the freshly precipitated material is much more reactive and usually dissolves in a few minutes.

An optional method consists in treating the manganese dioxide with an excess of standard ferrous sulfate, which reduces the manganese dioxide and is itself oxidized to the ferric state; the excess of the ferrous salt is then titrated with a standard permanganate solution. This method is commonly used when standard solutions of ferrous sulfate and permanganate are readily available and when it is desired to eliminate the use of the relatively expensive potassium iodide. A procedure for the use of this method is given in Note 3 below; this method can also be utilized for the analysis of pyrolusite ores. However, it is a different method, is not as rapid as the iodide method, and (where the amount of manganese is not approximately known, so that the excess of ferrous sulfate can be kept small) is not so conveniently performed as is the iodide method.

A very sensitive test for manganese can be made by oxidizing it in an acid solution to permanganate; the color thus obtained can be compared with known amounts of manganese and a colorimetric estimation can be made, or with larger amounts the permanganate can be reduced with a standard solution of a reducing agent. It is recommended that the presence of manganese in the sodium peroxide precipitate from the preliminary test in P. 71 be confirmed by this method; if it is desired, a colorimetric estimation can be made.

If the chlorate precipitate from P. 71 is small (25 mg or less), the presence of manganese in it can be confirmed and the amount present can be estimated by this procedure. A procedure for this purpose is given in Note 1 below.

In that procedure, sodium bismuthate is used as the oxidizing agent, the reaction taking place being represented by the following equation:

$$5HBiO_3 + 2Mn^{++} + 9H^+ = 2MnO_4^- + 5Bi^{+++} + 7H_2O.$$

The $HBiO_3$ is formed by adding commercial sodium bismuthate (usually a mixture of sodium bismuthate and bismuth tetroxide) to a nitric acid solution; $HBiO_3$ is unstable in acid solutions, oxygen and tripositive bismuth being formed. This oxidation of manganese to permanganate is frequently used as the basis of both colorimetric and oxidimetric determinations of manganese. The colorimetric method is restricted to small amounts (usually less than 2 mg in 100 ml), as the color comparison is unsatisfactory with more concentrated solutions; in the oxidimetric method the permanganate formed is titrated with a standard solution of a reducing agent, usually ferrous sulfate. In the oxidimetric method difficulty is experienced in obtaining complete oxidation of the manganese if more than 50 to 100 mg per 100 ml are present. Other oxidizing agents which are similarly used for oxidizing manganese to permanganate are lead dioxide, periodate, and peroxysulfate;[1] bismuthate is used here because it reacts rapidly in a cold solution.

Procedure 72: ESTIMATION OF MANGANESE. Transfer as much as possible of the MnO_2 precipitate (Note 1) on the filter back to the flask containing the remainder of it by tipping the perforated porcelain plate on edge and washing the precipitate and asbestos from the funnel with about 25 ml of water (Note 2). Dissolve 2 to 5 g of KI (or see Note 3) in 40 ml of water, add 10 ml of HCl, and then wash the funnel and plate with this solution, collecting it in the flask. Close the flask and gently swirl the contents until all of the MnO_2 precipitate has apparently dissolved. Titrate the solution with standard $Na_2S_2O_3$ until the iodine color becomes indistinct, add 5 ml of starch indicator solution, and again titrate until the blue color disappears. From the volume of $Na_2S_2O_3$ used, calculate the amount of manganese present.

[1] For discussions of these methods, see Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel*, Wiley, 1931, pp. 190–208.

Notes:

1. If the precipitate is small (25 mg or less), it can be estimated more quickly and a confirmatory test can be obtained by using the method given below. In this case proceed as follows:

Dissolve the precipitate on the filter by pouring dropwise through it 5 to 10 ml of HNO_3 to which has been added 2 ml of 3 per cent H_2O_2. Collect the solution in the original flask and dissolve any precipitate there; boil for 2 to 3 min. (to destroy the peroxide). Transfer the solution to a large test tube, washing the filter and flask with 3 n. HNO_3, and cool it to room temperature. The total volume should be from 20 to 50 ml, depending upon the amount of manganese thought to be present. Add 2 to 3 g of solid sodium bismuthate and allow the mixture to stand until the excess settles. (Purple color, presence of manganese.) If all of the bismuthate dissolves, add more, in 0.2-g portions, until an excess is present. Add standard permanganate to the same volume of 3 n. HNO_3 in a similar test tube until the colors match.

If the color is too intense to make a comparison, filter the mixture through a sintered-glass (or asbestos) filter, wash the residue with 25 ml of cold 0.6 n. HNO_3, and collect the filtrate and washings in a 200-ml flask. Add 2 ml of 85 per cent H_3PO_4 and titrate dropwise with standard ferrous sulfate solution until the permanganate color disappears. From the volume of ferrous sulfate used, calculate the amount of manganese present.

2. Possible loss of precipitate or solution is minimized by inserting a large wide-stem funnel in the flask.

3. As KI is an expensive chemical, the following method may be used instead of the one described if standard permanganate and ferrous sulfate solutions are available:

Add, with a 10- or 25-ml pipet, standard ferrous sulfate solution to the precipitate, running the first portions through the funnel and shaking the mixture vigorously after each addition. (The amount of ferrous sulfate required should be approximately calculated from the size of the precipitate, and a 20 to 50 per cent excess should be added.) Add 50 ml of 3 n. H_2SO_4, close the flask with a clean rubber stopper carrying an inlet and outlet tube (similar to that used for the H_2S treatment in P. 11), and sweep out the flask with a stream of carbon dioxide (from a tank or generator). Heat the mixture almost to boiling until all of the precipitate is dissolved (keeping a very slow stream, 1 or 2 bubbles a second, of CO_2 passing through the flask), immediately cool the solution to room temperature, add 3 ml of 85 per cent H_3PO_4, and titrate with standard permanganate solution until the first permanent pink color is obtained. From the volumes of standard ferrous sulfate and permanganate used, calculate the amount of manganese present.

If a standard solution of ferrous sulfate is not available, an equivalent amount of solid $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ can be weighed out and added. Solid sodium oxalate can be used in place of the ferrous sulfate; it reacts more slowly, but it has the advantage that it is not oxidized by oxygen of the air, and therefore the carbon dioxide can be dispensed with. The excess

oxalate is titrated with permanganate without the solution being cooled (see P. 87).

This procedure and the modifications mentioned can be used to determine the manganese dioxide (or so-called "available oxygen") in pyrolusite, native manganese dioxide. This is more resistant than the freshly precipitated material and has to be heated for a longer time. Proceed as follows:

> Weigh out a 0.25- to 0.5-g sample (which should have been ground to a very fine powder in an agate mortar and dried for at least 1 hr. at 120°C.) into a 300-ml flask and treat it with ferrous sulfate (or sodium oxalate) as directed in the procedure above. Continue the heating until no more dark particles of pyrolusite are present (a white silicious residue may remain).

P. 73. Precipitation of Aluminum

Discussion. After the oxalate has been destroyed, the aluminum can be precipitated as hydroxide by neutralizing the solution with ammonium hydroxide; the chromium, having been oxidized to chromate, remains in solution. The quantitative precipitation of aluminum has been carefully investigated by Blum,[2] and his results show that the hydroxide begins to precipitate when the hydrogen ion concentration of the solution is reduced to between 10^{-3} and 10^{-4} (depending upon the concentration of the aluminum and the anions present); that it is least soluble in an approximately neutral solution, where the precipitation is complete within usual quantitative limits; and that the precipitate becomes appreciably soluble if the hydrogen ion concentration is reduced to as low as 10^{-9} or 10^{-10}. This last effect is due to the amphoteric nature of aluminum hydroxide. By neutralization of the nitric acid with ammonium hydroxide a high concentration of ammonium salts is provided, and by the addition of only a small excess of ammonia the hydroxyl ion concentration is controlled at a very favorable value. As the precipitate tends to become colloidal and run through the filter, it is washed with an ammonium nitrate solution and not with water alone.

The precipitate produced by ammonia may consist of silicic acid or chromic hydroxide. Silica is frequently introduced during the analysis, especially by alkaline solutions which have stood in glass containers, or by the action of hot alkaline solutions on glass or porcelain vessels. Any chromium not oxidized by the chlorate or subsequently reduced would also produce a precipitate which would make the presence of aluminum doubtful. Because of this, if one

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[2] Blum, *J. Am. Chem. Soc.*, **38**, 1291 (1916).

is interested in the detection of small amounts of aluminum, the precipitate (if small or not of characteristic appearance) should be subjected to a confirmatory test. This is done by making use of the dyestuff ammonium aurintricarboxylate (commonly known by the trade name of Aluminon), which forms a compound with aluminum hydroxide in a very weakly acid solution, giving a bright red precipitate which is not rapidly decomposed when the solution is made alkaline with an excess of ammonium carbonate. Such colored compounds (which are frequently formed by adsorption processes) of a dyestuff with a hydrous oxide are known as "lakes." This particular compound does not form in an alkaline medium, but, once formed, it is stable in ammonium carbonate solution; chromium, if present, forms a similar lake, but this is decomposed by ammonium carbonate; alkaline earth elements give red compounds which are decomposed by carbonate; iron forms a violet precipitate which is changed to reddish-brown by ammonia and is thus likely to obscure the aluminum test; phosphates in excess prevent the color with aluminum, but after an ammonium hydroxide precipitation the ratio of aluminum to phosphate is usually such that the test is obtained; silicic acid gives a white precipitate.[3]

Procedure 73: PRECIPITATION OF ALUMINUM. Dilute the filtrate from the MnO_2 precipitate to 100 ml, heat it almost to boiling, and, while keeping the solution hot, add NH_4OH slowly until the solution just changes red litmus paper to blue. (White flocculent precipitate, presence of aluminum. Notes 1, 2.) If an excess of NH_4OH is added, make the solution just acid with HNO_3 and repeat the neutralization. Heat the solution for 2 to 3 min. and filter at once through an ashless paper filter. Wash the precipitate at once with 2–4 ten-ml portions of a hot wash solution containing 2 g. of NH_4NO_3 in each 100 ml of solution. Collect this wash water with the filtrate and treat it by P. 75 if chromium is present. Finish washing the precipitate with the same wash solution and treat it by P. 74.

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[3] The following articles give a discussion of this confirmatory test and of its use for the colorimetric estimation of aluminum: Hammett and Sottery, *J. Am. Chem. Soc.*, **47**, 142 (1925); Lundell and Knowles, *J. Ind. Eng. Chem.*, **18**, 60 (1926); Yoe and Hill, *J. Am. Chem. Soc.*, **49**, 2395 (1927); Middleton, *ibid.*, **48**, 2125 (1926); Corey and Rogers, *ibid.*, **49**, 216 (1927); Thrun, *J. Phys. Chem.*, **33**, 997 (1929); Winter, Thrun, and Bird, *J. Am. Chem. Soc.*, **51**, 2721 (1929); Roller, *ibid.*, **55**, 2437 (1933).

Notes:

1. For the reasons mentioned in the discussion, if only a small precipitate is obtained, the presence of aluminum should be confirmed. In that case filter and wash the precipitate and proceed as follows:

Dissolve the precipitate by pouring repeatedly through the filter 5 ml of warm 1.2 n. HCl. (If the precipitate is reddish colored, indicating iron, make this solution just alkaline with 6 n. NaOH, add 2 ml in excess, warm the mixture, filter out the precipitate, make the filtrate just acid with HCl, and add 1 ml in excess.) Add to the solution 5 ml of 3 n. $NH_4(C_2H_3O_2)$ and 5 ml of a 0.1 per cent solution of ammonium aurintricarboxylate (Aluminon). Allow the solution to stand for 5 min., make it just alkaline with 6 n. $(NH_4)_2CO_3$ reagent, and add 5 ml in excess. (Red precipitate, presence of aluminum.)

2. If it is important to know whether a small precipitate of aluminum is due to the presence of this element in the original substance, a blank analysis should be made by adding together in the same manner the reagents which have been used to produce the aluminum hydroxide precipitate. Aluminum is almost always introduced into an analysis in small quantities because of the action of reagents on vessels and containers and because of impurities in the chemicals used.

P. 74. Estimation of Aluminum

Discussion. Since no distinctive and rapid volumetric method for the estimation of aluminum is yet available, especially when the element may be present in greatly varying amounts, a gravimetric method is used. This consists in simply heating the precipitate of aluminum hydroxide (or more properly, of hydrous aluminum oxide), which is very indefinite in its composition, at a high temperature until it is converted to the oxide, Al_2O_3, which is then cooled and weighed. Blum[4] has shown that 5 to 10 min. at the highest temperature of the blast lamp is sufficient to bring most aluminum precipitates to constant weight. A somewhat longer time may be required for large precipitates.

For a general discussion of the heating of precipitates, see p. 128.

Procedure 74: ESTIMATION OF ALUMINUM. Place the funnel containing the paper with the precipitates in it in a drying oven at 100°C. (Notes 1, 2).

Select a clean porcelain crucible (20- to 30-ml capacity), cover it, and slowly heat it on a clean clay or nichrome triangle until the full heat of the blast lamp is used. Allow

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[4] Blum, *J. Am. Chem. Soc.*, **38**, 1282 (1916).

the crucible to cool until it is still noticeably warm when the hand is held near it. With a pair of crucible tongs place the crucible in a desiccator and allow it to cool to room temperature (Note 3). When it is cool, weigh the crucible to 0.1 mg. Take the funnel with the precipitate from the drying oven, and carefully remove the paper from the funnel. Fold the filter paper over the precipitate so that none can drop out, and place it in the crucible. If any precipitate adheres to the funnel, wipe it off with a clean piece of filter paper and put it in the same crucible.

Replace the crucible on the triangle, inclining it, and then very gradually heat it with the flame from a burner until the paper is dry and begins to char; then maintain a temperature such that the paper slowly chars and "smokes off" without at any time igniting (Note 5). After the paper has completely charred, increase the temperature to the full heat of the burner and maintain this temperature until most of the carbon from the filter has been burned. Turn the tilted crucible frequently. Finally place the crucible upright, cover it, and heat it at the full temperature of the blast lamp for 5 to 10 min. Cool the crucible as before and again weigh it. Repeat the heating with the blast lamp until a constant weight (Note 4) is obtained. From the weight of Al_2O_3 obtained, calculate the amount of aluminum present.

Notes:

1. If the precipitate is small (10 mg or less), an estimate of the amount of aluminum present can be made by dissolving the precipitate in 5 ml of HCl, collecting the solution in a test tube, neutralizing with NH_4OH, and comparing the precipitate with varying amounts of aluminum precipitated in a similar manner. A correction should be made for any aluminum found in the blank (Note 2, P. 73).

2. Aluminum oxide is not reduced by being heated with moist paper; therefore if a weighed crucible is ready, the moist precipitate can be transferred to the crucible and dried by direct heating. Care must be taken not to raise the temperature so rapidly as to cause spattering of the precipitate.

3. This cooling usually requires from 15 to 30 min. Do not keep the desiccator open any longer than absolutely necessary.

4. The complete dehydration of $Al(OH)_3$ may take considerable time. It is judged to have been accomplished when no further change (within a few tenths of a milligram) takes place in the weight of the precipitate.

5. Should the paper ignite, immediately extinguish it by momentarily placing the cover on the crucible.

P. 75. Estimation of Chromium

Discussion. After the ammonium hydroxide precipitation of aluminum, chromium (as chromate) is the only element of the Aluminum Group remaining in the solution. Therefore, by properly adjusting the acid concentration and adding an excess of iodide, the chromate is quantitatively reduced to the tripositive state and the iodine set free can be titrated with a standard thiosulfate solution. The procedure is essentially the same as that used for the standardization of a thiosulfate solution against potassium dichromate; for a discussion of the reaction and of the conditions affecting it, see the discussion of P. XIV.

If, through faulty procedure, any aluminum or manganese were present, they would not interfere with this estimation of chromate. Any chlorate not decomposed by the concentrated nitric acid in P. 71 reacts so slowly with the iodide under the conditions of the procedure that it does not cause an appreciable error.

Procedure 75: ESTIMATION OF CHROMIUM. If in P. 71 the presence of chromium has been indicated, evaporate the filtrate (from P. 73) to 70 to 80 ml and cool it.

If the amount of chromium present is thought to be less than about 50 mg (Note 1), transfer the cold solution to a 500-ml flask and treat it as directed in the last paragraph of this procedure.

If the amount of chromium present is thought to be more than 50 mg, transfer the cold solution to a 100-ml volumetric flask, dilute it to the mark, and thoroughly mix the solution. Pipet into a 500-ml flask a volume of solution thought to contain about 50 mg of chromium, dilute it to 80 ml, and treat it as directed in the next paragraph.

Add H_2SO_4 slowly, 1 ml at a time, until the solution changes from yellow to orange or quickly turns blue litmus red, and then add 6 ml more of H_2SO_4 and 2 g of KI. Close the flask with a clean rubber stopper, gently swirl the mixture until the KI is dissolved, and let it stand for 5 min., preferably in the dark. Add to the solution 200 ml of cold water (washing down the sides of the flask) and titrate it with standard 0.1 n. $Na_2S_2O_3$ until the brownish-yellow color of the iodine becomes indistinct (Note 2). Swirl the solution slowly as the thiosulfate is added. Add to the solution 5 ml of a starch indicator solution, and again titrate

until the blue starch color disappears (Note 2). From the volume of standard $Na_2S_2O_3$ used, calculate the amount of chromium present.

Notes:

1. The amount of chromium present can be judged by adding a standard chromate solution to a solution of the same volume containing 1 g of NH_4NO_3 and 1 drop of NH_4OH until the intensity of the yellow color in the two solutions is the same.

2. It should be remembered that the solution does not become entirely colorless, as the tripositive chromium gives it a greenish color.

TABULAR OUTLINE IX

The Analysis of the Alkaline Earth Group

Filtrate from the Ammonium Sulfide Group Precipitation: Alkaline Earth and Alkali Group Elements, Ammonium Salts
Evaporate, add 16 n. HNO_3, evaporate to dryness. (*Ignite if $HClO_4$ is present.*)
Dissolve residue. Add $(NH_4)_2CO_3$ and C_2H_5OH. (P. 81)

Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3 \cdot 6H_2O$, $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$
Dissolve in HNO_3; neutralize. Add $HC_2H_3O_2$ and $NH_4C_2H_3O_2$.
Add K_2CrO_4; heat. (P. 82)

Filtrate: Na^+ and K^+, $(NH_4)_2{}^+CO_3^-$, C_2H_5OH
(To P. 91)

Precipitate: $BaCrO_4$

Dissolve in HCl.
Ba^{++}, $Cr_2O_7^-$

Add KI.
(Ba^{++}, Cr^{+++}, I_3^-)

Dilute, titrate with $Na_2S_2O_3$; starch indicator.
(Ba^{++}, Cr^{+++}, I^-, $S_4O_6^-$)
(P. 83)

Filtrate: Sr^{++}, Ca^{++}, Mg^{++}, $HC_2H_3O_2$, $C_2H_3O_2^-$, $Cr_2O_7^-$
Add NH_4OH and C_2H_5OH (also more K_2CrO_4). (P. 84)

Precipitate: $SrCrO_4$

Dissolve in $HC_2H_3O_2$.
(Sr^{++}, $Cr_2O_7^-$)

Add $K_2C_2O_4$; make alkaline with NH_4OH.

Precipitate: $SrC_2O_4 \cdot H_2O$

Filtrate: *Discard.*

Dissolve in HCl, dilute.
(Sr^{++}, $H_2C_2O_4$)

Heat to 80° to 90°C.
Titrate with $KMnO_4$.
(Sr^{++}, CO_2, Mn^{++})
(P. 85)

Filtrate: Ca^{++}, Mg^{++}, $C_2H_3O_2^-$, CrO_4^-, NH_4OH, C_2H_5OH
Add NH_4Cl, $K_2C_2O_4$. (P. 86)

Precipitate: $CaC_2O_4 \cdot H_2O$

Dissolve in H_2SO_4.
($CaSO_4$, $H_2C_2O_4$)

Dilute; heat to 80° to 90°C.
Titrate with $KMnO_4$.
(CO_2, Mn^{++})

(P. 87)

Filtrate: Mg^{++}, $Mg(C_2O_4)_2^-$, $C_2H_3O_2^-$, CrO_4^-, C_2H_5OH, $C_2O_4^-$, NH_4OH
Add Na_2HAsO_4, NH_4OH.
(P. 88)

Precipitate: $MgNH_4AsO_4 \cdot 6H_2O$

Filtrate: *Discard.*

Dissolve in HCl.
(Mg^{++}, H_3AsO_4)

Add KI.
(Mg^{++}, H_3AsO_3, I_3^-)

Titrate with $Na_2S_2O_3$.
(Mg^{++}, H_3AsO_3, I^-, $S_4O_6^-$)
(P. 89)

The Analysis of the Alkaline Earth Group

P. 81. Precipitation of the Alkaline Earth Group

Discussion. Two general methods are used in systems of qualitative analysis for the precipitation of the elements known as the Alkaline Earth Group. In the most generally used of these, the filtrate from the Ammonium Sulfide Group precipitation is concentrated by evaporation and then ammonium carbonate is added. The large amount of ammonium chloride present, which has accumulated during the course of the analysis, tends to prevent the precipitation of magnesium; thus only barium, strontium, and calcium are included in the group. In the alternative method, which is used here, magnesium is caused to precipitate with the other elements of the group (1) by the removal of the ammonium chloride before the precipitation, (2) by using a high concentration of ammonium carbonate and ammonium hydroxide (the latter being added to repress the hydrolysis of the carbonate) and (3) by the addition of alcohol, as most inorganic salts, especially if they are ionized, are much less soluble in alcohol than in water. This method has been adopted because the experiments of Bray[1] have indicated that it is impossible to find conditions under which barium, strontium, and calcium can be completely precipitated with ammonium carbonate without causing partial precipitation of magnesium when it is present in large amounts. It is also true that the precipitation of the first three elements is much more rapid and complete under the conditions which cause complete precipitation of magnesium. Bray (*loc. cit.*) has also shown that, with conditions similar to those of this procedure, 0.5 mg of any element of the group will give a distinct turbidity in 15 min.; that with 500 mg of any element not more than 0.2 mg remained in the filtrate when the precipitates were filtered after 30 min.; that the precipitates became crystalline more rapidly and were more easily filtered if the mixtures were shaken frequently; and that, if the alcohol was omitted, no precipitates were obtained when 0.5 to 1 mg of calcium or magnesium was present. Gooch and Eddy[2] have shown that magnesium can be quantitatively precipitated by an ammonium carbonate reagent in the presence of

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[1] Bray, *J. Am. Chem. Soc.*, **31**, 611 (1909).

[2] Gooch and Eddy, *Am. J. Sci.* (4), XXV, 444.

alcohol and that neither sodium nor potassium are carried with the precipitate in significant amounts.

The Removal of Ammonium Salts. The ammonium chloride is removed from the solution, in the absence of perchlorate, by evaporation with concentrated nitric acid; in this process the ammonia is oxidized to nitrogen by the products of the reaction between the nitric acid and the chloride. This method is more convenient for removing ammonium salts and less liable to loss from spattering than the more familiar method of heating to a sufficiently high temperature to voltilize them. If perchlorate is present (from the use of perchloric acid in the preparation of the solution), it must be removed or destroyed in order to prevent the possible precipitation of the potassium as perchlorate with this group. It has been found by Noyes and Bray[3] that the perchlorate is destroyed by simple ignition because of its reaction with the ammonium salts present. Neither the ammonium chloride nor the perchlorate has to be quantitatively removed at this point, as a small amount of the first would not prevent the precipitation of magnesium, nor would a trace of perchlorate cause the precipitation of potassium; large amounts would cause these effects.

Either of these methods of removing the ammonium salts produce a vigorous oxidizing action, which results in the conversion of any sulfur or sulfur compounds present (various thionic acids, usually introduced into the analysis during the Hydrogen Sulfide and Ammonium Sulfide Group precipitations) into sulfate. This sulfate may cause the partial or, if they are present in small amounts, complete precipitation of barium and strontium; if it is present in large amounts, calcium may be partially precipitated. As the residue from the treatment to destroy ammonium salts is normally treated with water and any insoluble material is discarded, these elements may be partially, or even completely, lost.

To avoid this possibility, a treatment for the recovery of these elements is provided in Note 3 of the procedure. This consists in treating any insoluble residue with a solution containing sodium carbonate and a small amount of sodium hydroxide; the latter is added to repress the hydrolysis of the carbonate. It is intended that this treatment metathesize the sulfates into carbonates, as represented by the equation (for $BaSO_4$)

$$BaSO_{4(s)} + CO_3^{=} = BaCO_{3(s)} + SO_4^{=}.$$

[3] Noyes and Bray, *Qualitative Analysis for the Rare Elements*, Macmillan, 1927, p. 236.

The carbonate precipitate is then combined with the subsequent ammonium carbonate precipitate of this group and dissolved in nitric acid.

The Metathesis of Slightly Soluble Compounds. Upon reference to solubility data, it will be found that barium carbonate is considerably *more* soluble than barium sulfate; therefore it is appropriate to question to what extent the desired metathetical reaction will proceed. This can be approximately predicted as follows:

As soon as a precipitate of barium carbonate is formed, the solubility-product principle for both barium sulfate and barium carbonate can be applied (assuming that these precipitates are in equilibrium with the solution). Therefore the two solubility-product expressions can be written as follows:

$$[Ba^{++}][SO_4^{=}] = K_{BaSO_4}. \quad (1)$$

$$[Ba^{++}][CO_3^{=}] = K_{BaCO_3}. \quad (2)$$

As $[Ba^{++}]$ is common to both and has the same value (the expressions apply to the same solution), it can be eliminated and the two expressions can be combined to obtain the following:

$$\frac{[SO_4^{=}]}{[CO_3^{=}]} = \frac{K_{BaSO_4}}{K_{BaCO_3}}. \quad (3)$$

This expression shows that, in any solution which is saturated with both barium sulfate and barium carbonate, the ratio of the concentration of sulfate ion to that of carbonate ion will be determined by the ratio of the solubility product of barium sulfate to that of barium carbonate. For the case being considered, this ratio has the value

$$\frac{[SO_4^{=}]}{[CO_3^{=}]} = \frac{K_{BaSO_4}}{K_{BaCO_3}} = \frac{1 \times 10^{-10}}{7 \times 10^{-9}} = 0.014.$$

Therefore (assuming the conditions obtaining in the proposed treatment), if a solution 1.5 m. in carbonate is added to a $BaSO_4$ precipitate, metathesis will take place, the carbonate concentration decreasing and the sulfate concentration increasing until the above ratio is attained or the supply of $BaSO_4$ is exhausted. If it is assumed that an excess of $BaSO_4$ is present and if x represents the equilibrium sulfate concentration, then the carbonate concentration will be $1.5\text{-}x$.[4] Solving for x, we find the concentration of the sulfate to be

[4] This assumes (as is justified in this case because of the very slight solubility of these precipitates) that for each mole of $SO_4^{=}$ appearing in the solution a mole of $CO_3^{=}$ is precipitated.

0.021 m., which indicates that, with 25 ml of 3 n. sodium carbonate, approximately 0.12 g of barium sulfate should be metathesized.[6]

It is seen from these calculations that the amount of a given precipitate which can be metathesized into some other compound by such a process is determined by three factors: (1) the relative solubilities of the two compounds, (2) the concentration of the metathesizing ion, and (3) the volume of the metathesizing solution. It is possible, as was calculated above for the case of barium sulfate, and as is experimentally true, to cause the complete metathesis of a limited amount of a precipitate into a more soluble compound. However, as solubility data would indicate, a much larger amount of strontium or calcium sulfate is metathesized under the same conditions.

It is to be noted that, in applying the above principles to the metathesis of a precipitate into another of a different ionic type, the simple ratio of ion concentrations to solubility products does not hold; thus, for the metathesis of silver chloride into silver carbonate, which can be represented by the equation

$$2AgCl_{(s)} + CO_3^{=} = Ag_2CO_{3(s)} + 2Cl^-,$$

the expression

$$\frac{[Cl^-]^2}{[CO_3^{=}]} = \frac{(K_{AgCl})^2}{K_{Ag_2CO_3}}$$

is obtained. However, the same principles apply, and calculations similar to the one above can be made.

It will also be seen, particularly in the analysis of the Alkaline Earth Group, that the completeness with which two ions may be separated by a common precipitant can be predicted from the proper treatment of the solubility-product principle.

Procedure 81: PRECIPITATION OF THE ALKALINE EARTH GROUP. Make the filtrate from the Ammonium Sulfide Group precipitation acid with HCl and evaporate it in a large flask until salts begin to crystallize or the mixture begins to bump (Note 1).

If $HClO_4$ has *not* been used in the preparation of the solution, add to the mixture 5 to 10 ml of 16 n. HNO_3 and warm it gently as long as a vigorous evolution of gas takes place.

[6] It is to be emphasized that this figure should be considered as only a very approximate indication of the experimental facts. In these relatively concentrated solutions the activities of the ions are undoubtedly quite different from their concentrations.

Finally, evaporate the solution almost to dryness, keeping the mixture in constant motion or allowing the evaporation to take place on a steam or sand bath. Add 5 ml more of 16 n. HNO_3, washing the sides of the vessel, evaporate the mixture just to dryness, and treat it by the last paragraph of this procedure.

If $HClO_4$ has been used in the preparation of the solution, transfer the mixture to a capacious casserole, add 5 ml of 16 n. HNO_3 (Note 2), and evaporate it to dryness over a steam bath. Remove the casserole from the steam bath and keep a flame from a burner continuously moving over the surface of the residue until no more burning appears to take place and no more salts appear to be volatilized. Allow the dish to cool, moisten all parts of the residue with 1 to 2 ml of 3 n. NH_4Cl, and again heat as directed above. Finally, heat the dish, keeping it in constant motion, until no more fuming of the salts occurs. Do not heat the dish so intensely that the porcelain at any time shows a reddish glow.

Add to the residue 1 ml of HNO_3 and 10 ml of water, heat the solution just to boiling, and transfer it with the aid of 5 ml of water to a 200-ml flask (Note 3). Add slowly 20 ml of $(NH_4)_2CO_3$ reagent (Note 4) and 20 ml of 95 per cent C_2H_5OH and shake the solution frequently for 15 min.; or, preferably, let it stand for several hours. (White precipitate, presence of the Alkaline Earth Group elements.) If a large precipitate forms, add to the mixture 10 ml more of each of the last two reagents. Allow the precipitate to settle, and decant the solution through a paper filter. Wash the precipitate by decantation with three to five 5-ml portions of a solution containing 2 volumes of the $(NH_4)_2CO_3$ reagent to 1 volume of alcohol. Collect these washings with the filtrate and treat it by P. 91. Treat the precipitate by P. 82.

Notes:

1. If, on evaporation of the solution, there forms a precipitate of sulfur, or of traces of the sulfides of the previous groups, these should be filtered out and discarded in order to minimize the formation of sulfate in the subsequent treatment with HNO_3.

2. The HNO_3 is added to prevent the possibility of an explosion on evaporating the perchloric acid mixture (see the discussion of P. 4).

3. If there is a white residue after the solution is boiled, it probably con-

sists of the sulfates of barium, strontium, or calcium. In this case proceed as follows:

Filter the mixture through a small filter, wash the residue, and transfer it to a casserole with 10 to 25 ml of 3 n. Na_2CO_3 and 1 ml of 6 n. NaOH. Boil the mixture for 5 min. Reserve the mixture until the ammonium carbonate precipitate of the Alkaline Earth Group elements (last paragraph of the procedure above) has been washed, and then filter it through the same filter which has been used to collect the ammonium carbonate precipitate. Wash the precipitate with water and discard the filtrate. (Do not add this Na_2CO_3· NaOH filtrate, or the washings, to the filtrate from the ammonium carbonate precipitate, as the latter is to be treated by P. 91 and tested for the Alkali Group elements.)

Any sulfur or sulfur compounds introduced during the treatments with hydrogen or ammonium sulfide will be oxidized to sulfate during the evaporation with nitric acid and will precipitate the sulfates of the elements mentioned. By this treatment these small sulfate precipitates are converted into carbonates (see the discussion above) and can be united with the ammonium carbonate precipitate.

4. See the Appendix for the preparation of this reagent, which is 3 f. in $(NH_4)_2CO_3$ and 6 f. in NH_4OH.

THE SEPARATION OF THE ALKALINE EARTH GROUP ELEMENTS

General discussion. The elements included in the Alkaline Earth Group are all found in the second group of the periodic table; calcium, strontium, and barium appear in the same sub-group, and, as would be predicted, the compounds of these elements do not vary widely in their properties. They exhibit only one stable valence state; they are distinctly basic and show no amphoteric reactions; there is relatively little tendency toward complex ion formation; and the solubilities of their salts, on which their analytical detection and separation depend, vary gradually on passing from one member to the next of the series.

Although various separations were investigated, the method used for the separation of these elements is essentially that developed by Bray[6] for their qualitative separation. Briefly stated, this method consists in precipitating first the barium as chromate from a weakly acid solution, then strontium as chromate by making the solution alkaline with ammonia and adding alcohol, next calcium as the oxalate, and finally magnesium as magnesium ammonium arsenate. Because of the relatively small solubility differences existing between the compounds of the elements of this group, it has been necessary in precipitating these elements to adopt the expedient of adding at

[6] Bray, *J. Am. Chem. Soc.*, **31**, 611 (1909).

first only sufficient precipitant to give a sensitive test for the element being precipitated. If the amount needed to precipitate completely a large quantity were added at first, it would tend to precipitate the next least soluble of the remaining elements. If a large precipitate is obtained with the first addition, then sufficient precipitant is added to cause complete precipitation; as a definite amount of sample is taken for analysis, the amount of any two elements which can be present is limited.

Owing to the small difference in the solubility of their salts, and probably to their similar crystal structure, coprecipitation is found to occur to a marked extent. Various efforts are made to minimize this, such as adding the precipitant very slowly while vigorously shaking the solution; these conditions also favor the formation of precipitates which can be more easily filtered. In spite of these efforts, experiments have shown that, when large amounts of two elements adjacent in the periodic table are present, a considerable fraction of the soluble one may be found in the precipitate. A second expedient is therefore provided; this consists in filtering the solution by decantation, dissolving the main portion of the precipitate, and reprecipitating it in a manner involving a relatively small expenditure of time. When a more exact separation of the elements of this group is desired, this process can be utilized.

The results of confirmatory analyses of this group are shown in Table XXVIII. These analyses were begun with the ammonium carbonate precipitation of P. 81.

TABLE XXVIII

TEST ANALYSES OF THE ALKALINE EARTH GROUP ELEMENTS

Analysis No.	Amount of Each Element Taken and Found (mg)							
	Barium		Strontium		Calcium		Magnesium	
	Taken	Found	Taken	Found	Taken	Found	Taken	Found
1	125	127	119	116	124	127	120	121
2	50	51	1	1	297	293	240	243
3	250	251	440	432	1	5	240	243
4	50	49.6	0	0	37.5	37.6	0	0
5	0.3	0	0	0	37.5	41	36	35
6	0	0	72	70.6	0	0	36	37.2
7	25	26.2	24	25	0	Trace	0.3	0
8	1	4	0	0	25	26 6	96	94 6

Note: Analyses 4 to 8, inclusive, were carried out by a selected group of students in a sophomore course in analytical chemistry at the California Institute of Technology. They had had no previous experience with the analysis of this group.

P. 82. Precipitation of Barium

Discussion. The separation of barium is based upon the fact that, of the elements of this group, barium forms the least soluble chromate. Experiments have shown that, when a *limited* amount of chromate is added to an acid solution in which the hydrogen ion is closely controlled by means of a carefully regulated ratio of acetic acid to acetate, 0.5 mg of barium will give a perceptible precipitate, while 500 mg of strontium, which forms the next least soluble chromate, remain in solution. If a considerable precipitate is obtained, an additional amount of chromate is then added in order to precipitate the barium completely. Experiments[7] have shown that, when 250 mg each of barium and strontium are present, from 5 to 10 mg of the strontium will be found with the precipitate. Because of this, the precipitant is added, and the mixture is heated, shaken, and treated, in such a manner that the solution can be filtered by decantation and the precipitate can be quite completely retained in the flask. The precipitate is then dissolved in a minimum amount of hydrochloric acid and reprecipitated, and the filtration is carried out through the original filter; the entire process takes only a few minutes.

The confirmatory experiments of Bray[8] have shown that, if the chromate is added all at once and if 500 mg of barium are present, as much as 3 mg of strontium may be so completely carried out with the precipitate as to escape subsequent detection in the filtrate, but that, if the chromate is added slowly, 1 mg of strontium can be readily detected.

The effect of acid on the solubility of barium (and other chromates) is due, first, to the fact that chromic acid is not a highly ionized acid. The second hydrogen ion is ionized to about the same extent as is the first hydrogen ion of carbonic acid or the second one of phosphoric acid; the equilibrium constant for the reaction $HCrO_4^- = CrO_4^= + H^+$ has been estimated[9] to be 3.2×10^{-7}. In addition to this, there is an equilibrium between hydrochromic acid and dichromate ion, as follows:

$$2HCrO_4^- = H_2O + Cr_2O_7^=.$$

The equilibrium constant for this reaction is 43. Therefore, as

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[7] The author is indebted to Dr. Carter Gregory for an extensive experimental investigation of the methods for the analysis of this group.

[8] Bray, *loc. cit.*

[9] Neuss and Rieman, *J. Am. Chem. Soc.*, **56**, 2238 (1934).

there is usually only a small concentration of hydrochromate ion in solutions, the predominant equilibrium is between the chromate and the dichromate ions, as follows:

$$2CrO_4^- + 2H^+ = Cr_2O_7^- + H_2O.$$

The equilibrium constant for this reaction can be calculated from those given above to be 4.2×10^{14}. It is seen that the hydrogen ion enters into this equilibrium as the square of its concentration and that, by proper adjustment, the chromate ion concentration can be controlled quite closely and can be varied through a wide range. The dichromates are, in general, soluble.

Procedure 82: PRECIPITATION OF BARIUM. Transfer most of the $(NH_4)_2CO_3$ precipitate (from P. 81) from the filter to the flask with the aid of a stirring rod (Note 1). Dissolve the precipitate left on the filter by pouring dropwise through it a 5- to 25-ml portion of cold HNO_3 (collecting the acid in the flask with the precipitate) and wash the filter with 3 to 5 ml of water added dropwise. Add 15 n. NH_4OH until the solution is alkaline and then HNO_3 (dropwise) until it is again acid, and evaporate or dilute it until the volume is 35 ml. Add to the solution just 1 ml of $HC_2H_3O_2$ and 10 ml of neutral (Note 2) 3 n. $NH_4C_2H_3O_2$, heat nearly to boiling, and add, 2 drops at a time and shaking after each addition 3 ml of 3 n. K_2CrO_4 (Notes 3 and 4). Heat the solution nearly to boiling for 2 min., swirling it continuously. (Yellow precipitate, presence of barium.) If a considerable precipitate forms, add, in the same manner as above, 2 ml more of K_2CrO_4 and again heat the solution for 2 min. Allow the precipitate to settle completely and decant the solution through an asbestos filter.

If there is only a small precipitate (50 mg or less), wash it with two to three 5-ml portions of hot water, collecting the wash water with the filtrate. Treat the filtrate by P. 84. Wash the precipitate and filter with hot water, added dropwise, until the wash water is no longer colored (Note 5). Discard these washings. Treat the precipitate by P. 83.

If there is a large precipitate and if the presence of strontium is suspected (Note 6), dissolve the precipitate remaining in the flask with 2 to 5 ml of cold HCl and 5 ml of water (Note 7). Add 1 ml of K_2CrO_4 and then NH_4OH, a few drops at a time, until the color changes from orange

to light yellow, and 2 ml more. Then add $HC_2H_3O_2$ until the original color returns; heat the mixture almost to boiling for 2 to 5 min., shaking it frequently; allow the precipitate to settle and wash it as directed in the preceding paragraph. Treat the precipitate and filtrate as directed there.

Notes:

1. If the precipitate were treated on the filter with HNO_3, considerable loss by spattering might result from the evolution of CO_2.

2. The $NH_4C_2H_3O_2$ of commerce frequently contains $HC_2H_3O_2$ in considerable amounts; for this reason the reagent should be tested and, if acid, made neutral by addition of NH_4OH until litmus is turned neither red nor blue but remains an indeterminate purplish color. Neutral 3 n. $NH_4C_2H_3O_2$ can also be made by mixing equal volumes of exactly 6 n. $HC_2H_3O_2$ and 6 n. NH_4OH.

3. It is essential that the precipitation of the $BaCrO_4$ be made very slowly; otherwise it separates in such a finely divided form that it will not settle, may even pass through the filter, and will tend to carry down strontium.

4. The solution should be absolutely clear before the chromate is added, as it is difficult to detect the small yellow turbidity caused by 1 mg or less of barium. If the detection of these amounts of barium is of importance, the solution should be filtered after the chromate is added, even when it is apparently clear, and the filter should be washed and then examined.

5. This washing should be done with the smallest possible volume of water; however, the estimation of barium in the next procedure requires that the chromate be removed so completely that its color cannot be seen when 2 to 3 ml of the wash solution is collected in a test tube.

6. This next operation is carried out for the purpose of removing the strontium coprecipitated with the $BaCrO_4$. This amount will be small unless considerable amounts of both barium and strontium are present, and even then it should not exceed 10 mg. Therefore, this step should be omitted if the size of the $(NH_4)_2CO_3$ precipitate (P. 81) or a knowledge of the substance being analyzed indicates that strontium is unlikely to be present in considerable amount, or if a precise estimate of the two elements is not desired.

7. If a very small fraction of the precipitate has been carried onto the filter, only that in the flask need be dissolved. If a considerable portion of it is on the filter, it should be dissolved by pouring the HCl dropwise through it and then washing the filter with the water to be added.

P. 83. Estimation of Barium

Discussion. In the method used here for the estimation of barium, the precipitate of barium chromate (obtained and washed free from excess of chromate in P. 82) is first dissolved by means of cold

hydrochloric acid. (The effect of hydrogen ion on the solubility of the chromates has been pointed out in the discussion of P. 82.) The dichromate in the acid solution is then determined iodometrically, an excess of potassium iodide being added and the liberated iodine being titrated with standard thiosulfate. In an experimental study[10] of this process, results exact to 0.3 per cent have been obtained with amounts of barium varying from 50 to 350 mg. Hydrochloric acid is used because it very readily dissolves the precipitate from the filter and because it was found that barium chromate was not completely metathesized by sulfuric acid, even upon the addition of the iodide. This incomplete metathesis was probably due to mechanical inclusion of the chromate by the precipitated barium sulfate. It was found that, if the barium chromate was precipitated in P. 82 by rapid addition of the chromate, the results were likely to be from 1 to 1.5 per cent too high, probably because chromate is carried down by the precipitate. For a discussion of the conditions under which the dichromate-iodide reaction should be carried out, see the references cited in the discussion of P. XIV, "The Standardization of a Thiosulfate Solution Against Potassium Dichromate."

Procedure 83: ESTIMATION OF BARIUM. Dissolve the precipitate on the filter by pouring dropwise through it just 10 ml of HCl, collecting the solution in a 600-ml beaker, and washing the filter with just 40 ml of water (Note 1). Transfer the precipitate from the flask to the same beaker with the aid of just 50 ml of water. Break up the precipitate, stir it until it dissolves, add 2 to 3 g of solid KI, and gently swirl the mixture until the KI is dissolved. Cover the solution with a watch glass and allow it to stand in a dark place for 5 min.

Dilute the solution to 400 ml, titrate it with 0.1 n. $Na_2S_2O_3$ solution (Note 2) until the color of the iodine becomes indistinct, add 5 ml of a starch indicator solution, and again titrate the solution until the blue starch color changes to a light green. From the volume of standard $Na_2S_2O_3$ used, calculate the amount of barium present.

Notes:

1. If a very small precipitate (1 to 2 mg) has been obtained, it should be dissolved in 2 to 5 ml of HCl, treated by the last paragraph of P. 82, and then compared with known amounts of barium precipitated under similar

[10] Unpublished experiments by K. H. Lau.

conditions; or, if desired, the presence of barium can be confirmed by evaporating the HCl solution to 0.1 to 0.2 ml, dipping a platinum wire (one which has been cleaned and then held in a flame until it no longer causes a color) into it, and then holding the wire in a small colorless flame. A green color in the flame indicates the presence of barium.

2. For notes on this titration, see P. XIV.

P. 84. Precipitation of Strontium

Discussion. The precipitation of strontium is the next step in the analysis of this group. Strontium is also precipitated as the chromate. This is accomplished by the addition of an excess of ammonia to the acetic acid filtrate from the barium precipitation and by the addition of alcohol to the solution. As was pointed out in the discussion of P. 82, the chromate ion concentration is tremendously increased by decreasing the hydrogen ion concentration of the solution. Also, by changing from a solvent medium of water to one containing a considerable proportion of alcohol, the solubility of the strontium chromate is further reduced. As was explained in P. 82, only such amounts of these reagents are first added as will give a sensitive test for small amounts of strontium; larger amounts are added if they are needed to precipitate large quantities of strontium. Even if the larger amounts of alcohol and chromate are added, calcium chromate will not precipitate if calcium is present alone; however, it tends to be coprecipitated with the strontium chromate. For that reason, if a more complete separation of these elements is desired, a double precipitation should be made when considerable strontium is found and calcium is also likely to be present. Thus, it was found that, with 250 mg of each element, about 10 mg of calcium were coprecipitated; no calcium could be detected with the strontium after making a reprecipitation.

Procedure 84: PRECIPITATION OF STRONTIUM. Add 15 n. NH_4OH to the filtrate from the $BaCrO_4$ precipitation (which should have a volume of not over 60 ml) until the color changes from orange to yellow, and then add 5 ml more. Add to the solution 3 ml of 3 n. K_2CrO_4, cool, and then add, 2 ml at a time and shaking the mixture vigorously after each addition, 30 ml of 95 per cent C_2H_5OH (ethyl alcohol). If it is thought that more than 50 to 100 mg of strontium are present, add 3 ml more of 3 n. K_2CrO_4 and, as directed above, 10 ml more of C_2H_5OH. Let the mixture stand at least 10 min (Note 1). (Light yellow precipi-

tate, presence of strontium.) Let the precipitate settle and decant the solution.

If there is only a small precipitate (50 mg or less), wash it with 2 portions of a solution made by adding 1 ml of 15 n. NH_4OH to 10 ml of 50 per cent alcohol. Collect the washings with the filtrate. Treat the filtrate by P. 86. Treat the precipitate by P. 85.

If there is a large precipitate and calcium may be present (Note 2), do not wash it but completely drain the solution from it. Dissolve the precipitate in the flask in 5 to 10 ml of warm $HC_2H_3O_2$, neutralize the solution with 15 n. NH_4OH as directed above, add 2 ml more, and dilute it to 30 ml. Add 2 ml of 3 n. K_2CrO_4 and, as directed above, 20 ml of 95 per cent alcohol, and then let the mixture stand for 10 min. Allow the precipitate to settle and decant the solution through an asbestos filter, draining all the solution from the precipitate. Add this solution to the original filtrate and treat it by P. 86. Treat the precipitate by P. 85.

Notes:

1. If other operations can be carried out in the meantime, it is advisable to let this precipitate stand for 30 min. to 1 hr., as it is then much more readily filtered. If the flask is tilted during this time (by inclining it in a large casserole or clamping it), the precipitate so settles that it is not stirred up when the solution is decanted.

2. In the majority of cases, this procedure to remove any coprecipitated calcium may be omitted; the considerations discussed in Note 6, P. 82, also apply here.

P. 85. Estimation of Strontium

Discussion. It would seem that the strontium could be estimated by an iodometric process identical with that used with the barium chromate precipitate; however, washing the rather soluble strontium chromate precipitate free of chromate without appreciably dissolving it was found to be extremely difficult. The method which was adopted depends upon converting the strontium chromate to oxalate, washing this precipitate free from the excess of oxalate, dissolving it in hydrochloric acid, and then titrating the oxalate obtained with standard permanganate solution. The strontium chromate precipitate is readily dissolved in acetic acid, and, because strontium oxalate is less soluble than the chromate,

and also because of the presence of an added excess of oxalate, strontium oxalate precipitates as the solution is neutralized. Hydrochloric instead of sulfuric acid is used for dissolving the precipitate of strontium oxalate, since it avoids the formation of strontium sulfate, which tends to enclose particles of undissolved oxalate.

The titration of oxalate with permanganate, which has been used in P. XIV for the standardization of a permanganate solution against sodium oxalate, is preferably carried out in the presence of sulfuric acid; when hydrochloric acid is used, there is a pronounced tendency for chloride to be oxidized by the permanganate. However; studies by Gooch and Peters,[11] by Baxter and Zanetti,[12] and by Kolthoff[13] have established that, by titrating in the presence of a relatively high concentration of manganous ion or at an elevated temperature (70° to 80°C.), the oxalate-permanganate reaction can be made to proceed quantitatively and without significant reduction of the permanganate by the hydrochloric acid.

Procedure 85: ESTIMATION OF STRONTIUM. Dissolve the precipitate on the filter (Note 1) by pouring through it 3 to 5 ml of $HC_2H_3O_2$ and then wash the filter with 10 to 20 ml of water, collecting the solutions in the flask with the remainder of the precipitate. Warm the mixture until the precipitate dissolves, dilute it to 50 ml, and heat it to boiling.

Add to the solution, a few drops at a time and shaking after each addition, 3 to 5 ml of 3 n. $K_2C_2O_4$; slowly add NH_4OH until the solution is alkaline and then add 5 ml more (Note 2). Heat the mixture to boiling for 3 to 5 min., cool it with tap water, shake it vigorously, and let it stand until the precipitate settles. Decant the solution through a paper filter and wash the precipitate by decantation with 5- to 10-ml portions of hot 0.6 n. NH_4OH until no precipitate forms when 1 drop of 1 n. $Ca(NO_3)_2$ is added to a 5-ml portion of the wash water.

Dissolve the precipitate in the flask with 50 ml of warm (40° to 50°C.) 3 n. HCl and transfer the solution to a 400- to 600-ml beaker (Note 3). Remove the paper with the precipitate from the funnel, open it against the side of the

[11] Gooch and Peters, *Z. anorg. allgem. Chem.*, **21**, 185 (1899).
[12] Baxter and Zanetti, *Am. Chem. Jour.*, **33**, 500 (1905).
[13] Kolthoff, *Z. anal. Chem.*, **64**, 204 (1924).

beaker, and then wash the precipitate from the paper with a stream of water from a wash bottle until the total volume of the solution is 100 to 125 ml. Heat the mixture to 70° to 80°C., add to it 5 ml of the Zimmermann-Reinhardt "preventative" solution (see P. 53*A*), and titrate it slowly with 0.1 n. $KMnO_4$, stirring the solution constantly, until the first pink color is obtained. Shove the filter paper from the side of the beaker into the solution and again titrate until a pink color is obtained which remains for 10 sec. (Note 2, P. 87). From the volume of standard permanganate used, calculate the amount of strontium present.

Notes:

1. If only a small precipitate is obtained, it may be due to a small amount of barium which had not been precipitated in P. 82. In order to confirm the presence of strontium, proceed as follows:

Pour repeatedly through the filter a hot solution made by adding 10 drops of $HC_2H_3O_2$ and 1 ml of 1 n. K_2CrO_4 to 5 ml of 3 n. $NH_4C_2H_3O_2$. Add 15 n. NH_4OH until the orange color changes to yellow and 1 ml more; then add 5 ml of alcohol. (Yellow precipitate, presence of strontium.)

Barium chromate would not be dissolved by the solution which is poured through the filter; calcium chromate would be dissolved, but the amount that might be precipitated in P. 84 would not be likely to cause a precipitate here. Even 0.3 mg of strontium will give an easily perceptible turbidity upon addition of the alcohol. The amount present can be estimated by comparison with precipitates produced by known amounts of strontium.

Strontium gives a red color in a flame. An additional test can be made in the same manner as was suggested for the barium precipitate.

2. By adding the reagents in this manner a coarsely crystalline precipitate is obtained which is very readily washed by decantation; strontium oxalate precipitated from an alkaline solution by rapid addition of oxalate is likely to be difficult to filter.

3. If a large precipitate has been obtained, it is recommended that the HCl solution be poured repeatedly through the precipitate, cooled, and transferred to a 100-ml volumetric flask, the filter be washed with cold 3 n. HCl, and the solution be collected in the volumetric flask until the calibration is reached. After the contents are thoroughly mixed, portions may be pipeted out and duplicate titrations may be made.

P. 86. Precipitation of Calcium

Discussion. This procedure is based upon the conventional quantitative separation of calcium from magnesium by precipitation of calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$, from an alkaline solution.

When precipitated from a cold neutral or alkaline solution, calcium oxalate is so finely divided as to be difficult to filter and wash. Therefore in quantitative work the oxalate is usually added to a warm *acid* solution and ammonia is then slowly added in excess; by this means coarse, granular, easily filtered crystals can be obtained. This method cannot be used here, as in an acid solution the chromate previously added would be at least partially reduced by the oxalate and alcohol present. Therefore in the procedure below the oxalate is added dropwise to a hot solution; the precipitates thus produced usually can be filtered without undue difficulty. Potassium oxalate is used as the precipitant, as it is more soluble, and less coprecipitated, than either the ammonium or the sodium salt.

Magnesium oxalate is only moderately soluble in water (0.3009 g of $MgC_2O_4 \cdot 2H_2O$ per liter at 18°C.); therefore it would appear to be impossible to effect a separation of calcium from considerable amounts of magnesium by this procedure. That such a separation is possible is due to two specific properties of magnesium oxalate solutions. First, magnesium oxalate forms unusually stable supersaturated solutions in which the normal solubility can be greatly exceeded. W. M. Fischer[14] has shown that under certain conditions a solution of magnesium oxalate will remain supersaturated to 60 times its normal solubility for ½ hr.; to 40 times for 2 hr.; to 25 times for 4 hr.; to 10 times for 40 hr.; and to 4 times for greater than 10 weeks. The time for which the solution will remain supersaturated is decreased by the presence of other ions, by scratching of the containing vessel, by mechanical agitation, and by increase in temperature, the latter effect being quite pronounced above 80°C. Second, the solubility of magnesium oxalate is *increased*, rather than decreased, by an excess of oxalate, being about seven times as great in a solution approximately 0.35 f. in ammonium oxalate as in pure water.[15]

It has long been known that calcium oxalate was more soluble in solutions of magnesium salts than in water, and the effect has been attributed to the formation of either un-ionized magnesium oxalate or to a complex ion; the data cited above, showing a marked

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[14] Fischer, *Z. anorg. allgem. Chem.*, **153**, 62 (1926).

[15] Bobtelsky and Malkawa-Janowskaja, *Z. angew. Chem.*, **40**, 1436 (1927), present extensive data showing that the solubility of magnesium oxalate becomes greater in solutions of ammonium oxalate, oxalic acid, and ammonium chloride.

increase in solubility with an excess of oxalate, indicate complex ion formation. Because of this it is necessary to add sufficient oxalate, not only to precipitate the calcium, but to combine with the magnesium and convert it into the complex ion. Too large an excess should not be added here, as it has been shown by Hall[16] that the subsequent precipitation of magnesium may be thereby prevented. A considerable amount of ammonium chloride has also been found to aid in preventing the precipitation of magnesium oxalate with the calcium oxalate.[17]

Procedure 86: PRECIPITATION OF CALCIUM. To the filtrate from P. 84 add 5 g of solid NH_4Cl, heat the solution to 70° to 80°C., and add to it, dropwise and swirling the mixture continuously, 3 to 12 ml of 3 n. $K_2C_2O_4$ (Notes 1, 2). Let the solution stand for 10 min., shaking it frequently (Note 3). (White precipitate, presence of calcium.)

If a small precipitate forms, let it settle. Decant the solution through a paper filter and wash the precipitate by decantation with four 5-ml portions of warm water, collecting these washings with the filtrate in a 400- to 600-ml conical flask. Treat the filtrate by P. 88. Wash the precipitate with hot 0.6 n. NH_4OH until no precipitate forms when 1 drop of $Ca(NO_3)_2$ solution is added to a 5-ml portion of the wash water. Transfer most of the precipitate to the filter during the washing. Treat the precipitate by P. 87.

If there is a large precipitate and magnesium may be present (Note 4), decant the solution through a paper filter. Add 5 to 15 ml of water to the precipitate, heat to boiling, let the precipitate settle, and decant the solution. Repeat this washing once and collect the washings with the filtrate in a 400- to 600-ml conical flask. Dissolve the precipitate on the filter by pouring dropwise through it 5 to 10 ml of HCl, collecting the solution with the precipitate in the flask. Wash the filter with 5 to 10 ml of water added dropwise.

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[16] Hall, *J. Am. Chem. Soc.*, **50**, 2707 (1928).

[17] A detailed discussion of the quantitative precipitation of calcium as oxalate and the separation of calcium from magnesium is given by Kolthoff and Sandell, *Quantitative Inorganic Analysis*, Macmillan, 1936, pp. 323-337. Kolthoff and Sandell, *J. Phys. Chem.*, **37**, 443, 459 (1933), have also investigated the coprecipitation of various substances by calcium oxalate precipitates.

Add to the mixture in the flask 3 g of NH_4Cl and swirl it until most of the precipitate dissolves (Note 5); then add to it 40 ml of water and 1 ml of 3 n. $K_2C_2O_4$. Add 15 n. NH_4OH dropwise to the solution, shaking vigorously, until it is just alkaline, and then add 2 ml more. Heat the mixture to 70° to 80°C. until the precipitate settles rapidly. Decant the solution through the original filter, wash the precipitate as directed in the paragraph above, and add the filtrate and the first two washings to the original filtrate. Treat the filtrate by P. 88. Treat the precipitate by P. 87.

Notes:

1. The volume of $K_2C_2O_4$ used should be based upon the total amount of calcium *and of magnesium* thought to be present. This can be estimated by the size of the ammonium carbonate precipitate obtained in P. 81 and by the amount of barium and strontium already found present.

2. The more slowly the $K_2C_2O_4$ is added to the solution the more favorable are the conditions for obtaining a precipitate that can be readily filtered. A coarse crystalline precipitate of calcium oxalate can be obtained by beginning the precipitation in an acid solution and then slowly neutralizing. This cannot be done here, however, as chromate is reduced by both alcohol and oxalate in hot acid solution.

3. The precipitate should not be allowed to stand for much longer than 10 min. because of the possible precipitation of magnesium oxalate from its supersaturated solutions.

4. In the majority of cases, this procedure to remove any coprecipitated magnesium may be omitted; the considerations discussed in Note 6, P. 82, also apply here.

5. This acid mixture should not be heated, because of the possible reduction of the chromate by the oxalate present.

P. 87. Estimation of Calcium

Discussion. The principle involved in this estimation of calcium is the same as that in the procedure for the estimation of strontium; that is, the oxalate precipitated with the calcium is titrated with permanganate after the precipitate has been dissolved in acid. The procedure is varied somewhat, depending upon whether a large or small precipitate is obtained. If less than 100 mg of calcium are thought to be present, the precipitate is dissolved in sulfuric instead of hydrochloric acid, because the end-point obtained when oxalate is titrated with permanganate is more stable in this acid (the possible oxidation of chloride by the permanganate is avoided) and because any small precipitate of calcium sulfate which may be

obtained would cause no trouble. If a large precipitate is obtained, it is desirable that only a portion of the solution be titrated, because of the excessive volume of permanganate which would be required. Therefore, because hydrochloric acid more effectively dissolves the precipitate of calcium oxalate, and in order to avoid a large precipitate of calcium sulfate (which may enclose calcium oxalate particles), this acid is then used; the conditions for the titration of the hydrochloric acid solution are the same as those in the estimation of strontium.

The precise titration of oxalate in a sulfuric acid solution has been discussed in P. XIV. There, in order to obtain very accurate results, most of the calculated volume of permanganate is added rapidly to the cold solution of the oxalate. This procedure is not practical when unknown amounts of oxalate are present and is not justified in this procedure, as the titration can be more conveniently carried out in a hot solution and as the titration errors caused by so doing (see the discussion of P. XIV) are smaller than those likely to arise from solubility and coprecipitation effects.

Procedure 87: ESTIMATION OF CALCIUM. If the precipitate is thought to contain less than 100 mg of calcium (Note 1), transfer that in the flask to a 600-ml beaker with the aid of 50 to 100 ml of water and add to it 30 ml of H_2SO_4. Remove the paper with the remainder of the precipitate from the funnel, open it against the side of the beaker, and wash the precipitate from the paper with a stream of water from a wash bottle, using 50 to 100 ml of water. Dilute the solution to approximately 200 ml, heat it to 80° to 90°C., and titrate it with standard 0.1 n. $KMnO_4$. Stir the solution constantly and do not add the $KMnO_4$ more rapidly than its color is bleached. When the first permanent pink color is obtained, push the filter paper into the solution and again titrate the mixture slowly until a pink color is obtained which remains for 30 sec. (Note 2). From the volume of standard $KMnO_4$ used, calculate the amount of calcium present.

If the precipitate is thought to contain as much as 100 mg of calcium, remove the paper with the precipitate from the funnel, open it against the side of a 400-ml beaker, and wash the precipitate to the bottom of the beaker with a stream of water, using not over 25 ml. Dissolve the precipitate in the

flask in 20 ml of hot 3 n. HCl and pour this solution into the beaker. Wash the beaker with 30 ml of hot 3 n. HCl, pouring this solution slowly over the filter paper as well. Wash the paper with 10 ml of hot water and discard it. Finally cool the solution to room temperature, transfer it to a 100-ml volumetric flask, dilute it exactly to the mark, and thoroughly mix the contents. Pipet that volume of the solution which is thought to contain 50 to 75 mg of calcium into a 400-ml flask, dilute it to 100 to 125 ml with 1 n. HCl, add to it 5 ml of the Zimmermann-Reinhardt preventative solution (P. 53*A*), and heat it to 70° to 80°C. Titrate the solution slowly with 0.1 n. $KMnO_4$ solution until the first pink color is obtained which remains for 10 sec. From the volume of standard $KMnO_4$ used, calculate the amount of calcium present.

Notes:

1. If a very small precipitate is obtained, it should be estimated by comparison with known amounts of calcium precipitated under similar conditions. Any strontium not precipitated in P. 84 would appear here. If desired, the presence of calcium in the precipitate may be confirmed as follows:

Pour repeatedly through the precipitate 5 ml of H_2SO_4 containing just 0.5 ml of 95 per cent C_2H_5OH. Add to the clear solution 10 ml of C_2H_5OH. (White precipitate, presence of calcium.)

A small amount of any calcium oxalate present is always dissolved by the sulfuric acid (oxalic acid being less ionized than sulfuric), and is reprecipitated as $CaSO_4 \cdot 2H_2O$ by the addition of the large amount of alcohol. Strontium oxalate would be metathesized to $SrSO_4$ by the sulfuric acid but, in the presence of the small amount of alcohol first added, does not dissolve in appreciable amounts. Magnesium sulfate is so soluble that, even if present, it does not precipitate on the addition of the alcohol. Calcium salts give an orange-red color to a flame; however, the intensity of the color is not adequate for a sensitive confirmatory test.

2. If the paper were introduced into the solution at the beginning of the titration, it would be disintegrated and make the detection of the end-point more difficult; also, it would cause an error by reducing an appreciable amount of the permanganate.[18] When the titration is carried out as directed, this effect is negligible.

P. 88. Precipitation of Magnesium

Discussion. In both qualitative and quantitative methods, magnesium is usually precipitated as magnesium ammonium phosphate. This compound is relatively soluble and tends to form

[18] McBride and Scherrer, *J. Am. Chem. Soc.*, **39**, 928 (1917); Simpson, *J. Ind. Eng. Chem.*, **13**, 1152 (1921).

supersaturated solutions. Therefore the precipitation is most effectively made from a small volume of cold solution and by means of a large excess of phosphate, ammonium ion, and ammonium hydroxide. The ammonium hydroxide is added to repress the hydrolysis reaction,

$$MgNH_4PO_{4(s)} + HOH = Mg^{++} + NH_4OH + HPO_4^{=},$$

which is a large factor in the solubility of the compound in water. A more detailed discussion of the solubility of this compound is given in the discussion of P. 162.

As would be predicted from their periodic relationships, phosphoric and arsenic acids are very similar in many of their properties. This is especially true in regard to the solubilities of their salts, and magnesium can be effectively precipitated as magnesium ammonium arsenate under conditions similar to those of the phosphate precipitation. This substitution is made here because it provides a means for the rapid volumetric estimation of magnesium in P. 89. With the large volume of solution which is present here, precipitation would be very slow if the alcohol added in P. 84 were not present. The alcohol decreases both the solubility of the precipitate and its tendency to form supersaturated solutions. In spite of the increased solubility of the magnesium salt in the presence of the excess of oxalate added in P. 86, experiments have shown that by this procedure 0.5 mg of magnesium can be easily detected and that larger amounts are quantitatively precipitated.

Procedure 88: PRECIPITATION OF MAGNESIUM. To the filtrate from P. 86 add 10 ml of 15 n. NH_4OH and then, 1 ml at a time and shaking after each addition, 10 to 25 ml of 1 f. Na_2HAsO_4 solution. Cool the solution and let it stand for at least 15 min., shaking it vigorously at frequent intervals. (White precipitate, presence of magnesium.) Allow the precipitate to settle and decant the solution through a paper filter, using suction; then wash the precipitate with 10-ml portions of 1.2 n. NH_4OH until 1 drop of $Ca(NO_3)_2$ solution gives no precipitate when added to a 5-ml portion of the washings. Discard the filtrate and washings. Treat the precipitate by P. 89.

P. 89. Estimation of Magnesium

Discussion. The method used here for the estimation of magnesium is based upon the iodometric determination of the arsenic in the magnesium ammonium arsenate precipitate.

In this method the magnesium ammonium arsenate precipitate is dissolved in hydrochloric acid, and the arsenic acid thus produced is reduced by the addition of potassium iodide to arsenious acid.[19] The iodine thus liberated is then titrated with standard thiosulfate solution. The reaction

$$H_3AsO_4 + 2H^+ + 3I^- = H_3AsO_3 + I_3^- + H_2O$$

is the reverse of the one discussed in P. XII and P. 43 and, as was stated there, can be caused to proceed quantitatively in either direction by proper control of the hydrogen ion concentration. However, in solutions in which the hydrogen ion concentration is such that it would be calculated that the reaction as written above would proceed quantitatively to the right, the rate is likely to be too slow for the method to be practical.

Williamson,[20] Gooch and Morris,[21] Rosenthaler,[22] Fleury,[23] Kolthoff,[24] and others too numerous to tabulate have studied experimentally the effects caused by the equilibrium and the rate of the reaction between arsenic acid and iodide, and by other factors involved in the determination, such as the oxidation of iodide in the strongly acid solution by the oxygen of the air. They have also investigated the influence of various conditions, such as the volume of the solution, the concentration of the iodide, the amount of acid present, and the temperature.

To review briefly these experimental studies: It has been found that, if the concentration of acid is below approximately 4 n., permanent end-points are not obtained, and that with this concentration of acid some time should be allowed for completion of the reaction. With too high a concentration of iodide and of acid, a yellow precipitate of arsenious iodide is formed which obscures the end-point. With the relatively high concentrations of iodide and acid which are present, the air has to be excluded from the reaction to avoid "oxygen error." The solution should be stirred vigorously

[19] Washburn, *J. Am. Chem. Soc.*, **35**, 682 (1913), has shown that in acid solutions as concentrated as the one used here the tripositive arsenic exists to a considerable extent as AsO^+. The volatility of arsenious chloride and bromide and the possible precipitation of arsenious iodide in this procedure show that in concentrated solutions of these halogen acids there also exists an appreciable concentration of the corresponding arsenic halide.

[20] Williamson, *J. Soc. Dyers and Colorist*, **1896**, 86–89.

[21] Gooch and Morris, *Z. anorg. allgem. Chem.*, **25**, 227 (1900).

[22] Rosenthaler, *Z. anal. Chem.*, **45**, 596 (1906).

[23] Fleury, *J. de Pharmacie et de Chemie*, **21**, 385 (1920).

[24] Kolthoff, *Z. anal. Chem.*, **60**, 399 (1920).

as the thiosulfate is added, to avoid the decomposition of the latter by the high concentration of acid which is present. Also, the acid concentration is so high that the use of starch is not advisable; the end-point can be determined solely by the disappearance of the iodine from the otherwise clear solution, or some organic solvent for iodine, such as carbon tetrachloride, may be used.

Experiments have shown that under the conditions of the procedure given below, results precise to within 0.3 per cent can be readily attained in the iodometric determination of arsenic acid.

As the other alkaline earth elements form insoluble phosphates and arsenates and would be precipitated in P. 88 if they had not been previously completely removed, a confirmatory test for the presence of magnesium is desirable if only a small precipitate is obtained. This can be made by precipitating magnesium hydroxide in the presence of the colored organic compound para-nitrobenzene-azo-resorcinol, whereby the precipitate is colored blue as a result of the formation of an adsorption compound (a lake) between the precipitate and the organic dyestuff.[25] The method can be used for the detection of very small traces of magnesium, and experiments[26] have shown that, as carried out below, 0.01 mg can be easily detected. The presence of arsenate (and phosphate) in the absence of other alkaline earth elements did not interfere with the test; calcium, strontium, and barium did not give any color; and when 10 mg of calcium and arsenate were both present, the colorless precipitate of calcium arsenate was so milky that it was impossible to detect less than 0.1 mg of magnesium. When ammonium salts, phosphate, or arsenate are present, sufficient excess of a strong base must be added to insure the precipitation of the magnesium hydroxide; a tenfold excess of sodium hydroxide over that specified below did not diminish the intensity of the color with given amounts of magnesium.

Procedure 89: ESTIMATION OF MAGNESIUM. Dissolve the precipitate on the filter and wash the filter by pouring slowly through it 20 to 50 ml of 6 n. HCl, collecting the solution with the precipitate in the flask (Note 1). Dissolve the precipitate in the flask and cool the solution to room temperature.

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[25] Suitsu and Okuma, *J. Soc. Chem. Ind., Japan*, **29**, 132 (1926); Ruigh, *J. Am. Chem. Soc.*, **51**, 1456 (1929); Stone, *Science*, **72**, 322 (1930).

[26] By Erwin Baumgarten.

If less than 50 mg of magnesium are thought to be present (Note 2), add to the cold solution, 0.2 g at a time and shaking after each addition, 1 g of solid $NaHCO_3$ and then 1 g of solid KI. Close the flask, swirl the mixture until the KI is dissolved, and allow it to stand for 5 min. Slowly titrate the mixture with 0.1 n. $Na_2S_2O_3$, swirling the solution continuously, until the iodine color disappears (Note 3). From the volume of standard $Na_2S_2O_3$ used, calculate the amount of magnesium present.

If more than 50 mg of magnesium are thought to be present, transfer the cold solution to a 100-ml volumetric flask, dilute it to the mark with HCl, and thoroughly mix the contents. Pipet that volume of the solution which is thought to contain 30 to 40 mg of magnesium into a 200-ml flask (preferably one fitted with a ground-glass stopper), and treat it as directed in the paragraph above.

Notes:

1. If only a small precipitate (corresponding to 3 to 5 mg) is obtained or only a qualitative confirmation of the presence of magnesium is desired, proceed as follows:

Dissolve the precipitate in 2 to 5 ml of HCl (if there is a large precipitate, take only an amount corresponding to 5 to 10 mg of magnesium). Add 1 drop of the para-nitrobenzene-azo-resorcinol reagent (a 0.5 per cent solution in 0.3 n. NaOH), make the solution alkaline with NaOH, and add 1 ml in excess. Shake the mixture for 10 to 15 sec. and allow it to stand for 2 min. (Blue precipitate, presence of magnesium.) If uncertain as to a bluish-colored precipitate, because of the reddish-violet color of the reagent, filter the mixture through a small paper filter and wash the precipitate and filter dropwise with 5 to 10 ml of cold water to which has been added 3 drops of NaOH.

2. As the amount of iodide added is based on not more than an amount of arsenic corresponding to 50 mg of magnesium being present, it is essential that only a portion of the solution be taken when larger amounts have been precipitated. If more than 1 g of KI is added, a precipitate of AsI_3 is likely to separate.

3. The color of iodine in a solution containing iodide is so pronounced that this end-point can be readily placed within 1 drop (0.02 to 0.04 ml) of 0.1 n. $Na_2S_2O_3$. If desired, 3 to 5 ml of carbon tetrachloride can be added and the solution can be titrated until no more color is observed in this solvent. If this method is used, it is essential that the solution be thoroughly shaken as the end-point is approached, in order that equilibrium between the aqueous and carbon tetrachloride solutions be attained; also, the thiosulfate should not be added more rapidly than the color is removed from the aqueous layer, as it is rapidly decomposed by this concentration of acid.

The Analysis of the Alkali Group

P. 91. The Detection of the Alkali Group and Estimation of the Total Amount of Sodium and Potassium Present

Discussion. Sodium and potassium, which constitute the Alkali Group, should have remained in the solution through all the previous group separations and now have to be detected in the filtrate from the Alkaline Earth Group precipitation. This is done by first removing the ammonium salts, then precipitating the potassium as perchlorate from a mixed alcohol-ether solution, and, finally, precipitating the sodium as chloride by saturating the alcohol-ether solution with hydrogen chloride gas. Ammonium, which has many of the properties of an alkali metal ion, behaves similarly but cannot be tested for in this solution because it has been introduced as a reagent in the preceding group separations. However, because of the striking similarity of ammonia to an alkali metal, a procedure for its detection and estimation, using another portion of the sample of the original material, is given immediately after the procedures for the analysis of this group.

Before beginning the analysis of the Alkali Group, it is necessary that the ammonium salts introduced in precipitating the Alkaline Earth Group be completely removed, as potassium is separated from sodium by precipitation as the perchlorate, and as ammonium perchlorate is insoluble under the same conditions. The ammonium salts are removed by treatment with concentrated nitric acid (see the discussion of P. 81) and by heating at a temperature sufficiently high to cause their complete volatilization. Also, if, after volatilizing the ammonium salts, there is no residue, further procedures are unnecessary.

Sulfate has to be tested for and removed, as sodium sulfate is insoluble in a mixed alcohol-ether solution and would cause the precipitation of sodium with the potassium perchlorate. Even if sulfate is not present in the original material, sulfur compounds are frequently introduced into the analysis during the hydrogen sulfide and ammonium sulfide precipitations. These compounds are then oxidized to sulfate by the nitric acid treatment (P. 81) used to destroy the ammonium salts. The sulfate can be precipitated as either the barium or the lead salt; the latter is used, as lead can be removed from the solution by hydrogen sulfide, whereas the barium

TABULAR OUTLINE X

The Analysis of the Alkali Group

Filtrate from the Alkaline Earth Group Precipitation: Na^+, K^+, NH_4^+, $CO_3^=$, $SO_4^=$, (ClO_4^-), NH_4OH, C_2H_5OH

Evaporate, add 16 n. HNO_3, evaporate to dryness, heat just below dull redness.
Add $Pb(NO_3)_2$ until no more precipitate forms. (P. 91)

Precipitate: $PbSO_4$
Discard.

Filtrate: Na^+, K^+, Pb^{++}, NO_3^-
Saturate with H_2S. (P. 91)

Precipitate: PbS
Discard.

Filtrate: Na^+, K^+, NO_3^-, H_2S
Evaporate to dryness. Add HCl, evaporate.
Heat at 300°C.
Weigh residue of NaCl and KCl. (P. 91)

Dissolve residue in H_2O. Add $HClO_4$; fume; cool.
Add 15 ml 95 per cent C_2H_5OH and 15 ml $(C_2H_5)_2O$.
Filter the precipitate on a weighed crucible. (P. 92)

Precipitate: $KClO_4$
Heat crucible and precipitate to 300° to 350°C.
Cool and weigh.
(P. 93)

Filtrate: $NaClO_4$ in C_2H_5OH and $(C_2H_5)_2O$
Cool in ice water. Saturate with HCl gas. (P. 94)

Precipitate: NaCl
Method I:
Heat and weigh.
Method II:
Dissolve in H_2O. Add K_2CrO_4.
Titrate with $AgNO_3$.
Precipitate: AgCl; Ag_2CrO_4 (reddish) (P. 95)

Filtrate.
Discard.
(Caution)

The Detection and Estimation of Ammonia (P. 96)
Heat a portion of the original material with NaOH.
Detection: *Test escaping gas (NH_3) with litmus.* (Red litmus changes to blue.)
Estimation: *Distill into standard HCl solution.*
Distillate: NH_4^+ in excess HCl. *Titrate excess HCl with standard NaOH.* (P. 96)

has to be removed by precipitation with ammonium carbonate, which again introduces ammonium salts into the solution. It is an advantage that the alkali metal salts have been converted to nitrates, as this prevents the possible precipitation of lead chloride.

Upon evaporation of the filtrate and removal of the hydrogen sulfide, the elements present are changed from their nitrates to their chlorides, which are more stable under heat, and the total weight of sodium and potassium chloride is determined. This often eliminates the subsequent precipitation and estimation of sodium, as, after estimating the potassium, the amount of sodium present can be obtained by difference.

Optional Method for the Qualitative Detection of Sodium and Potassium. In case only small amounts of these two elements are present, or only their qualitative detection is desired, there is provided in Note 4 of the procedure below an optional method for this purpose, which is much shorter than the perchlorate separation. In this procedure the residue obtained after the ammonium salts are removed is dissolved, and this solution is divided into two portions. One portion is tested for potassium by the addition of a sodium cobaltinitrite ($Na_3Co(NO_2)_6$) reagent. Even 0.2 mg of potassium causes the formation of a detectable yellow precipitate, potassium sodium cobaltinitrite ($K_2NaCo(NO_2)_6$), similar to that used for the optional separation of cobalt from nickel (P. 64). The other portion is tested for sodium by addition of a reagent containing magnesium acetate, uranyl acetate ($UO_2(C_2H_3O_2)_2$), and acetic acid.[1] As little as 0.3 mg of sodium causes the formation of a voluminous, greenish-yellow, crystalline precipitate having the composition $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 9H_2O$.

Procedure 91: DETECTION OF THE ALKALI GROUP. Evaporate the filtrate from the Alkaline Earth Group precipitation (P. 81) to a volume of 5 to 10 ml, filter out any precipitate on a small filter, and wash the filter with a few milliliters of cold water. Collect the filtrate and washings in a 50-ml casserole. (Discard the precipitate. Note 1.) Cover the casserole with a clock glass, evaporate the filtrate almost to dryness, add 2 to 5 ml of 16 n. HNO_3, and care-

[1] This reagent was proposed for use in the quantitative determination of sodium by Blanchetière, *Bull. Soc. Chim.* (4), **33**, 807 (1923); it, and a similar reagent in which the magnesium acetate is replaced by zinc acetate, have been investigated by Barber and Kolthoff, *J. Am. Chem. Soc.*, **50**, 1625 (1928).

fully evaporate the solution to dryness, keeping the mixture in motion or allowing the evaporation to take place on a steam bath. Wash the clock glass and the sides of the flask with 1 to 2 ml of 16 n. HNO_3, and again evaporate the solution to dryness. Remove the clock glass and heat the casserole over a flame at a temperature just below dull redness until fumes are no longer given off (Note 2). (White residue, presence of the Alkali Group.)

Dissolve the residue in 10 ml of hot water (Notes 3 and 4) and add to it 0.1 ml of 1 n. $Pb(NO_3)_2$. If a white precipitate forms, continue adding the $Pb(NO_3)_2$ in 0.1-ml portions until precipitation ceases. Shake the mixture and let the precipitate settle after adding each portion of the $Pb(NO_3)_2$; avoid a large excess. Filter the solution through a small paper filter, and wash the precipitate with 3 to 5 ml of cold water added dropwise, collecting the filtrate and washings in a 100-ml flask. (Discard the precipitate.) Saturate the solution with H_2S under pressure (not by passing the gas through the solution—Note 3, P. 11), heat the mixture almost to boiling, and at once filter out the precipitate on a small paper filter. Wash the precipitate with 5 to 10 ml of hot water, added dropwise, and collect the wash water with the filtrate in a 100-ml flask (Note 5) which has been previously heated to 250° to 300°C. and then allowed to cool in a desiccator and weighed. Immediately evaporate the solution to dryness (Note 6), moisten it with 12 n. HCl, and again evaporate it, repeating this process once. Finally, heat the flask to 250° to 300°C. for 10 min., allow it to cool in a desiccator, and weigh it. Note the total weight of alkali metal chloride present. Treat the residue by P. 92.

Notes:

1. Traces of the alkaline earth elements, of aluminum hydroxide, or of silica may precipitate as the solution is evaporated. These should be carefully filtered out through a small filter so that, in case alkali elements are absent, no residue will remain after the ammonium salts are removed.

2. The sides and entire bowl of the casserole should be heated in order to remove all traces of ammonium salts. The vessel should not be heated to a red heat, as the alkali salts would then be appreciably volatile.

3. An insoluble residue which is dark in color is usually due to organic material introduced into the analysis from filter papers or in the reagents, especially alcohol. A white residue of silica may also be obtained. These are usually not sufficiently large to interfere with the $Pb(NO_3)_2$ treatment and can be filtered out with the $PbSO_4$.

4. If it is desired only to detect the presence of the two metals, treat the solution as follows:

Detection of Potassium: Pour half of the solution into a test tube, add 5 ml of $Na_3Co(NO_2)_6$ reagent, and let the solution stand, shaking it frequently, for 10 min. (Yellow precipitate, presence of potassium.) Compare the precipitate with known amounts of potassium precipitated under similar conditions. (If the mixture is allowed to stand until the precipitate settles in the bottom of the test tube, 0.2 mg of potassium can be detected. Ammonium salts must be removed, as they cause a similar precipitate.)

Phosphate would be precipitated by the uranium in the magnesium uranyl acetate reagent; therefore, if phosphate has been found present (see P. 54), it should be removed before testing for sodium. This can be done by the procedure given above for removing sulfate; therefore, if it is present, proceed as follows:

Treat the second half of the solution with $Pb(NO_3)_2$ and H_2S as directed in the second paragraph of the procedure above, evaporate the H_2S filtrate to dryness, dissolve the residue in 5 ml of hot water, and treat it as directed in the next two paragraphs.

Detection of Sodium: If less than 10 mg of potassium are present (in the half portion), pour the remaining half of the solution into a test tube, add 10 ml of magnesium uranyl acetate reagent, and let the solution stand, shaking it frequently, for 10 min. (Pale greenish-yellow crystalline precipitate, presence of sodium.)

If more than 10 mg of potassium are present, evaporate the solution in the flask almost to dryness and add to it 5 ml of 12 n. HCl and 5 ml of 95 per cent C_2H_5OH. Cool the mixture and decant the solution through a small filter. Evaporate the solution just to dryness, dissolve the residue in 5 ml of water, and treat it by the paragraph above.

If the mixture is allowed to stand for 10 min., 0.3 mg of sodium can be detected. Not more than 20 mg of potassium can be present without likewise causing a precipitate; therefore, larger amounts are removed by treating the residue with a mixture of hydrochloric acid and alcohol. Only about 20 mg of sodium remain in the alcoholic solution, so that the estimation of larger amounts than this should be made from the original residue and from the amount of potassium found.

5. If only a qualitative separation of the alkali elements is desired, it is not necessary to weigh the residue. In this case the solution should be collected in a 200-ml flask and treated directly by P. 92.

6. The solution should not be allowed to stand for any length of time before expelling the H_2S, as the latter may oxidize on contact with the air and form a white precipitate of sulfur. In case such a precipitate does form, it should be carefully filtered out.

P. 92. Precipitation of Potassium

Discussion. This method for the precipitation of potassium and its separation from sodium is based upon the difference in solu-

bilities of the perchlorates of the two elements. As potassium perchlorate is relatively soluble in water, it has been customary to effect the separation in nearly anhydrous ethyl alcohol, 97 to 99 per cent, and even in some cases to saturate this alcohol first with potassium perchlorate.[2] As a substitute for the ethyl alcohol, various other organic solvents have been investigated, and the use of a mixture of butyl alcohol and ethyl acetate has been recommended.[3]

This reagent, while very effective, may not be available, especially as the solvents should be anhydrous, and the butyl alcohol often contains impurities which give it an offensive odor. A study by Walter

TABLE XXIX

THE SOLUBILITY OF SODIUM AND POTASSIUM PERCHLORATES IN VARIOUS SOLVENTS

The dry perchlorates were shaken with the reagents indicated at room temperature (approximately 20°C.) for 20 min.; then 50-ml portions were analyzed.

Expt.	Volume Taken (ml)				Solubility (g in 50 ml)	
	Water	$HClO_4$	C_2H_5OH (94 per cent)	$(C_2H_5)_2O$	Sodium	Potassium
1	....	...	.....	50	0.000	0.0000
2	....	...	50.0	.. ..	2.039	0.0049
3	3.0	...	31.25	31.25	1.130	0.0020
4	3.0	...	15.63	46.88	0.996	0.0011
5	3.0	...	20.50	105.0	0.336	0.0003
6	0	...	50.0	105.0	0.2085	0.00001
7	2.60	0.4	15.63	46.88	.....	0.0004
8	2.20	0.8	15.63	46.88	0.603	0.0003

D. Wilkensen, Jr., has shown that the addition of ethyl ether to ethyl alcohol very markedly decreases the solubility of potassium perchlorate and that, although a decrease in the solubility of sodium perchlorate is also caused, the ratio of the solubility of the sodium salt to that of the potassium is greatly increased. Thus, as can be calculated from the data shown in Table XXIX (Experiment 2), with 94 per cent ethyl alcohol this ratio of the formal solubilities

[2] Davis, *J. Agr. Sci.*, **5**, 52, 512 (1912); Gooch and Blake, *Am. J. Sci.*, **44**, 381 (1917); Baxter and Kobayashi, *J. Am. Chem. Soc.*, **39**, 249 (1917); **42**, 735 (1920).

[3] Willard and Smith, *J. Am. Chem. Soc.*, **44**, 2816; **45**, 293 (1923); G. F. Smith, *ibid.*, **47**, 762 (1925); Smith and Ross, *ibid.*, **47**, 774, 1020 (1925).

is approximately 700, while with a mixture of 1 volume of 94 per cent alcohol and 3 volumes of ethyl ether it is about 50 times as great (Experiment 6).

It is an advantage that the solubilities of the salts are so reduced that, instead of treating a dry mixture with the solvent and extracting the sodium, it is possible to dissolve the salts in a small amount of water and to precipitate the potassium perchlorate gradually by slowly adding first the alcohol and then the ether; by this precipitation process there should be less tendency for sodium to be carried out with the potassium precipitate. The quantitative value of this

TABLE XXX

THE SEPARATION OF POTASSIUM AND SODIUM

A slight excess of perchloric acid was added to the alkali salts and the mixture was evaporated just to complete dryness. Water was then added, 1 ml at a time, the mixture being heated after each addition, until the residue was dissolved; the solution was then evaporated until just 1 ml of water remained. The mixture was cooled and 15 ml of 95 per cent C_2H_5OH and 45 ml of $(C_2H_5)_2O$ were slowly added; then the mixture was allowed to stand for 10 min., with frequent shakings. The solution was decanted through a Gooch-type filter, and the precipitate was washed with 50 ml of a solution containing 1 volume of alcohol to 3 volumes of ether. The precipitate was dried at 350°C. and weighed. The filtrate was evaporated to dryness, dried at 350°C., and weighed.

Expt.	Potassium (g)		Sodium (g)	
	Taken	Found	Taken	Found
1	0.3642	0.3670	0.2916	0.2899
2	0.3642	0.3641	0.2916	0.2917
3	0.0009	0.0011	0.3871	0.3870
4	1.4449	1.4445	0.0008	0.0011
5	0.4642	0.4638	0.0015	0.0019
6	0.3641	0.3636	None	0.0005

method was tested by the procedure given with Table XXX, and the results obtained are shown there.

For the purpose of this system, where the occlusion of small amounts of perchloric acid within the potassium perchlorate precipitate would not introduce serious errors, and where the presence of phosphate and borate would cause the sodium salts to precipitate from a neutral solution, it seemed more expedient to use a solvent containing a small amount of perchloric acid and equal volumes of alcohol and ether. In testing the procedure given below, it was found that 0.5 mg of potassium gave an easily detected precipitate

and also that, when 250 mg each of sodium and potassium were taken, less than 1 mg of sodium was found in the precipitate and no detectable amount of potassium remained in the filtrate.

Potassium is often separated from sodium and gravimetrically determined by precipitation as the chloroplatinate (K_2PtCl_6); this method is not used here because of the cost of the reagent and because of the necessity of removing the excess of the reagent before the precipitation of the sodium can be made.

Procedure 92: PRECIPITATION OF POTASSIUM. Transfer the residue obtained by P. 91 to a 200-ml conical flask with the aid of as little water as possible. Add to the solution 1 to 3 ml of 9 n. $HClO_4$ and evaporate until dense white fumes are copiously evolved and not over 1 ml of $HClO_4$ remains (Note 1). Keep the contents of the flask in constant motion during this evaporation. Let the residue cool somewhat, add 1 ml of water, warm the mixture, and shake it until the residue dissolves or is thoroughly mixed. Cool the flask to room temperature with tap water, add slowly 15 ml of 95 per cent alcohol, and then add 15 ml of ethyl ether. Shake the mixture and let it stand for 5 min. in a beaker of ice water. (White crystalline precipitate, presence of potassium.) Filter the mixture through a sintered-glass crucible (Notes 2, 3) which has been previously heated to 300° to 350°C., cooled, and weighed (Note 4). Wash the precipitate with 20 to 30 ml of a cold solution made by adding 1 volume of alcohol to 2 volumes of ether. Transfer all of the precipitate from the flask by squirting this wash solution from a small wash bottle onto the precipitate while the flask is held in an inclined position. Collect the washings with the filtrate in a large test tube (25 mm by 200 mm) and treat it by P. 94. Treat the precipitate by P. 93.

Notes:

1. Enough $HClO_4$ should be added to combine with all of the alkali elements present. If, after adding the $HClO_4$ and evaporating, no fumes are evolved before the mixture becomes nearly dry, 1 ml more acid should be added and the mixture should again be evaporated; an excess of more than 1 ml of $HClO_4$ should be avoided.

2. If available, sintered-glass crucibles should be used here. These crucibles are rapidly prepared for use and brought to constant weight, and are very satisfactory in this determination. If they are not available, Gooch-type asbestos filters can be used.

3. *Caution:* Ether should not be handled near a flame (see the second paragraph of Note 8, P. 52).

4. The heating prior to weighing may be conveniently carried out in a manner similar to the final heating and drying of the precipitate in P. 93 (see also Note 2 of that procedure).

P. 93. Estimation of Potassium

Discussion. A gravimetric method is used for estimating the potassium, because this element has been detected and separated as the perchlorate (which can be conveniently heated and then weighed) and because no rapid volumetric estimation of either the potassium or the perchlorate is available. Smith and Ross[4] have shown that it is necessary to heat the precipitate to approximately 350°C. in order to expel the occluded perchloric acid. If only a very small precipitate is obtained, the presence of potassium can be confirmed by dissolving the precipitate and reprecipitating the potassium as potassium sodium cobaltinitrite, $K_2NaCo(NO_2)_6$, as directed in Note 4, P. 91. This confirmatory test is advisable, as, if either chloride or sulfate were left with the alkali metals, sodium chloride or sulfate would separate out from the alcohol-ether solution. The only other anions likely to be present are phosphate and borate; however, these are almost completely removed with sulfate by the treatment with lead in P. 91 and are much less ionized than perchloric acid and do not cause the sodium to precipitate.

Procedure 93: ESTIMATION OF POTASSIUM. Place the crucible with the precipitate from P. 92 (Note 1) in an oven at 110°C. until it is dry (Note 2), suspend it well down in a large iron or nickel crucible by means of a nichrome or clay-covered triangle, and heat it to between 300° and 350°C. for 10 min. Place the crucible in a desiccator, allow it to cool to room temperature, and weigh it. Repeat the heating and weighing until the precipitate no longer changes weight. From the weight of precipitate obtained, calculate the amount of potassium present (Note 3).

Notes:

1. If only a small precipitate is obtained, the presence of potassium should be confirmed by dissolving the precipitate in 5 ml of water and treating the solution as directed in Note 4, P. 91.

2. The crucible and precipitate may be more quickly dried by placing it directly in the metal crucible next used and then very gradually raising the temperature; too abrupt heating will cause spattering. A thermometer

[4] Smith and Ross, *J. Am. Chem. Soc.* 47, 774 (1925).

should be suspended inside the crucible so that the temperature can be controlled. If an electric furnace with temperature control is available, it can be used to advantage.

3. If only an approximate estimation of the amount of sodium present is desired, this may be calculated from the amount of potassium found here and the total weight of the alkali chlorides found in P. 91.

P. 94. Precipitation of Sodium

Discussion. As the filtrate should now contain only sodium perchlorate, perchloric acid, alcohol, and ether, the obvious method of detecting the sodium would be to evaporate the solution to dryness and note if any residue remains. However, if the evaporation of solutions containing alcohol and perchloric acid is not carried out under very carefully controlled conditions, a violent and dangerous explosion will result. Because of this, and because a salt which is more readily estimated is obtained, the sodium is precipitated as the chloride by saturating the filtrate with dry hydrochloric acid gas. By this means, 0.3 mg of sodium can be detected and larger amounts can be completely precipitated. Any potassium not precipitated by the perchloric acid will also be precipitated.

The precipitate has to be washed free from perchloric acid with ether, as any perchloric acid which remains on the precipitate will displace the more volatile hydrochloric acid from the salt when it is dried. This would result in a mixture of perchlorate and chloride and cause an error in the subsequent estimation of the sodium.

> **Procedure 94:** PRECIPITATION OF SODIUM. Immerse the test tube containing the filtrate from P. 92 in a mixture of ice and water and pass a fairly rapid stream of dry HCl gas (Note 1) through the solution until it is saturated, as shown by the gas no longer being absorbed. (White crystalline precipitate, presence of sodium.) Filter the solution through a sintered-glass filter (Note 2) which has been moistened with alcohol and then sucked dry. Wash the precipitate with three to five 5-ml portions of ether, and dry it at 110°C. for 20 min. (see the second paragraph of Note 8, P. 52). Treat the precipitate by P. 95. *Caution: Discard the filtrate; do not heat or evaporate it* (Note 3).

Notes:

1. The dry gaseous HCl should be generated as follows: Fit a 500-ml conical flask with a two-hole rubber stopper carrying in one hole a delivery tube and in the other a thistle tube. Place in the flask the necessary amount

of solid NaCl. Support a short test tube upright on the bottom of the flask by having the end of the thistle tube extend just below the top of the test tube. Pour 95 per cent H_2SO_4 through the thistle tube until the test tube overflows; thereafter, add the acid as it is needed to cause a vigorous flow of gas. After a volume of acid equal in milliliters to the grams of salt taken is added, the mixture should be heated to 60° to 80°C. as the gas is needed. When the gas is no longer needed, the evolution can be stopped by cooling the flask. Whatever the type of generator used, it should be provided with an efficient safety tube, since the HCl is so vigorously absorbed at first that it tends to suck the alcohol-ether solution back into the generator.

2. If desired, the sodium may be estimated by drying at 350°C. and weighing the NaCl precipitate. In this case, the precipitate should be collected on a sintered-glass or Gooch-type asbestos filter which has previously been dried at 350°C., cooled, and then weighed. If a volumetric estimation is to be made, a simple asbestos filter is satisfactory (see the discussion of P. 95 in regard to these optional procedures).

3. Solutions containing perchloric acid and alcohol should not be heated, as a violent explosion may result. Noyes and Bray[5] have found, and repeated experiments have confirmed, that it is possible to evaporate solutions containing perchloric acid and alcohol by the following procedure:

> Transfer the solution to a casserole, dilute it with one-fourth its volume of water, and evaporate it on a steam bath until the volume is only slightly greater than that of the 9 n. perchloric acid present (*do not cause the $HClO_4$ to fume*). Cool the solution and add 16 n. HNO_3, a drop at a time, as long as any reaction is observed, and then add 5 ml more. Finally evaporate the solution to dryness, taking care that, should an explosion occur, a minimum of danger will result.

It is therefore possible to detect the sodium by evaporating the filtrate from P. 92 as indicated above and noting if any residue of sodium perchlorate remains. If it is desired to estimate sodium after detecting it by this process, the perchlorate can be converted to chloride as follows: Add to the casserole 0.5 to 2 g of solid NH_4Cl, just moisten the entire mass, and then heat the casserole as was directed for removing ammonium salts in P. 91. If a large amount of sodium is present, the process should be repeated to insure complete decomposition of the perchlorate.

P. 95. Estimation of Sodium

Discussion. Several methods are available for estimating the amount of sodium present. First, after the total weight of the chlorides has been obtained in P. 91 and the potassium has been separately estimated in P. 93, the sodium present can be calculated. This is a difference method and is subject to error when the amount

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[5] Noyes and Bray, *Qualitative Analysis for the Rare Elements*, Macmillan, 1927, pp. 259 and 472.

of sodium is small, the more so since the precision in weighing the relatively heavy flask with its large surface (in P. 91) would probably be low.

Second, as the crucible has been weighed before the filtration, the crucible and precipitate can be heated so as to dry the salt completely and a gravimetric determination can be made.

Finally, after the precipitate of sodium chloride has been heated until it is free of hydrogen chloride, the sodium can be determined indirectly by either of two volumetric methods for determining the chloride. First, with standard solutions of silver nitrate and thiocyanate available, the chloride present can be estimated by adding an excess of the silver nitrate and then titrating this excess as was done in estimating bismuth in P. 27. Or, second, the chloride can be determined by a titration with a standard silver nitrate solution and the end-point can be determined either (1) by adding a soluble chromate to the solution and noting the appearance of the first reddish precipitate of silver chromate—this is known as the Mohr titration—or (2) by the use of an adsorption indicator. This direct titration with a standard silver nitrate solution (using either means of determining the end-point) is recommended because of the precision and rapidity with which it can be carried out; procedures are given below which permit the optional use of either end-point. Because it has been so extensively used, especially for the determination of the chloride in drinking waters, the principles involved in the Mohr method of obtaining the end-point will be discussed in detail. A general discussion of adsorption indicators has been given in P. VI, "The Standardization of a Thiocyanate Solution."

The Use of Chromate as an Indicator in Titrating Chloride with Silver Ion. In both methods of determining the end-point, the sodium chloride is dissolved and a neutral solution is thus obtained. Then for carrying out the Mohr titration, chromate is added as an indicator, and the solution is titrated with standard silver nitrate; silver chloride is formed until the chloride ion concentration is reduced to a very low value, when a reddish precipitate of silver chromate begins to form, and the first appearance of this color is taken as the end-point. This method, which is one of the older analytical processes, was first described by Mohr[6] and has been extensively investigated. The theoretical accuracy of the method can be calculated as follows: At the end-point it is desired that the equivalents of silver added be equal to the equivalents of chloride

[6] Mohr, *Liebig's Ann. d. Chem.*, **97**, 335 (1856).

originally present. Therefore, the percentage titration error, T.E., will be the total equivalents of silver added, Σ Eq.Ag, minus the total equivalents of chloride present, Σ Eq.Cl, times 100, divided by the total equivalents of chloride present, thus:

$$\text{T.E.} = \frac{\Sigma\ \text{Eq.Ag} - \Sigma\ \text{Eq.Cl}}{\Sigma\ \text{Eq.Cl}} \times 100 \qquad (1)$$

The silver which has been added is present at the end-point as the silver chloride precipitate, as the silver chromate precipitate, and as silver ion; the chloride is present as the silver chloride precipitate and as chloride ion.

As, at the end-point, the total equivalents of silver, Σ Eq.Ag, are equal to the equivalents of silver chloride, Eq.AgCl, plus the equivalents of silver chromate, Eq.Ag_2CrO_4, plus the equivalents of silver ion, Eq.Ag^+, and as the total equivalents of chloride, Σ Eq.Cl, are equal to the equivalents of silver chloride, Eq.AgCl, plus the equivalents of chloride ion, Eq.Cl^-, Equation 1 can be rewritten

$$\text{T.E.} = \frac{(\text{Eq.AgCl} + \text{Eq.}Ag_2CrO_4 + \text{Eq.}Ag^+) - (\text{Eq.AgCl} + \text{Eq.}Cl^-)}{\Sigma\ \text{Eq.Cl}} \times 100. \qquad (2)$$

If these quantities can be evaluated, the titration error can be calculated.

It is seen that the equivalents of the silver chloride precipitate drop from the equation; this is obvious, as the equivalents of silver and of chloride are equal in the precipitate. The equation then reduces to the form

$$\text{T.E.} = \frac{(\text{Eq.}Ag_2CrO_4 + \text{Eq.}Ag^+) - (\text{Eq.}Cl^-)}{\Sigma\ \text{Eq.Cl}} \times 100. \qquad (3)$$

The equivalents of silver chromate represent the amount of that precipitate which is required before it is visible. This quantity is variable, being dependent upon the individual observer, the concentration of the chromate, the coagulation of the precipitate, and the conditions obtaining at the time of the observation; under favorable conditions it appears to range from between 0.08 and 0.2 mg of silver chromate, but, if care is not taken, it will be much larger. Thus, in a series of observations made with 100 ml of a solution which was 1.2×10^{-2} n. (6×10^{-3} f.) in potassium chromate, it was found that 0.28, 0.24, and 0.22 ml—or an average of 0.25 ml—of 0.01 n. silver nitrate was required to give the first perceptible

color change. Assuming that an equilibrium was attained in these experiments, and taking the average value given above, it is seen that 2.5×10^{-6} equivalent of silver has been added. As the silver added is small in comparison to the chromate, it can be assumed that the initial and final chromate ion concentrations have approximately the same value, that is, 6×10^{-3} m.[7] The solubility product of Ag_2CrO_4 is

$$[Ag^+]^2[CrO_4^{=}] = 2 \times 10^{-12}.$$

Therefore it is calculated that the silver ion concentration in equilibrium with the above concentration of chromate is 1.8×10^{-5}, or that there will be 1.8×10^{-6} equivalent of silver as silver ion remaining in the 100 ml of solution; therefore, 0.7×10^{-6} equivalent of silver chromate has been precipitated. Applying these conditions to a titration and taking the solubility product of silver chloride as

$$[Ag^+][Cl^-] = 10^{-10},$$

it is seen that, in a solution in which the silver ion concentration is 1.8×10^{-5}, the chloride ion concentration will be 5.6×10^{-6}, or in 100 ml of solution there will be 0.56×10^{-6} equivalent of chloride ion. If we assume some quantity of chloride initially present, say 25 ml of 0.1 n. solution or 2.5×10^{-3} equivalent, all of the quantities are available for substitution in Equation 3 above for the titration error, thus:

$$\text{T.E.} = \frac{(0.7 \times 10^{-6} + 1.8 \times 10^{-6}) - (0.56 \times 10^{-6})}{(2.5 \times 10^{-3})} \times 100$$

$$= 0.04 \text{ per cent, positive error.}$$

From an inspection of the factors in the expression, it is seen that the percentage error is determined by the following: (1) The amount of Ag_2CrO_4 precipitated. As stated, this quantity is dependent upon the individual observer and upon the conditions, such as background and lighting used, and under most conditions will be greater than the value calculated above, thus leading to a larger positive error. It was found that the sensitivity of the detection was apparently somewhat increased in the presence of a white precipitate, but that with too high a chromate concentration the color of the solution

[7] If the hydrogen ion concentration of the solution is less than 10^{-7}, the fraction of the chromate existing as $Cr_2O_7^{=}$ or $HCrO_4^-$ can be neglected for an approximate calculation.

begins to mask the first appearance of the precipitate. (2) The chromate ion concentration. This is the most important factor involved, as it can be controlled over a considerable range; and, as can be seen, increasing its concentration causes an increase in the chloride ion concentration and a decrease in the silver ion concentration. Practically, the chromate concentration cannot be increased beyond the point that its color becomes objectionable. (3) The equivalents of chloride taken. This quantity is limited by the volume of solution required for the titration. It is apparent that the error becomes quite serious if 0.01 n. solutions are used, as the term Eq.Cl (in the denominator of Equation 3) becomes smaller for a given volume of standard solution.

Practically, the error is most effectively reduced by applying an "end-point correction." This consists in subtracting from the silver nitrate required for the titration a volume equivalent to the end-point error, that is, referring to Equation 3, $(\text{Eq.Ag}_2\text{CrO}_4 + \text{Eq.Ag}^+) - (\text{Eq.Cl}^-)$.

In the case considered, the correction would be 1.94×10^{-6} equivalent of silver nitrate, corresponding to 0.02 ml of 0.1 n. $AgNO_3$ solution. Frequently such an "end-point correction" is approximated experimentally by adding the silver nitrate solution to a solution containing the same concentration of chromate as was used in the titration until a precipitate comparable to that occurring in the titration is obtained. The volume of the silver nitrate thus used represents the correction applied.

The accuracy of the method is also dependent upon the hydrogen ion concentration, which should be between 5×10^{-7} and 10^{-10}. The upper limit is fixed by the solubility of silver chromate in acid solutions and the lower limit by the solubility of silver oxide in alkaline solutions. As the solubility of silver chromate increases rapidly with the temperature, the solution should not be much above 20°C. during the titration.

A further factor which affects the accuracy of the method and which is not considered in the theoretical calculations shown above is the tendency of a silver chloride precipitate to adsorb chloride ion and thus cause a premature end-point. This is minimized by vigorously shaking the solution as the end-point is approached and noting if the first color obtained is permanent.[8] This Mohr titration

[8] Meldrum and Forbes, *J. Chem. Ed.*, **5**, 205 (1928), advocate boiling the solution after obtaining a preliminary end-point, cooling, and then titrating to a permanent end-point.

can be used for the determination of bromide as well as chloride, but, because of adsorption effects, it is not suitable for the determination of iodide or thiocyanate.

The Use of Adsorption Indicators in Titrating Chloride with Silver Ion. The conditions are ideal here for the use of an adsorption indicator, as the chloride is present as a neutral solution of pure sodium chloride; because of this and because difficulty is sometimes experienced in detecting the silver chromate end-point, the use of an adsorption indicator is recommended for this titration. As was stated in the discussion of these indicators in P. VI, their usefulness is limited in the presence of a high concentration of neutral salt or hydrogen ion.

Fluorescein is used here because it gives an excellent end-point and is commonly available; it can be used satisfactorily only when the *p*H of the solution is between 7 and 10. If it is desired to carry out the titration in an acid solution (up to *p*H 3), dichlorofluorescein may be used. Eosin (tetra brom fluorescein) may be used for the titration of bromide, iodide, or thiocyanate in solutions with a *p*H up to 3 but, as it is appreciably adsorbed before the equivalence-point, it cannot be used for titrating chlorides.

Procedure 95: ESTIMATION OF SODIUM. *Gravimetric Method.* Treat the crucible and precipitate as directed in P. 93. Calculate the amount of sodium present from the weight of sodium chloride found (Note 1).

Volumetric Method. Dissolve the precipitate by pouring dropwise through the filter 10 to 35 ml of hot water and then collecting the solution in a 200-ml flask. Cool the solution.

If less than 100 mg of sodium are thought to be present, treat the solution as directed in either of the last two paragraphs of this procedure.

If more than 100 mg of sodium are thought to be present, transfer the solution to a 100-ml volumetric flask, dilute it to the mark, mix it well, and pipet into a 200-ml conical flask that volume which is thought to contain 50 to 75 mg of sodium.

Using Chromate as Indicator. Dilute the solution to 50 ml; if it reacts acid to litmus, make it *just neutral* with 1 f. $NaHCO_3$ (Note 2), and add to it 5 drops of 3 n. K_2CrO_4.

Titrate the solution slowly with 0.1 n. $AgNO_3$, swirling vigorously, until the first permanent reddish precipitate is produced (Note 3). From the volume of standard $AgNO_3$ used, calculate the amount of sodium present (Note 4).

Using an Adsorption Indicator. Dilute the solution to 50 ml; if it reacts acid to litmus, make it just neutral with 1 f. $NaHCO_3$ (Note 2), and add to it 5 drops of 0.2 per cent fluorescein indicator solution. Titrate the solution slowly with 0.1 n. $AgNO_3$, swirling vigorously, until a transient pink color is observed; thereafter add the silver nitrate dropwise until the precipitate suddenly turns a reddish-pink color.

Notes:

1. If the crucible has not been weighed before the filtration, the estimation can still be made, though less precisely, by weighing the crucible with the precipitate as directed, washing the crucible with hot water until the washings give no test for chloride with $AgNO_3$, and again drying, heating, and weighing the crucible.

2. The solution is neutralized with $NaHCO_3$ in preference to NaOH, since a slight excess will not unduly increase the alkalinity of the solution; a large excess of $NaHCO_3$ should be avoided, as it tends to cause the Ag_2CrO_4 to coagulate and makes the end-point more difficult to detect. Na_2CO_3 is objectionable because an excess of it would cause the precipitation of silver carbonate instead of silver chromate.

3. The titration should be made slowly in order that adsorbed chloride may be removed from the precipitate before the appearance of the end-point. The mixture should be shaken vigorously in order to coagulate the precipitate, thus facilitating the detection of the end-point.

4. If a precise titration is desired, an end-point correction should be made. This is done by adding the standard $AgNO_3$ to the amount of chromate and volume of solution to be used in the titration until the first perceptible coloration is obtained. The effect of the presence of the silver chloride precipitate can be approximated by triturating 0.2 g of calcium carbonate with a few milliliters of water in a mortar and adding this suspension to the solution. The "end-point" thus obtained should be kept beside the solution being titrated as a reference standard.

P. 96. Detection and Estimation of Ammonia

Discussion. Ammonia (NH_3) will be found most frequently in materials as the ammonium ion (NH_4^+), although it may be present as ammonia in various complex salts (coördination compounds such as $Co(NH_3)_5Cl \cdot Cl_2$ and $Cd(NH_3)_4(ClO_4)_2$) and in some ammoniated

compounds such as $CaCl_2 \cdot 2NH_3$, where it is similar to the water of hydrates.[9] Both the detection and the estimation of ammonia are based upon the fact that ammonia compounds are decomposed by, and the gaseous ammonia is expelled from, hot sodium hydroxide solutions. Because ammonium hydroxide is a weak base, it will be displaced from its salts in the presence of an excess of a strong base. From the constant for the ionization equilibrium,

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5} \text{ at } 25°\text{C.},$$

it is seen that in case the $[OH^-]$ is made 1 m., by addition of any strong base, the ratio

$$\frac{[NH_4^+]}{[NH_4OH]} = 1.8 \times 10^{-5}.$$

It is also seen that there will have been practically quantitative conversion of any ammonium salt to ammonium hydroxide and

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[9] Upon being boiled in a strongly alkaline solution, various other nitrogen compounds will also evolve ammonia. This is true of the inorganic amides, imides, nitrides, cyanamides, and cyanides; all of these are hydrolysis reactions which are accelerated under the conditions of the procedure below. Typical reactions are as follows:

Sodium amide:

$$NaNH_2 + HOH = Na^+ + OH^- + NH_3.$$

Sodium imide:

$$Na_2NH + 2HOH = 2Na^+ + 2OH^- + NH_3.$$

Sodium nitride:

$$Na_3N + 3HOH = 3Na^+ + 3OH^- + NH_3.$$

(It is seen that the amides, imides and nitrides can be considered as ammonia derivatives in which the hydrogen atoms are successively replaced by other metals.)

Calcium cyanamide:

$$CaCN_2 + 3HOH = CaCO_{3(s)} + 2NH_3.$$

Sodium cyanide:

$$CN^- + 2HOH = COOH^- + NH_3.$$

ammonia, and, as ammonia is volatile, it is readily expelled from boiling solutions.[10]

The detection of the ammonia can be made by means of its odor above the solution, by its effect on red litmus, or by the intense yellow to orange precipitate (usually colloidal) which it produces in an alkaline solution containing the complex ion $HgI_4^{=}$. This solution is prepared by dissolving mercuric iodide in an excess of potassium iodide and making the solution strongly alkaline with sodium or potassium hydroxide; it is the so-called Nessler reagent. According to Nichols and Willets,[11] this precipitate has the composition $Hg_2NH_2I_3$. The reaction occurring may be represented as follows:

$$2HgI_4^{=} + NH_3 + OH^- = Hg_2NH_2I_3 + H_2O + 5I^-.$$

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[10] In the above equilibrium expressions $[NH_4OH]$ represents not just the concentration of the ammonia existing as ammonium hydroxide, but the total ammonia in the solution, $[NH_4OH + NH_3]$. Two equilibria exist in ammonia solutions:

$$NH_4OH = NH_3 + H_2O \qquad (1)$$

and

$$NH_4OH = NH_4^+ + OH^-. \qquad (2)$$

These are represented by the following equilibrium expressions:

$$\frac{[NH_3]}{[NH_4OH]} = K_1 \qquad (1)$$

and

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_2. \qquad (2)$$

As the value of the first constant is uncertain (the equilibrium is probably shifted towards the right), it is more convenient to express the second constant in terms of the total ammonia concentration. Therefore, as

$$[NH_4OH] = \frac{[NH_3 + NH_4OH]}{K_1 + 1};$$

the expression is formulated:

$$\frac{[NH_4^+][OH^-]}{[NH_4OH + NH_3]} = K = 1.8 \times 10^{-5}.$$

Similarly, such equilibria as

$$Ag(NH_3)_2^+ = Ag^+ + 2NH_3$$

are commonly expressed

$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = K.$$

Here $[NH_3]$ again represents the total ammonia concentration $[NH_3 + NH_4OH]$ in the solution.

[11] Nichols and Willets, *J. Am. Chem. Soc.*, **56**, 769 (1934).

The estimation of ammonia can be made by absorbing it in an excess of standard acid and titrating the excess with standard base, or, if only a very small amount of ammonia is present, by comparing the color produced by the Nessler reagent with suitably prepared standards. The latter method is extensively used in the determination of the ammonia in potable waters.

Procedure 96: DETECTION OF AMMONIA. Fit an 18 by 150-mm test tube with a stopper carrying a short piece of glass tubing into the lower end of which has been inserted a piece of red litmus paper. Transfer approximately 0.2 g of the sample to the test tube, add 2 to 3 ml of 6 n. NaOH (Note 1), insert the stopper with the tube and paper, and heat the mixture just to boiling, while carefully swirling the solution in the tube (Note 2). (Red litmus turning to blue, presence of ammonia. Note 3.)

Notes:

1. As NaOH may contain small amounts of ammonia, it should have been previously boiled before being used for this purpose.

2. The mixture should be so swirled as to prevent bumping and spattering. The litmus paper should show a gradual development of blue color from the bottom upwards. Spots would indicate that droplets of the alkaline solution had come in contact with it, probably in the form of spray. This is minimized by enclosing the paper in the tube, which also increases the sensitivity of the test, as all escaping vapors must pass through the tube.

3. The presence of ammonia gas can be very sensitively detected by its characteristic odor. A still more sensitive test is made by means of the mercuric iodide reagent discussed in Note 4 of the procedure below.

ESTIMATION OF AMMONIA. Weigh out a 0.2 to 1-g sample (Note 1) of the material for analysis and transfer it to a 300-ml Kjeldahl flask (Note 2). Insert glass wool in the neck of the flask so that a loose wad about 1 in. long is formed about 2.5 in. below the mouth of the flask (Note 3). Connect the flask by means of glass tubing and rubber stoppers to a small condenser fitted with an adapter as is shown in Fig. 31. Pipet 25 to 50 ml of standard 0.2 n. HCl (Note 4) into a 200-ml flask, add 2 drops of methyl red indicator solution (Note 5), and arrange the flask so that the end of the condenser adapter just touches the surface of the liquid. Add 50 ml of water to 10 ml of NaOH (both ammonia free), pour this into the distilling flask, and im-

mediately connect the flask to the condenser (Note 6). Rapidly heat the solution to boiling and boil continuously until approximately 25 ml have been collected in the receiving flask (Note 7). Lower the receiving flask until the end of the adapter is just above the solution, remove the flame from the distilling flask, disconnect the adapter from the condenser, and wash it, collecting the washings in the receiving flask. Cool the solution in the receiving flask and titrate it with standard 0.2 n. NaOH until a change from

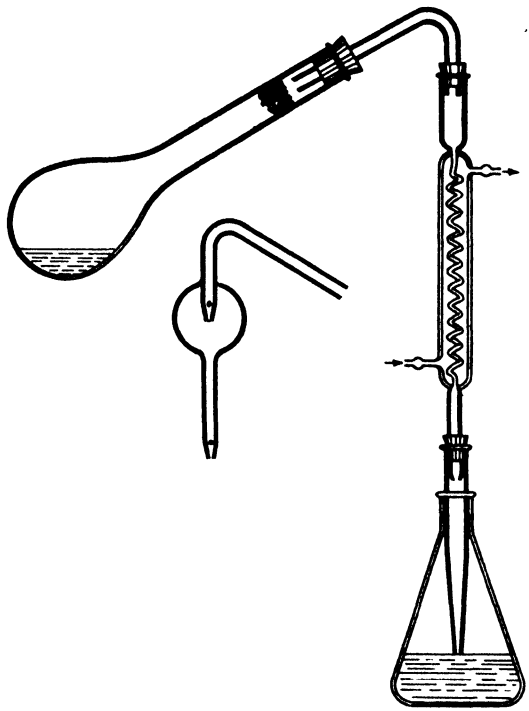

Fig. 31. Apparatus for the Distillation of Ammonia

red to yellow is obtained (Note 8). From the volumes of standard HCl and NaOH used, calculate the amount of ammonia (or ammonium) present.

Notes:

1. The size of the sample taken should be adjusted to the amount of ammonia thought to be present from previous information, or from the evidence obtained in the detection; 25 ml of 0.2 n. acid is equivalent to 85 mg of NH_3.

2. If the Kjeldahl flask (a pear-shaped flask with a long neck) is not

available, an ordinary round-bottom, long-neck flask (preferably of resistance glass) can be used.

3. The need for the glass wool may be eliminated by the use of a spray trap (shown in Fig. 31) between the flask and the condenser. It is necessary that some means be employed to prevent spray from the NaOH solution from passing into the receiving solution.

4. If it is desired to detect or estimate very small amounts of ammonia, a few milligrams or less, proceed with the distillation as directed in this procedure, but collect the distillate in a 50-ml test tube or, preferably, a Nessler tube (a long cylindrical tube with a flat bottom which facilitates the comparison of colored solutions). Cool the distillate and add to it 1 ml of K_2HgI_4 reagent. Compare the precipitate or color thus produced with known amounts of an ammonium salt in similar tubes.

This test is so sensitive that an ammonia free NaOH solution should be first distilled in the distilling apparatus until the distillate gives no color with the K_2HgI_4 reagent; the distillation should be carried out in a laboratory that is free of ammonia fumes.

5. Methyl orange can be substituted for methyl red, although the latter gives a somewhat sharper and more exact end-point in this titration. The indicator is added at this point so that warning will be given if all of the acid is neutralized by the ammonia passing over. In such a case, immediately add more of the standard acid.

6. As ammonia will be liberated as soon as the NaOH is added, the distilling flask should be immediately connected to the condenser in order to avoid loss.

7. Care is necessary during the distillation in order to avoid sucking the distillate into the condenser and distilling flask. The distilling flask should be heated uniformly, so that there is continuous and steady boiling, and, in addition, the adapter tube should just touch the surface of the receiving solution, so that no appreciable amount of solution can be pulled back. Under no conditions should the flame be removed unless the receiving solution is lowered from the adapter. The distillation should proceed so that approximately 5 ml of solution are collected per minute.

8. The end-point can be more precisely obtained by adding to the same volume of water and indicator as is present in the titrated solution approximately the same number of equivalents of pure NH_4Cl as there are thought to be equivalents of ammonia present; the titration should then be continued until the color of the solutions match.

Part III

THE SYSTEM OF ANALYSIS FOR THE ACIDIC CONSTITUENTS

The Analysis of the Acidic Constituents

General discussion. The fundamental objective of the system for the analysis of the acidic constituents differs from that of the basic constituents and is more difficult of attainment. Thus in the basic analysis there is sought the detection of certain elements without regard to their state of oxidation or combination in the original material. In the acidic analysis there is desired not only the detection of certain elements but also definite information as to the oxidation state and state of association of these elements. As examples, not only is it desired to detect the presence of the element chlorine, but it is desired to know whether it is present as chloride, hypochlorite, chlorate, or perchlorate; it is usually important to know, not that nitrogen is present, but whether it is combined as cyanide, thiocyanate, nitrite, or nitrate.

The problem is further complicated by the possibility that one or more of these constituents may exist in the same solution under certain conditions—for example, when it is alkaline—and may decompose or interact with the formation of other constituents under other conditions—that is, when the alkaline solution is made acid. Thus nitrite ion is stable in alkaline solutions but decomposes into nitrate ion and nitric oxide in acid solutions; the oxygen acids are in general much more reactive in acid solutions. Because of these facts, recourse has often been made mainly to individual tests for each constituent, often without proper precautions to prevent other constituents from interfering with the particular test being applied, and only relatively recently have attempts been made to develop methods for the analysis of the acidic constituents on a systematic basis similar to that for the basic constituents.[1]

In the following procedures an attempt has been made to provide a scheme for the acidic analysis approaching the systematic nature of that for the basic elements. However, the limitations stated above have made it impossible at the present time to include all of the important acids, and therefore it has been necessary to provide supplementary tests for certain individual constituents.

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[1] Systematic procedures, including varying numbers of the more common acidic constituents, have been recently proposed by Duschak and Sneed, *J. Chem. Ed.*, **8**, 1177, 1386, (1931); Dobbins and Ljung, *ibid.*, **12**, 586 (1935); Flosdorf and Henry, *ibid.*, **13**, 274 (1936); Yamamura, *J. Chem. Soc. Japan*, **57**, 761, 877, 1048, 1067 (1936); **58**, 42, 149, 275, 410, 685 (1937).

TABULAR OUTLINE XI

Separation of the Acidic Constituents into Groups

Solution Obtained from a Treatment of the Sample with a Sodium Carbonate Solution. *Transfer to distilling apparatus. Make just acid with $HC_2H_3O_2$. Draw air through solution. Collect evolved gases (H_2S, HCN, CO_2) in solution containing NaOH, NH_4OH and $AgNO_3$.* (P. 121)

Distillate: Ag_2S, $Ag(CN)_2^-$, Sulfide-Cyanide Group *Treat by P. 121–123.*

Distillate: Na_2SO_3, Sulfite *Treat by P. 125.*

Solution: Remaining anions: $HC_2H_3O_2$, $C_2H_3O_2^-$. *Add $HClO_4$; again draw air through the solution. Collect evolved gas (SO_2) in NaOH.* (P. 124)

Solution: Remaining anions: $H^+ClO_4^-$, $HC_2H_3O_2$. *Add $Cd(NO_3)_2$.* (P. 131)

Precipitate: $Cd_2Fe(CN)_6$, $Cd_3(Fe(CN)_6)_2$, Ferrocyanide Group *Treat by P. 132–134.*

Filtrate: Remaining anions: $HC_2H_3O_2$, $H^+ClO_4^-$, Cd^{++}, NO_3^- *Add $AgNO_3$.* (P. 141).

Precipitate: AgI, AgSCN, AgBr, AgCl, ($AgIO_3$, $Ag_2C_2O_4$), Halide Group *Treat by P. 141–148.*

Filtrate: Remaining anions: $HC_2H_3O_2$, H^+ClO_4, Cd^{++}, Ag^+, NO_3^- *Add $NaNO_2$, $AgNO_3$.* (P. 151)

Precipitate: AgBr, AgCl, AgI (from P. 141), Oxy-Halogen Group *Treat by P. 142–148.*

Filtrate: Remaining anions: $HC_2H_3O_2$, $H^+ClO_4^-$, Cd^{++}, Ag^+, NO_3^-, HNO_2 *Add NaOH, then $HC_2H_3O_2$, $AgNO_3$.* (P. 161)

Precipitate: Ag_3PO_4, Ag_3AsO_4, Ag_3AsO_3, $Ag_2C_2O_4$, Phosphate Group *Treat by P. 162–166.*

Filtrate: Remaining anions: $C_2H_3O_2^-$, $HC_2H_3O_2$, Cd^{++}, Ag^+, NO_3^-, NO_2 *Add HNO_3, $Ba(NO_3)_2$.* (P. 171)

Precipitate: $BaSO_4$

Filtrate: as above; also Ba^{++} $(NO_3^-)_2$ *Neutralize with NH_4OH. Add $Ca(NO_3)_2$.* (P. 172)

Precipitate: CaF_2

Filtrate: *Discard. (Test separately for $C_2H_3O_2^-$, ClO_4^-, NO_3^-, BO_2^-, CO_3^- NO_2^-.)*

The Separation of the Acidic Constituents into Groups. The methods used for the separation of the acidic constituents into groups are shown in Tabular Outline XI. As is shown there, a solution of the original material is prepared by treating the sample with sodium carbonate. The first group to be removed is composed of sulfide and cyanide. Hydrogen sulfide and hydrogen cyanide are such weak acids in aqueous solutions and are so volatile that they can be removed by drawing a current of air at room temperature through a solution which has been buffered to a *p*H of approximately 6 by providing the proper ratio of acetate and acetic acid. Carbonate is similarly removed but has been added in preparing the solution; therefore it has to be detected in a separate portion of the original sample. Sulfurous acid is too highly ionized to be volatilized from the acetate–acetic acid solution, but, by the addition of an excess of a strong acid (perchloric is used), it can be similarly volatilized with a current of air. Sulfide, cyanide, and sulfite could be volatilized in one step from a strongly acid solution; however, the method as outlined provides for the separation of sulfite from all other constituents, and, furthermore, this separation has to be carried out only when reducing agents have been found to be present. The second group to be removed (called for convenience the Ferrocyanide Group) is composed of the two complex iron cyanides; these anions are precipitated from a strongly acid solution as their cadmium salts. Following this, those anions which form silver salts insoluble in a solution half normal in perchloric (or nitric) acid are removed; these include chloride, bromide, iodide, and thiocyanate and are designated as the Halide Group. Iodate is precipitated with this group but is removed from it and combined with the next group. The halogen oxy-acids, chlorate and bromate (which form soluble silver salts), are then reduced by the addition of nitrite and are precipitated as the corresponding silver halides; these (together with the iodate precipitated with the Halide Group) constitute the Oxy-Halogen Group (periodate and perchlorate are not reduced or precipitated). By lowering the hydrogen ion concentration to approximately 10^{-5} m., the silver salts of a group of weak acids are precipitated; included in this group are phosphate, arsenate, arsenite, and oxalate. Phosphite is oxidized by silver ion under these conditions and is precipitated as silver phosphate, an equivalent amount of silver also being formed. The constituents of this precipitate constitute the Phosphate Group. Sulfate is then separately precipi-

tated as barium sulfate, and fluoride as calcium fluoride. Acetate, perchlorate, nitrate, nitrite, and borate are detected in separate portions of the sodium carbonate solution of the material.

It is to be noted that, because it has been found much more satisfactory to carry out certain of the group separations in strongly acid solutions, the results which are obtained may be misleading unless they are properly interpreted in those exceptional cases where oxidizing and reducing agents have been simultaneously present in the solid material or an alkaline solution has been submitted for analysis. Partly to aid in this interpretation, and frequently to enable the subsequent analysis to be much simplified and shortened, there have been provided a limited number of preliminary group tests, which establish the presence or absence of certain classes and groups of constituents. The groups thus tested for are those constituents which (1) act as reducing agents, (2) act as oxidizing agents, (3) form silver salts insoluble in acids, and (4) form barium or calcium salts insoluble in an acetate–acetic acid solution.

It is also to be pointed out, as is done by A. A. Noyes,[2] that the number of acidic constituents which may be present is often limited by a knowledge of the history of the material. Thus *native* materials (minerals, ores, and substances which have been subjected to long periods of weathering action) and substances which have been submitted to high temperatures cannot, in general, contain the more unstable and reactive acidic constituents.

Methods for the estimation of the amounts of the constituents found present are provided in these procedures. However, the values so obtained are subject to the limitations stated above, involving loss in preparing a solution of the material for the analysis, in interference from other constituents, and in imperfect separations. Therefore, it is urged that a careful consideration of these factors be made to prevent according the results obtained from these estimations with too great a degree of accuracy.

This system for the analysis of the acidic constituents has been developed with the coöperation and assistance of Theodore Vermeulen, R. W. Dodson, D. K. Beavon, and R. N. Wimpress; its present form is largely the result of their efforts. Erwin Baumgarten, F. C. Ingalls, Bernard Love, and W. B. Scarborough have given valuable assistance in developing many of the procedures.

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[2] Noyes, *Qualitative Analysis*, Macmillan, 1922.

P. 111. Preparation of a Solution for the Analysis of the Acidic Constituents

Discussion. In the selection of a method for the preparation of a solution of a material for an analysis of the acidic constituents, certain requirements have to be considered which are not necessary in this operation in an analysis of the basic elements. There the principal object is to obtain the basic elements in a soluble form, while in this process for the acidic analysis two additional requirements have to be met, namely: (1) The procedure must be so carried out that no changes in the constituents as they exist in the original material are caused by decomposition or by oxidation-reduction effects; and (2) it is desirable to remove, insofar as possible, most of the basic elements from the solution, as these are likely to interfere with the subsequent analysis by forming precipitates either when reagents are later added or when the solution is made alkaline or by producing colors which mask certain tests for acidic constituents.

Because of the first of these requirements, oxidizing or reducing agents cannot be used, nor can strong acids. Because of the second requirement, concentrated hydroxide solutions are unsatisfactory, as they would cause amphoteric elements—such as aluminum, chromium, and antimony—to pass into the solution with the acidic constituents.

Recourse is therefore made to metathesizing agents. Of these, the phosphates and carbonates most generally cause the formation of insoluble compounds with the basic elements. Upon being treated with an excess of an alkaline phosphate, such as Na_3PO_4, most of the basic elements would be metathesized and precipitated. Phosphate, however, is undesirable in the solution for three reasons: (1) It is likely to form precipitates with the reagents later to be added; (2) by its buffering action, it makes difficult the proper adjustments of the acid concentration in later procedures; and (3) it is difficult to remove once it is introduced into the analysis. Upon being treated with an excess of a soluble carbonate, most of the metallic elements form insoluble carbonates, basic carbonates, or hydroxides; therefore a carbonate solution is an effective metathesizing agent, both precipitating the metallic elements from solution, and (by metathesis) causing the decomposition of many of their insoluble compounds. In addition, carbonate can be readily removed from a solution by acidification. For these reasons the solution for the acidic analysis is prepared by boiling the material with a sodium carbonate solution

and then filtering out any residue or precipitate which results. Unfortunately, many insoluble compounds (sulfides, phosphates, silver halides, complex cyanides, and so forth) are not decomposed by the carbonate treatment, and therefore this residue has to be examined further before being rejected.

Procedure 111: PREPARATION OF THE SOLUTION. If the material is a non-metallic solid, weigh out a sample of approximately 5 g and transfer it to a 200-ml flask (Note 5; see also Notes 1–3, P. 5).

If the material is a solution, measure out into a flask that volume which is estimated to contain 5 g of solid material (see P. 4), make it just alkaline with Na_2CO_3, and evaporate it to 5 to 10 ml.

Add to the sample 50 ml of 3 n. Na_2CO_3 and 0.5 ml of NaOH, and heat the mixture just to boiling until no further action appears to be taking place (Notes 1, 2). Filter out the precipitate and wash it with hot water, collecting the wash water with the filtrate until it has a volume of approximately 90 ml. Treat the precipitate by P. 191 (Note 3). Cool the filtrate, transfer it to a 100-ml volumetric flask, dilute it to the mark, mix the contents thoroughly, and treat portions of it by P. 112 to P. 185 (Note 4).

Notes:

1. The information obtained in the preparation of the solution of the basic constituents should be considered here. However, even if the material is soluble in water, the sodium carbonate solution should be added, as the hydrogen ion concentration in certain subsequent procedures is adjusted by neutralizing the carbonate and then adding a certain amount of the acid, thus producing a definite ratio of the concentration of the salt to that of the acid.

2. If ammonia is one of the constituents of the material (indicated by its smell above the boiling solution), the mixture should be boiled until it is completely expelled; otherwise those basic elements which form ammonia complexes may be carried into the sodium carbonate solution.

3. As mentioned in the discussion, certain compounds are attacked very slightly by the sodium carbonate treatment. This residue is therefore treated by P. 191 to insure the detection of any of these acidic constituents which may be present.

4. In the subsequent analysis it is to be remembered that certain amphoteric elements may be found in the sodium carbonate solution. Thus copper, tin, antimony, aluminum, and chromium are dissolved in appreciable amounts. Basic elements, such as manganese and chromium, which form oxygen acids in their higher oxidation states will also be found in the solution.

Basic elements which form complex ions may also be present; thus the presence of cyanide may cause iron, cobalt, nickel, silver, and mercury to pass into the solution, and mercury may dissolve if much iodide is present.

5. As has been mentioned previously, if the sample is a native material (a mineral, or from an ore) or is the product of a high-temperature process, the number of acidic constituents which may be present is greatly limited. Therefore, in such cases, careful consideration should be given to the possibility of carrying out the much shorter system of analysis which is suggested in the second paragraph of the general discussion of the analysis of the residue from the sodium carbonate treatment, p. 493.

Preliminary Tests for Certain Groups of the Acidic Constituents

General discussion. As previously mentioned, it has seemed advisable to provide preliminary tests for certain groups of the acidic constituents. From the information thus obtained it is often possible to reduce greatly the number of operations required for the complete analysis. These tests are shown in Tabular Outline XII.

TABULAR OUTLINE XII

PRELIMINARY TESTS FOR CERTAIN GROUPS OF THE ACIDIC CONSTITUENTS

Treat 5-ml portions of the Na_2CO_3 solution as follows:

Acidify with H_2SO_4. Add KI. Shake with CCl_4.	*Acidify with H_2SO_4. Add KIO_3. Shake with CCl_4.*	*Add $AgNO_3$ and HNO_3. Add $NaNO_2$.*	*Acidify with $HC_2H_3O_2$. Add $Ba(NO_3)_2$ and H_2O_2. Add $Ca(NO_3)_2$.*
Iodine color in CCl_4, presence of OXIDIZING ANIONS	Iodine color in CCl_4, presence of REDUCING ANIONS	Precipitate, presence of CYANIDE, HALOGEN OR OXY-HALOGEN Groups	Precipitate, presence of SULFATE, CHROMATE, OXALATE, SULFITE, or FLUORIDE
(BrO_3^-, $CrO_4^=$, IO_3^-, MnO_4^-, $Fe(CN)_6^=$, NO_2^-, IO_4^-, $S_2O_8^=$)	($S^=$, $SO_3^=$, I^-, SCN^-, $S_2O_3^=$, $Fe(CN)_6^{\equiv}$, $AsO_3^=$)	($S^=$, CN^-, $Fe(CN)_6^=$, $Fe(CN)_6^{\equiv}$, Cl^-, Br^-, I^-, SCN^-, IO_3^-, BrO_3^-, ClO_3^-)	
P. 112	P. 113	P. 114	P. 115

P. 112. Detection of Oxidizing Anions

Discussion. This test for the oxidizing acidic constituents (oxidizing basic constituents such as ferric iron or cupric copper having been removed by the sodium carbonate treatment) depends upon the fact that certain of the acidic constituents provided for in this

system will cause in an acid solution the oxidation of iodide ion to iodine.[3]

Experiments have shown that, under the conditions of this procedure, 0.3 mg of bromate, chromate, iodate, periodate, permanganate, persulfate, ferricyanide, or nitrite are readily detected; the color with persulfate and ferricyanide is less intense because of their high equivalent weight. Even after 20 min. no color is produced in the absence of oxidizing agents; the carbon dioxide evolved upon acidifying the sodium carbonate solution tends to prevent oxidation of the iodide by oxygen of the air. Chlorate reacts so slowly with iodide in this concentration of hydrogen ion that 1 mg gives a perceptible color only after 30 min.; 100 mg of nitrate did not give a color until after more than an hour. Upon the addition of 5 ml of 12 n. hydrochloric acid, 0.5 mg of chlorate or arsenate can be detected in 2 to 3 min. In experiments to determine the effect upon this test of the presence of reducing agents, it was found that 1 mg of iodate or permanganate could be detected in the presence of much larger amounts of sulfite, arsenite, or thiocyanate, but not when thiosulfate or sulfide were present.

Procedure 112: DETECTION OF OXIDIZING ANIONS. Pipet 5 ml of the Na_2CO_3 solution (P. 111) into a test tube or small flask (Note 1) containing 5 ml of CCl_4. Add 5 ml of H_2SO_4 and then, 1 ml at a time, 2 to 5 ml of a solution made by dissolving 2 g of solid KI in 5 ml of water (Note 2). Shake the mixture for 10 to 15 seconds. (Purple to violet color in the CCl_4, presence of oxidizing constituents. Notes 3, 4.)

Notes:

1. This operation can be advantageously carried out in a small conical flask with a ground-glass stopper, as such a flask permits the solution to be shaken without loss. By inverting the flask and collecting the carbon tetrachloride in the neck, the presence of any color can be conveniently noted.

2. Iodide solutions are not stable, because of oxidation by the air; therefore this solution should be prepared only as needed. As iodine forms the tri-iodide ion with an excess of iodide, only a small amount of the potassium iodide solution is added at first so that small amounts of iodine may be more completely extracted by the carbon tetrachloride. However, if large amounts of a strong oxidizing agent, such as permanganate, were present, the iodide might be oxidized to iodate (or to iodine monochloride, if chloride were present); for this reason a larger amount of iodide is finally added.

[3] See p. 68 for a discussion of the oxidation and reduction reactions of iodine and the detection of free iodine by various agents.

3. If no color is obtained and information is desired as to the probable presence of arsenate and chlorate, add gradually 0.25 g of solid $NaHCO_3$ and 5 ml of 12 n. HCl; close the flask and allow it to stand for 5 min. An iodine color indicates the presence of chlorate or arsenate. The test is not entirely conclusive for small amounts of these constituents, as it is difficult to prevent some oxidation of iodide by any oxygen present in solutions of this acidity; the $NaHCO_3$ is added to minimize this effect.

4. If oxidizing constituents are present and an estimation of the amount desired, transfer the mixture to a larger flask, add 50 ml of water and 4 ml of the KI solution, and titrate the mixture with standard 0.1 n. $Na_2S_2O_3$, shaking after each addition, until the violet color disappears from the CCl_4. From the volume of thiosulfate used, calculate the equivalents of oxidizing constituents present. For a discussion of the principles involved in the above estimation, see the discussion and notes to P. XIV.

P. 113. Detection of Reducing Anions

Discussion. This test depends upon the fact that in an acid solution many reducing agents will be oxidized by iodate. With the stronger reducing agents, the reaction would proceed to iodide if they were present in excess, but with an excess of iodate the reduction product is iodine, as, in an acid solution, iodide is oxidized to iodine by iodate. If a high concentration of hydrochloric acid were provided, iodine would be quantitatively converted to iodine monochloride by the excess of iodate, the reaction being represented as

$$2I_2 + IO_3^- + 6H^+ + 5Cl^- = 5ICl + 3H_2O.$$

Because of this fact, the solution is acidified with sulfuric acid and only a small excess is added.

Experiments have shown that, under the conditions of the procedure, 0.3 mg of sulfite, iodide, thiocyanate, thiosulfate, and ferrocyanide are readily detected, while arsenite gives only a very faint color. Nitrite and phosphite give a distinct color within 1 min. only when present in amounts above 50 mg; bromide causes a bromine color in amounts above 25 mg; only with more than 200 mg is an iodine color also evident.

Procedure 113: DETECTION OF REDUCING ANIONS. Pipet 5 ml of the Na_2CO_3 solution (P. 111) into a test tube or small flask (Note 1, P. 112) containing 5 ml of CCl_4, make the solution acid to litmus with H_2SO_4, add just 1 ml in excess, and dilute it with 10 ml of water. Add slowly to the solution, noting any changes taking place (Note 1), 5 ml of 1 n. KIO_3. (Purple to violet color in the CCl_4, presence of reducing constituents. Note 2.)

Notes:

1. With the first portion of KIO_3, no iodine color, or only a transitory one, may be produced, because of reduction of the iodate to iodide by an excess of reducing agent. As explained in the discussion, this iodide is oxidized to iodine by the additional iodate.

2. If the reducing group is present and an estimation of the amount is desired, transfer the mixture to a short-stem separating funnel and draw off the CCl_4 layer into a 200-ml flask; add two successive 5-ml portions of CCl_4 to the aqueous layer, separating and collecting these with the first.

Add 50 ml of water to the CCl_4 extracts, and titrate the mixture with 0.1 n. $Na_2S_2O_3$, shaking vigorously, until the two layers are colorless. From the volume of thiosulfate used, calculate the equivalents of reducing constituents present.

P. 114. Detection of Constituents of the Cyanide, Halide, and Oxy-Halogen Groups

Discussion. This test is provided to determine, first, the presence of those constituents which form silver salts insoluble in dilute nitric acid. These constituents comprise the halogen acids, cyanide, thiocyanate, the complex iron cyanides, and sulfide. Experiments have shown that, under the conditions of the procedure below, 0.3 mg of sulfide, cyanide, ferro- or ferricyanide, chloride, bromide, iodide, iodate, or thiocyanate can be readily detected. If more than about 75 mg of bromate are present, a precipitate will be obtained.

By the addition of a reducing agent, nitrite in this procedure, bromate and chlorate are reduced to the halides and corresponding precipitates are obtained. Iodate is precipitated as silver iodate and is not appreciably reduced by the nitrite; perchlorate and periodate are not reduced under the conditions of this procedure.

It is essential that the concentration of the nitric acid be sufficiently high to prevent the precipitation of the insoluble silver salts of various weak acids. Thus, in a neutral solution, phosphate, arsenate, arsenite, oxalate, chromate, carbonate, and borate would cause precipitates.

Procedure 114: DETECTION OF CONSTITUENTS OF THE CYANIDE, HALIDE, AND OXY-HALOGEN GROUPS. Pipet 5 ml of the Na_2CO_3 solution (P. 111) into a 100-ml flask, dilute with 5 ml of water, and add 5 ml of $AgNO_3$ and 5 ml of HNO_3 (Note 1). (Precipitate, presence of the Halogen or Cyanide Groups. Notes 2, 3.) Filter out any precipitate and add 0.5 ml of $NaNO_2$ to the filtrate. (Precipitate, presence of halogen oxyacids. Note 4.)

Notes:

1. Upon the addition of silver nitrate to the sodium carbonate solution, a precipitate of silver carbonate, or of the silver salts of any of the weak acids mentioned in the discussion above which are present, will be obtained; these precipitates are dissolved by the nitric acid. The reagents are added in this order to prevent partial loss of volatile constituents such as cyanide or sulfide, which would tend to be swept from the solution by the carbon dioxide liberated when the carbonate solution is acidified, and to prevent the interaction of certain constituents such as thiocyanate and iodate, which are stable in an alkaline solution but which would react with the formation of other products upon acidification.

2. Acidification of the sodium carbonate solution with nitric acid may produce a precipitate which would obscure the silver salts. Thus, on acidification of the sodium carbonate solution, the presence of any of the following substances would cause precipitates to be formed which might obscure the test for constituents of the Halogen and Cyanide Groups: Silicate, which would give a precipitate of silicic acid; certain amphoteric elements, such as antimony or tin, which would precipitate as their hydrous oxides; elements forming sulfo-acids, such as arsenic, antimony, or tin, which would be precipitated as sulfides; sulfur, which would precipitate as a result of being held in solution as disulfide, S_2^-, or as a result of the simultaneous presence of sulfide and sulfite or of sulfide and an oxidizing agent; the less stable complex cyanides, $Ag(CN)_2^-$, $Cu(CN)_3^-$, $Cd(CN)_4^-$, and $Ni(CN)_4^-$ (but not the iron and cobalt compounds), which would be decomposed by the acid and precipitate as the simple salt.

Because of this, if a precipitate which is not characteristic of the silver salts is obtained (see Note 3), another portion of the sodium carbonate solution should be acidified, the precipitate filtered out, and silver nitrate added to this filtrate.

3. The colors of the various silver precipitates are as follows: Sulfide, black; ferricyanide, red-orange; iodide, yellow; bromide, pale yellow; and the others white. If thiosulfate is present in appreciable amounts, it causes a white or yellowish precipitate which changes within a period of approximately 30 sec. through reddish-brown to black. The first precipitate is silver thiosulfate and the final one is silver sulfide; although various intermediate products may be formed,[4] the equation for the complete reaction may be written as follows:

$$Ag_2S_2O_3 + H_2O = Ag_2S + HSO_4^- + H^+.$$

It has been shown[5] that 0.1 mg of thiosulfate in 100 ml of solution can be detected by this reaction.

4. Chlorate, which does not give a satisfactory test in the procedure for detecting oxidizing constituents, because of the slowness with which it reacts with iodide, is rapidly reduced and precipitated here. Therefore, if no test for the oxidizing group is obtained but the presence of the oxy-halogen acids is indicated, the presence of chlorate is conclusively shown.

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[4] For an extensive discussion of the decomposition of thiosulfate with acid and with various metals, see Bassett and Durrant, *J. Chem. Soc.*, **1927**, 1401.

[5] Hackl, *Chem. Ztg.*, **47**, 174 (1923).

P. 115. Detection of Sulfate, Sulfite, Oxalate, Fluoride, or Chromate

Discussion. This test is made by adding successively barium and calcium salts to a portion of the sodium carbonate solution which has been buffered with acetate and acetic acid to a hydrogen ion concentration of approximately 2×10^{-5}. Under the conditions of the procedure below, 0.3 mg of sulfate (or sulfite after it is oxidized to sulfate with peroxide) or chromate gives a precipitate with the barium; upon addition of the calcium salt, 0.3 mg of oxalate or 0.6 mg of fluoride can be detected. This preliminary test is of value in that, when a negative result is obtained, the procedures for the separations of these constituents can be eliminated, and much time can be saved.

When more than 5 to 10 mg of iodate are present, a precipitate of barium iodate will be obtained; if more than 50 mg of fluoride are present, it will partially precipitate as barium fluoride; and if more than 200 mg of phosphate are present, an almost immediate precipitate of barium phosphate will result—even 100 mg will cause a precipitate if allowed to stand for more than 30 min.

Procedure 115: DETECTION OF SULFATE, SULFITE, OXALATE, FLUORIDE, OR CHROMATE. Pipet 5 ml of the Na_2CO_3 solution (P. 111) into a 100-ml flask, add 5 ml of H_2O, make the solution just acid to litmus with $HC_2H_3O_2$, noting the volume required, and then add the same amount in excess. Filter out and discard any precipitate. Add to the clear solution 1 to 5 ml of $Ba(NO_3)_2$, shaking the mixture after each addition (Note 1). Let any precipitate settle and add to the solution 2 to 5 ml of $Ca(NO_3)_2$ solution (Notes 1, 2). If in P. 113 reducing anions have been found present, add to the mixture 2 ml of H_2O_2 (Note 2). (Precipitate, presence of sulfate, sulfite, oxalate, fluoride, or chromate.)

Notes:

1. If no precipitate is obtained, only 1 ml of the precipitant should be added in order to avoid possible precipitation of other constituents; if an immediate permanent precipitate is obtained, the additional reagent should be added in 1-ml portions, the effect of each additional portion being noted.

2. If desired, any precipitate already present can be filtered out so that the effect of the addition of the next reagent can be more easily noted.

TABULAR OUTLINE XIII

The Analysis for Sulfide, Cyanide, and Sulfite

Na_2CO_3. Solution (containing all acidic constituents)

Make just acid with $HC_2H_3O_2$. Draw a rapid stream of air through the solution. Pass air through receiving solution containing NaOH, NH_4OH, and $AgNO_3$. (P. 121)

Receiving solution: Ag_2S, $Ag(CN)_2^-$, CN^-, $S^=$ ($Ag(NH_3)_2^+$, NH_4OH, Na^+OH^-) *Add excess $AgNO_3$.* (P. 121)		Residual solution: Remaining anions, $HC_2H_3O_2$, $C_2H_3O_2^-$ *Add $HClO_4$. Draw air through solution. Pass air through NaOH.* (P. 124)	
Precipitate: Ag_2S *Dissolve in HNO_3.* *Add $Fe(NO_3)_3$, as indicator.* *Titrate with KSCN.* AgSCN (precipitate) $Fe \cdot Fe(SCN)_6$ (red color) P. 122	Filtrate: $Ag(CN)_2^-$, $Ag(NH_3)_2^+$ (NH_4OH, NaOH) *Add excess standard silver nitrate.* *Acidify with HNO_3.* Precipitate: AgCN Solution: excess Ag^+, NH_4^+, Na^+, NO_3^- *Add $Fe(NO_3)_3$, as indicator.* *Titrate with KSCN.* AgSCN (precipitate) $Fe \cdot Fe(SCN)_6$ (red color) P. 123	Receiving solution: $SO_3^=$, Na^+OH^- *Acidify with $HC_2H_3O_2$.* *Titrate with standard KI_3 solution.* ($SO_4^=$, I^-, $HC_2H_3O_2$, $C_2H_3O_2^-$) *Add HCl, $Ba(NO_3)_2$.* Precipitate: $BaSO_4$ P. 124	Residual solution: Remaining anions *Treat by P. 131.*

The Analysis for Sulfide, Cyanide, and Sulfite

P. 121. Volatilization and Detection of Sulfide and Cyanide

Discussion. This procedure is based upon the fact that, of the acidic constituents to be tested for in the sodium carbonate solution, the only ones forming very slightly ionized and very volatile acids are hydrogen sulfide and hydrogen cyanide.

By neutralization of the sodium carbonate solution with acetic acid and addition of sufficient acid to give a *p*H of about 5.5, a solution buffered with acetic acid and acetate is obtained, and upon the passage of a current of air through the solution, hydrogen sulfide and hydrogen cyanide are completely removed and can be collected in a suitable receiving solution. The receiving solution contains sodium hydroxide, silver nitrate, and ammonium hydroxide. The sodium hydroxide solution serves as an efficient absorbing agent for hydrogen sulfide and hydrogen cyanide, because it rapidly converts them to sulfide and cyanide ions. The silver nitrate is added, primarily, to indicate the presence of sulfide so that the distillation process may be shortened in its absence; also, the oxidation of sulfide ion by oxygen in alkaline solutions is minimized. Sufficient ammonia must be present to prevent the precipitation of silver oxide.

Carbonate, which is volatilized from the solution as carbon dioxide, is not tested for because it has been used in preparing the solution. At this hydrogen ion concentration, sulfurous and hydrofluoric acids are ionized to such an extent that the partial pressures of sulfur dioxide and hydrogen fluoride are so low that they are not volatilized; borates are converted largely to the un-ionized acid, but this is not volatile under these conditions.

Experiments have shown that, under the conditions of the procedure given below, 0.2 mg of either sulfide or cyanide can be readily detected and that with 250 mg the distillation is complete in 15 min.; under these same conditions, neither sulfite nor fluoride is carried over in significant amounts. There is a slight decomposition of thiosulfate with precipitation of sulfur, but this does not interfere with the process. It was also found that neither ferrocyanide or ferricyanide is sufficiently decomposed to give a test for cyanide even when the distilling solution had 2 ml of 6 n. $HC_2H_3O_2$ added in addition to the amount necessary to acidify the solution.

Procedure 121: DETECTION OF SULFIDE AND CYANIDE. If in P. 114 the Halogen-Cyanide and Oxy-Halogen Group constituents were not found present and if either the reducing anions (P. 113) or sulfite (P. 115) have been found to be *absent* (Note 9), pipet 10 ml of the sodium carbonate solution (P. 111) into a 200-ml flask, make it just acid to litmus with $HC_2H_3O_2$, filter out and discard any precipitate, dilute the solution to 40 ml, and treat it by P. 161.

If the Halogen-Cyanide Group constituents were not found present in P. 114, but reducing anions were found present in P. 113 and the possible presence of sulfite was also indicated in P. 115, proceed as directed in the next paragraph of this procedure (omitting the second test tube from the apparatus), acidify the sodium carbonate solution with $HC_2H_3O_2$, and further proceed as directed in P. 124.

If in P. 114 the Halogen-Cyanide Group constituents were found present, pipet 10 ml of the sodium carbonate solution (P. 111) into a test tube $\frac{7}{8}$ in. by 7 in. or larger (Note 1) and drop into it a small square of blue litmus paper. To a second test tube add 50 ml of water, 10 ml of 6 n. NaOH, 5 ml of 6 n. ammonium hydroxide, and (from a buret or pipet) 2 ml of standard 0.1 n. silver nitrate solution (Note 8), and connect it to the first test tube as shown in Fig. 32. The first test tube is fitted with a rubber stopper carrying a glass tube—a thistle tube can be used to advantage—extending to its bottom and an outlet tube which is bent so as to pass through a second rubber stopper and serve as an inlet tube to the second test tube, which is 1.5 in. by 8 in.; the stopper of the second test tube also carries an outlet tube, which is connected to a water aspirator (Note 2).

Draw a moderate current of air (3 bubbles/sec.) through the apparatus and add slowly $HC_2H_3O_2$ through the thistle tube until the solution is just acid to litmus (Notes 3, 4, 5). Continue the current of air for 1 min. (Brown-black precipitate in receiving test tube, presence of sulfide.)

If sulfide is present, maintain a moderate current of air for 5 min., followed for 10 min. by a current at the maximum rate consistent with retaining the solution (Note 6). Treat the distillate mixture by P. 122. Treat the residual solution by P. 124.

If sulfide is absent, draw a rapid current of air through the apparatus for 5 min. Pipet 5 ml of the solution from the receiving test tube into a test tube containing 2.00 ml of standard 0.1 n. $AgNO_3$. Add to the solution 5 ml of HNO_3 (Note 7). (White precipitate, presence of cyanide.)

If cyanide is absent, treat the residual solution by P. 124; discard the distillate.

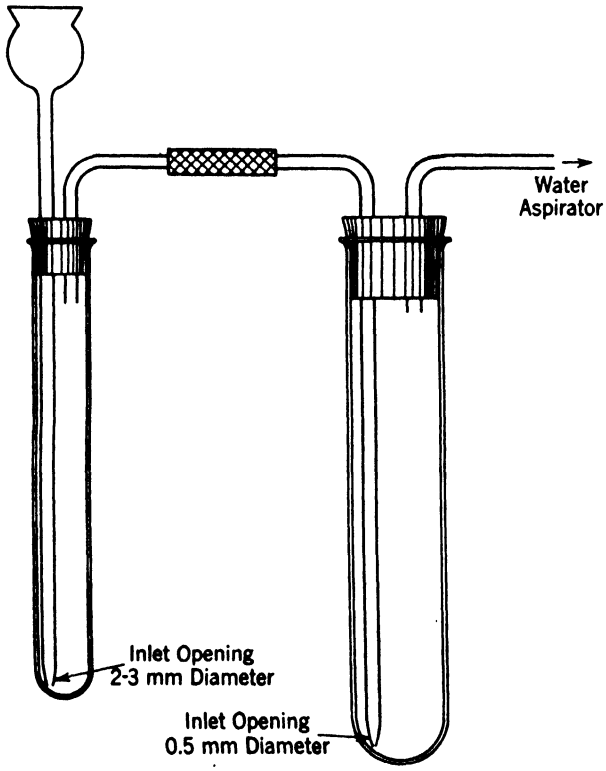

Fig. 32. Apparatus for Separation of Cyanide and Sulfide.

If cyanide is present, make the test mixture alkaline with ammonia, return it to the receiving test tube, and again pass a rapid current of air through the apparatus for 10 min. Stop the current of air and remove the receiving test tube; as the apparatus is disconnected, rinse into the respective test tubes any solution adhering to the inlet and outlet tubes. If cyanide is present, treat the contents of the receiving test tube by P. 123. Treat the residual solution by P. 124.

Notes:

1. If test tubes of the specified size are not available, 100-ml and 125-ml round-bottom long-neck flasks may be substituted.

2. The efficiency of the separation is dependent upon the size of the air inlets to the two flasks. If the inlets are too large, absorption is incomplete because of large bubble size; if the inlets are too small, incomplete expulsion may result, because the rate of flow of air is cut down too much. Expulsion and absorption are satisfactory when the inlet to the first solution is about 2 to 3 mm in diameter and the inlet to the receiving solution is about 0.5 mm in diameter. More flexibility in assembling and using the apparatus is obtained if the single tube serving as combined outlet and inlet is cut at the top and joined with rubber tubing as shown in Fig. 32.

3. If too great an excess of acid is added, sulfite may be lost in small quantities from the solution. Under the specified conditions, less than 0.5 mg of sulfite or fluoride are volatilized from 250 mg of each constituent.

4. When large quantities of sulfide are present, the litmus tends to become decolorized and sluggish in its action. In general, the amount of $HC_2H_3O_2$ added should be from 4 to 6.5 ml. When sulfide is present in large enough quantities to cause this trouble, disulfide is usually also present in sufficient quantity to cause a milky precipitate in the solution. As acid is added, the solution becomes yellow. When a slight excess of acid has been added. the precipitate of sulfur becomes a milky white. Other precipitates which may be formed have been discussed in Note 2, P. 114.

Sulfide may be present in the sodium carbonate solutions as a thio salt of arsenic or antimony. On acidification of such a solution, the sulfides would be precipitated and no test for sulfide would be obtained. If a precipitate characteristic of arsenic or antimony sulfides is obtained, it should be filtered from the residual solution before P. 131 is carried out and it, or a portion of the original material, should be treated by P. 191 for the detection of sulfide. Arsenic and antimony would be detected in the analysis for the basic constituents.

5. If iodide or bromide are present together with an oxidizing agent, such as bromate or chromate, iodine or bromine may be liberated when the solution is acidified. If these are apparent, the addition of 5 ml of CCl_4 to the distilling flask will tend to retain them in the solution. At the end of this procedure, the CCl_4 should be separated, by means of separating funnels, from the aqueous solution, reserved, and then shaken with the $(NH_4)_2S$ solution to be used in P. 142. By this means the halogens will be reduced, will pass into the aqueous solution, and will be detected in their proper place.

6. When large quantities of sulfide are present, a vigorous initial current of air may cause some of the hydrogen sulfide to pass through the receiving solution without time for absorption. This difficulty is not experienced with cyanide.

7. By this means, a test for cyanide is made, and, if it is absent, the passage of air for the longer period of time is avoided. The receiving solution is added to the solution containing an excess of silver before it is acidified, in order to avoid possible loss of HCN; this would occur if a solution containing considerable cyanide were acidified, especially when carbonate is present and large amounts of CO_2 are evolved. If no test for cyanide is obtained in the

small portion, the amount present is so small that the entire distillate can be safely acidified and examined for any precipitate.

8. The amount of silver added must be accurately known, as it permits a later estimation of the cyanide to be made.

9. If in P. 114 the Halogen-Cyanide Group was absent but the Oxy-Halogen Group was present, the solution obtained as directed in the first paragraph of this procedure should be treated directly by P. 141 and then by P. 151, after 5 ml of 9 n. $HClO_4$ is added.

P. 122. Separation and Estimation of Sulfide

Discussion. Sulfide is separated from cyanide by precipitation from an ammoniacal solution with standard silver nitrate solution; silver cyanide is soluble in ammoniacal solution. A known volume of standard silver nitrate solution is used as the precipitating agent in order that the subsequent estimation of cyanide may be simplified. The quantity of sulfide present is estimated by dissolving the silver sulfide precipitate in hot concentrated nitric acid and titrating the silver with standard thiocyanate solution, with a ferric salt as indicator. For a treatment of this titration, see the discussion and notes of P. VI, "The Standardization of a Thiocyanate Solution."

Procedure 122: SEPARATION AND ESTIMATION OF SULFIDE. Transfer the receiving solution to a 500-ml flask, add 5 ml of 6 n. NH_4OH, and then add standard 0.1 n. $AgNO_3$ from a buret until precipitation of Ag_2S has ceased (Note 1). Stopper the flask, shake the mixture vigorously for 1 min., and note the effect of more $AgNO_3$ (Note 2). Decant the solution through a paper filter, and wash the residue in the flask with three 5-ml portions of hot water, pouring the washings through the filter. Wash the residue on the filter paper with 10 ml of water added dropwise. Collect the washing with the filtrate. Reserve the filtrate for treatment by P. 123 (Note 5).

Transfer the filter paper to the flask containing the remainder of the Ag_2S precipitate (Notes 3, 4). Add 10 ml of 16 n. HNO_3, heat the mixture to boiling (hood), and swirl it until action seems to have ceased and only a residue of filter-paper pulp and coagulated sulfur remains. Add 100 ml of distilled water and boil until no more brown fumes are evolved. Cool, add 2 ml of 1 n. $Fe(NO_3)_3$ solution, and titrate the solution with standard 0.1 n. thiocyanate solution to the appearance of the first perceptible pink color

which remains permanent when the solution is vigorously shaken. From the volume of thiocyanate solution used, calculate the weight of sulfide present.

Notes:

1. When precipitation of Ag_2S has ceased, a transient precipitate of brown Ag_2O will be formed. This can be seen to better advantage if the silver nitrate solution is added down the side of the flask. When there is doubt, this point can be more surely detected by shaking the solution to coagulate the precipitate already present before adding more silver.

2. If the mixture is not thoroughly shaken, especially when cyanide is present, as much as 0.2 mg of sulfide may remain in solution and cause a dark precipitate when the filtrate is acidified.

3. If only a slight precipitate is present, it should all be transferred to the filter and the presence of sulfide should be confirmed as follows:

Tear off the part of the filter containing the precipitate and insert it in a test tube. Add 1 g of granulated lead and 5 ml of 6 n. HCl. Moisten a strip of filter paper with sodium plumbite solution (made by adding NaOH dropwise to a few milliliters of $Pb(C_2H_3O_2)_2$ solution until the precipitate first formed is largely dissolved). Hold it in the mouth of the test tube and heat the mixture to 60° to 80°C. (Darkening of the plumbite, presence of sulfide.)

By the treatment with metallic lead in a hydrochloric acid solution, the silver sulfide is reduced to metallic silver with evolution of hydrogen sulfide. This darkens the plumbite solution because of the formation of PbS. A blank should be run with the lead and acid to insure that they are sulfide free.

4. Tear off and discard all of the filter paper except that on which there is a residue in order to decrease as far as possible the introduction of extraneous material into the solution.

5. If it is found or known that cyanide is not present, the sulfide can be estimated more rapidly by acidifying the filtrate with HNO_3 and adding 10 ml in excess, and then adding 2 ml of $Fe(NO_3)_3$ and titrating with a standard thiocyanate solution as directed above to determine the excess silver present. The total volume of silver nitrate added being known, that precipitated by sulfide can be found.

P. 123. Detection and Estimation of Cyanide

Discussion. If cyanide is present, it will be combined with the excess of silver as the complex ion $Ag(CN)_2^-$. When the solution is acidified, the precipitation of silver cyanide can be formulated by one of the two following reactions, depending on the relative concentrations of silver and cyanide present. If silver is present in excess, the reaction is usually represented by the first equation; if cyanide is present in excess, it is usually represented by the second.

$$Ag(NH_3)_2^+ + 2H^+ + Ag(CN)_2^- = Ag \cdot Ag(CN)_{2(s)} + 2NH_4^+. \quad (1)$$

$$Ag(CN)_2^- + H^+ = AgCN_{(s)} + HCN. \quad (2)$$

However, the results of X-ray investigations fail to show any difference in the structures of the two precipitates, and do not indicate which is the correct formula; because of this uncertainty, the simple formula will be used without implication as to the actual structure. The solubility-product expression may be written either as $[Ag^+][CN^-] = K'$, or $[Ag^+][Ag(CN)_2^-] = K''$; care should be taken in making use of the value for this constant that there is no confusion as to which expression is to be used.

On acidification of the solution, 1 mg. of cyanide produces an opalescence which is clearly visible against a black background. When the amount of cyanide present is very small, it should be confirmed by converting it to thiocyanate and forming the red $Fe \cdot Fe(SCN)_6$.

After the solution is acidified, an excess of standard silver nitrate is added, the precipitate is filtered, and the excess is determined by titration with thiocyanate. From the known total volume of standard silver nitrate added to the solution in order to precipitate sulfide in P. 121 and P. 122, the amount of sulfide found present, and the result of this last titration, the amount of cyanide present can be calculated.

Procedure 123: DETECTION AND ESTIMATION OF CYANIDE. If cyanide is or may be present (Note 4), transfer the filtrate from the sulfide precipitation (P. 122), or, if sulfide was absent, the distillate from P. 121, to a 200-ml flask, add from a buret 10 to 50 ml of standard $AgNO_3$ (Note 1), and make the solution just acid to litmus with HNO_3. (White precipitate or opalescence, presence of cyanide.) Add $AgNO_3$ until no further precipitation occurs. Stopper and shake the mixture vigorously for 1 min. Decant the solution through a paper filter (Note 2). Wash the precipitate with two 5-ml portions of water, pouring the washings through the filter. Wash the residue on the filter with 10 ml of water, adding the washing to the filtrate (Note 3). Discard the residue. Add 10 ml of HNO_3 and 2 ml of 1 n. $Fe(NO_3)_3$ to the filtrate. Titrate with standard 0.1 n. thiocyanate solution to the first perceptible pink color which is permanent on shaking. From the volume of thiocyanate used, the amount of sulfide found present, and the total amount of silver added to the solution, calculate the amount of cyanide present.

Notes:

1. The silver nitrate is added in excess so that, when the solution is acidified, all the cyanide will be precipitated as silver cyanide; the loss of any HCN by volatilization is thus prevented.

The amount of silver nitrate to be added can be roughly estimated from the size of the precipitate obtained in the preliminary test for cyanide in P. 121, or, if it is desired not to run the risk of losing any HCN, a similar test on a portion of the ammoniacal solution can be made at this time.

2. Test the filtrate with a few drops of $AgNO_3$ to be sure that an excess has been added.

3. If the precipitate is very small, omit the subsequent procedure and confirm the presence of cyanide as follows:

> Pour 2 ml of warm ammonium sulfide reagent and 2 ml of water through the residue on the filter. Evaporate the filtrate to 1 to 2 ml, dilute it to 10 ml, make it just acid with H_2SO_4, boil it for 30 sec. to expel H_2S, cool it, and add to it 1 ml of 1 n. $Fe(NO_3)_3$. (Red color, presence of cyanide.)

4. If cyanide is known to be present (as a result of the test made in P. 121), the following estimation can be carried out very rapidly:

> Add to the ammoniacal solution 2 drops of 1 n. KI solution and titrate with standard 0.1 n. $AgNO_3$ to the appearance of the first permanent yellowish turbidity. If a precipitate appears upon addition of the KI, it indicates that an excess of silver has already been added. In this case, titrate with 0.2 f. KCN solution until the precipitate is just dissolved. The amount of cyanide present can be calculated from the amounts of silver added in P. 121 and P. 122, the amount of sulfide found in P. 122, and the result of this titration.

For a discussion of this method and the principles involved, see P. 23, "The Estimation of Silver."

5. If nitrobenzene is available, the subsequent filtration of the precipitate can be avoided by proceeding as follows:

> Add to the mixture 3 ml of nitrobenzene, stopper the flask, and shake the mixture vigorously for 1 min. Treat the mixture as directed in the last paragraph of the procedure above.

The principles involved in the use of nitrobenzene for coagulating the silver cyanide precipitate so that it will not be metathesized by the thiocyanate during the subsequent titration is discussed in P. 27. It has been shown[1] that precise results can be obtained provided the nitrobenzene is added and the precipitate is thoroughly coagulated before the ferric nitrate indicator is added.

P. 124. Separation and Estimation of Sulfite

Discussion. In the procedure below, sulfite is separated from the remaining anions by adding an excess of a strong acid and again passing a current of air through the solution; the sulfur dioxide thus removed is collected by passing the air through a sodium hydroxide

[1] Experiments by Bertram Scarborough.

solution. In the strongly acid solution the sulfite is converted into the un-ionized acid, which exists in aqueous solutions in equilibrium with the volatile sulfur dioxide. This equilibrium is maintained as the sulfur dioxide is removed (by boiling or the passage of another gas through the solution), so that quantitative volatilization can be obtained. In this strongly acid solution it might be expected that hydrofluoric acid would be volatilized, as it exists largely as the un-ionized acid; however, the partial pressure of the gaseous hydrogen fluoride above the solution is so small that no appreciable volatilization takes place. It has been shown[2] that, under the conditions of the procedure below, 0.5 to 1 mg of sulfite can be detected; with 250 mg of fluoride, less than 0.5 mg is volatilized; and no significant decomposition of either ferrocyanide or ferricyanide occurs in the strongly acid solution.

An estimation of the amount of sulfite present is made by acidifying the sodium hydroxide receiving solution and titrating with a standard iodine solution. This estimation can give only approximate results, as there is always oxidation of the sulfite during the volatilization process, especially in the alkaline receiving solution. In addition, the titration of sulfite solutions with iodine is subject to error because of an induced oxidation of the sulfite by oxygen; this can be largely eliminated by adding the sulfite solution *to an excess of the iodine solution*, and for precise determinations this order should be used. Experiments have shown that, under the conditions of the procedure below, when 200 mg of sulfite are originally present, the titration gives values ranging from 5 to 15 per cent low; with 50 mg of sulfite present, the values were approximately 25 per cent low. The sodium hydroxide solution is acidified with acetic acid, as the acidity of the resulting solution is such that no loss of sulfur dioxide results.

When thiosulfate is present in an amount greater than a few milligrams, it will be partially decomposed into sulfur and sulfurous acid by the perchloric acid, and consequently a test for sulfite will be obtained. Thus, it has been found that, when 250 mg of thiosulfate are treated by this procedure, 71 per cent is decomposed, as shown by titrating the residual solution with iodine, and 76 per cent of this amount appears as sulfite in the receiving solution; with 100 mg of thiosulfate present, these figures were 41 per cent and 80 per cent, respectively; with 2 mg of thiosulfate present, no sulfur was visible

[2] Experiments by Bernard Love and Bertram Scarborough.

in the distilling solution and no sulfite could be detected in the receiving solution.

Upon the addition of a soluble barium salt to the solution after the titration with iodine, a precipitate of barium sulfate will result. This confirmatory test for the presence of sulfite is given in Note 1 of the procedure below.

Procedure 124: SEPARATION AND ESTIMATION OF SULFITE. If either the reducing anions (P. 113) or sulfite (P. 115) have been found to be *absent*, treat the residual solution from P. 121 directly by P. 131.

If reducing constituents were found present in P. 113 and the possible presence of sulfite was indicated in P. 115, leave the residual solution in the apparatus described in P. 121, connect a receiving test tube containing 15 ml of NaOH and 50 ml of water, add 5 ml of 9 n. $HClO_4$ to the residual solution through the thistle tube (Note 2), and draw air through the apparatus, as rapidly as is possible without loss, for 5 min.

Remove the receiving test tube, washing off the inlet and outlet tubes, transfer the NaOH solution to a 200-ml flask, make it acid with $HC_2H_3O_2$, and titrate it with standard 0.1 n. iodine solution until the first iodine color is apparent in the solution (Note 1). From the volume of standard iodine used, calculate the amount of sulfite present. Treat the residual solution by P. 131.

Notes:

1. If only a small amount of the iodine solution is used, a confirmatory test for the presence of sulfite should be made as follows:

Add 5 ml of $Ba(NO_3)_2$ to the titrated solution and allow it to stand for several hours, preferably overnight. (White crystalline precipitate, presence of sulfite.)

As small amounts of reducing materials may be present in the acetic acid or other reagents used, this more distinctive test for sulfite should be made when only small amounts of iodine are used.

Starch may be used as the indicator for the iodine titration if more than 0.5 to 1 ml of the iodine is required for the titration. It should not be used with smaller amounts, as it would tend to interfere with the detection of small amounts of precipitate in the above confirmatory test for sulfite.

2. A coarsely crystalline precipitate of $KClO_4$ may result if large amounts of potassium salts are present in the material being analyzed. Such a precipitate is easily recognizable and should be neglected, as it does not interfere with this procedure and will be filtered out before P. 131 is carried out.

TABULAR OUTLINE XIV

The Analysis for Ferrocyanide and Ferricyanide

(See P. 133 and P. 134 for the Estimation of Ferrocyanide and Ferricyanide.)

Filtrate from distillation of sulfite (P. 124)
Add $Cd(NO_3)_2$. (P. 131)

Precipitate: $Cd_2Fe(CN)_6$, $Cd_3(Fe(CN)_6)_2$
Boil with NaOH. (P. 132)

Filtrate:
Remaining acidic constituents
To P. 141

Residue:
$Cd(OH)_2$
Discard.

Filtrate:
$Fe(CN)_6^{\equiv}$, $Fe(CN)_6^{=}$, Na^+OH^-
Add NH_4NO_3, NH_4OH, *and* $AgNO_3$. (P. 132)

Precipitate:
$Ag_4Fe(CN)_6$
Treat with HCl and $FeCl_3$.

Precipitates:
$Fe_4(Fe(CN)_6)_3$ (blue), AgCl

Filtrate:
$Fe(CN)_6^{=}$, $Ag(NH_3)_2^+$, NH_4^+, NH_4OH, NH_3
Acidify with HNO_3.
Precipitate:
$Ag_2Fe(CN)_6$ (red-brown)
Solution:
NH_4^+, Ag^+, $H^+NO_3^-$

The Analysis for Ferrocyanide and Ferricyanide

P. 131. Precipitation of Ferrocyanide and Ferricyanide

Discussion. After sulfide and cyanide have been removed from the solution, the separation of another group of constituents has to be considered. Because their presence makes subsequent group separations and analyses extremely complicated, it would be expedient to remove the complex iron cyanides. Methods of precipitating these constituents from the acetic acid–acetate buffered solution immediately after the sulfide-cyanide volatilization were first investigated. Nickel, zinc, and cadmium were considered as possible precipitants. The use of zinc was eliminated because its amphoteric nature caused difficulty in the subsequent group analysis, and cadmium was selected because its precipitates seemed to form more quickly and to be more readily handled than did those obtained with nickel. Detection of 0.5 mg and complete precipitation of larger amounts of either constituent could be obtained with any one of these precipitants, but certain difficulties were encountered; namely, the precipitation of ferricyanide took place somewhat slowly, the precipitates were very difficult to handle, and, finally, oxalate, phosphate, and arsenate were found to be precipitated more or less completely from the acetic acid–acetate solution.

As the result of experiments to determine the effect of the acid concentration on the solubility of the latter precipitates (and on that of the cadmium complex cyanides), it was found that their precipitation could be prevented if the solution was above 0.5 n. in nitric or perchloric acid and that, moreover, the precipitation of the complex cyanides was much more rapid and complete. This indicates that the compound formed between cadmium and acetate ions must be quite stable. Because of the possible presence of nitrous acid in nitric acid solutions, and because of experiments showing that under certain conditions cadmium ferrocyanide precipitates may be oxidized in nitric acid solutions, perchloric acid is used for acidifying the solution. If $HClO_4$ is not available, an equivalent amount of 6 n. HNO_3 may be used; it should be free of nitrous acid, the solution should not be subsequently heated, and the cadmium ferrocyanide precipitates should be washed free of nitric acid before they are allowed to stand for more than a few minutes.

Experiments have shown that, under the conditions of the pro-

cedure below, 0.5 mg of either ferrocyanide or ferricyanide will give a readily perceptible precipitate, and that, with that amount of both present, they can be separated and detected by the subsequent procedures.

Procedure 131: PRECIPITATION OF FERROCYANIDE AND FERRICYANIDE. If the solution has come from P. 121 and ferricyanide may be present, as is indicated if oxidizing anions were found present in P. 112 and the solution is not colorless (Note 4), transfer it to a 200-ml flask. (Filter the solution if it is not perfectly clear (Note 1), wash the residue with not over 5 ml of water added dropwise, and discard the residue or treat it as directed in the second paragraph of Note 4, P. 121. Collect the washings with the filtrate.) Warm the solution to 80° to 90°C. and add dropwise, while shaking it vigorously, 2 to 5 ml of 1 n. $Cd(NO_3)_2$ (Note 2); *cool* to room temperature (Note 6), then add 5 ml of 9 n. $HClO_4$ (Note 7), and let the resulting mixture stand for 5 min., shaking it frequently. (White or yellow precipitate, presence of the ferrocyanide group.) Treat the mixture by the last paragraph of this procedure.

If the solution has come from P. 124, transfer it to a 200-ml flask. (Filter the solution if it is not perfectly clear (Note 1), wash the residue with not over 5 ml of *cold* water added dropwise, and discard the residue or treat it as directed in Note 4, P. 121. Collect the washings with the filtrate.) Add *dropwise*, while shaking the cold solution vigorously, 2 to 5 ml of 1 n. $Cd(NO_3)_2$ (Notes 2, 3), and let the resulting solution stand for 5 min., shaking it frequently. (White precipitate, presence of ferrocyanide. Note 4.)

Filter the mixture through an asbestos filter and wash it with 5 ml of a solution made by adding 1 ml of $Cd(NO_3)_2$ and 2.5 ml of 9 n. $HClO_4$ to 15 ml of water, collecting this solution with the filtrate (Note 5). Wash the mixture with the remainder of the above wash solution, discarding the wash water. Treat the precipitate by P. 132. Treat the filtrate by P. 141.

Notes:

1. The solution may be turbid, owing to fibers from litmus paper or to precipitated sulfur, or it may contain a precipitate of some of the substances mentioned in Note 2, P. 114. In order that a very small precipitate of the complex cyanides may be detected, the solution should be perfectly clear.

2. Only 2 ml of the $Cd(NO_3)_2$ should be added at first in order to prevent the partial precipitation of cadmium iodate or cadmium oxalate when these anions are present in large amounts. Thus it was found that if 5 ml of $Cd(NO_3)_2$ were added when 250 mg of iodate were present, as much as 100 mg would be precipitated; with the smaller amount of cadmium, there is also less danger that any cadmium oxalate which may form locally will not be completely dissolved.

3. If the cadmium nitrate were added rapidly, the precipitate would separate in such a finely divided colloidal form that it would be extremely difficult to filter or wash. The solution should be cold in order to avoid decomposition of complex cyanides, which would lead to a greenish-blue precipitate.

4. Information as to the constituents present may be obtained from the appearance of the precipitate: Cadmium ferrocyanide is white; cadmium ferricyanide is orange-colored. When as little as 0.5 mg of ferricyanide is present, the solution prior to precipitation will be distinctly yellow, and the group precipitate will be distinctly yellow. Therefore, *if the solution is colorless before the precipitation, the absence of ferricyanide is shown* and only ferrocyanide should be present in the precipitate. In this case, if only the qualitative detection of ferrocyanide is desired, the precipitate can be treated directly with a solution of HCl and $FeCl_3$, as directed in the fourth paragraph of Note 3, P. 132.

It is to be noted that the only other colored acidic constituents which are likely to be present here are chromate (yellow, or in acid solution the reddish-yellow dichromate) and permanganate (pink to violet).

5. It is not necessary to transfer the precipitate to the filter, as it can be next treated in the same flask.

It is necessary to use the wash solution specified, as the precipitate will become colloidal and pass through the filter if it is washed with water; it was found that small amounts of the complex cyanides would often completely escape detection if this precaution was not taken.

6. It has been found that, if, when ferricyanide is present, the cadmium nitrate is added rapidly to the cold acetic acid solution, or if the $HClO_4$ is added first, the cadmium ferricyanide precipitate separates in such a finely divided colloidal form that it is extremely difficult to filter. The solution should be cold before the $HClO_4$ is added, in order to avoid decomposition of the complex cyanides, which would lead to a greenish-blue precipitate.

Sulfite and ferricyanide cannot exist in the same solution; therefore, if P. 124 has been carried out, ferricyanide cannot be present and the cadmium nitrate can be added directly to the perchloric acid solution from P. 124.

7. A coarsely crystalline precipitate of $KClO_4$ may result if large amounts of potassium salts are present in the material being analyzed. It is readily dissolved by slightly warming the solution or slightly increasing the volume. As stated above, an equivalent amount of HNO_3 may be substituted for the $HClO_4$ if this acid is not available or if it is desired to avoid its use.

P. 132. Separation and Detection of Ferrocyanide and Ferricyanide

Discussion. In the procedure below, the cadmium precipitate is treated with 3 n. NaOH, which metathesizes the cadmium to the

hydroxide, leaving the complex cyanides in solution. Ferricyanide ion has such an intense yellow color that as little as 0.2 mg can be readily detected in this solution.

Optional procedures are provided for the cases, first, that only small amounts are present or only a qualitative separation of these constituents is wanted and, second, that considerable amounts of the constituents are present and an estimation of these amounts is desired.

In the first case, the method of separation is based upon the fact that silver ferrocyanide is so insoluble that it can be precipitated quite completely from an ammoniacal solution containing relatively large amounts of ferricyanide. Several factors have to be considered in the adjustment of the conditions for this precipitation. First, there has to be sufficient ammonia in the solution to keep the ferricyanide in solution, the reaction being represented as follows:

$$Ag_3Fe(CN)_{6(s)} + 6NH_3 = 3Ag(NH_3)_2^+ + Fe(CN)_6^{\blacksquare}.$$

Second, the oxidation of ammonia by ferricyanide has to be avoided; the reaction for this oxidation can be represented by the equation

$$6Fe(CN)_6^{\blacksquare} + 2NH_3 + 6OH^- = 6Fe(CN)_6^{\blacksquare\blacksquare} + N_2 + 6H_2O.$$

An inspection of this equation indicates—as was found to be the case—that it would be desirable to reduce the hydroxyl ion concentration (by adding an excess of ammonium ion), and also to keep the ammonia concentration to the minimum value necessary to hold the maximum amount of ferricyanide in solution. The procedure given below is the result of a large number of experiments carried out in a study of these effects, and it has been found that, under the conditions obtaining there, it is possible to detect 0.5 mg of ferrocyanide, while, with even 250 mg of ferricyanide, the reduction to ferrocyanide takes place so slowly that no precipitate is obtained within 5 min. However, because of the slow oxidation of ammonia by ferricyanide in the presence of silver ion, the precipitation and filtration of the ferrocyanide, the subsequent acidification of the solution, and the precipitation of the silver ferricyanide have to be carried out without delay. It has been found that the effect of this oxidation in the ammoniacal filtrate can be minimized, but not entirely prevented, by the addition of a small quantity of peroxysulfate; this inhibiting effect is probably due to the ferrocyanide being more rapidly oxidized by peroxysulfate than is ammonia. The peroxysulfate also oxidizes any nitrous acid which may be pres-

ent in the nitric acid and may prevent reduction of the ferricyanide by this agent.

In investigating methods for separating ferrocyanide and ferricyanide, efforts were made to take advantage of the fact that cadmium ferricyanide is relatively soluble in ammonia solutions, while the ferrocyanide is only slightly soluble. However, no conditions were found under which large amounts of ferricyanide could be kept in solution without several milligrams of the ferrocyanide being dissolved; it was also found that upon treatment with ammonia the cadmium ferrocyanide precipitate tended to become so colloidal as to make the filtration unsatisfactory. The oxidation of ammonia by ferricyanide did not take place at an appreciable rate in these solutions but is appreciable in the presence of silver ion.

If a quantitative estimation of the ferrocyanide and ferricyanide is desired, the filtrate from the sodium hydroxide metathesis of the cadmium precipitates is treated by P. 133 and P. 134.

Procedure 132: SEPARATION AND DETECTION OF FERROCYANIDE AND FERRICYANIDE. With a flattened stirring rod, transfer as much as possible of the cadmium precipitate back to the flask in which it was precipitated (Note 1). Add 20 ml of 3 n. NaOH (washing the funnel with this), heat the mixture to boiling, stopper the flask securely with a clean rubber stopper, and shake it for 2 min. Filter the mixture through a thin pad of asbestos. (Yellow color in the filtrate, presence of ferricyanide.) Wash with two 10-ml portions of hot water. Discard the residue.

If only small amounts of the complex cyanides are present or if, when either small or large amounts are present, only a qualitative detection is desired, treat the filtrate as directed below.

If a quantitative estimation of the amount of ferrocyanide and ferricyanide present is desired, treat the filtrate as directed in P. 133.

Prepare an asbestos filter (Note 2), cool the NaOH filtrate (volume, 40 ml), and add 4 g of NH_4NO_3, 15 ml of NH_4OH, and, while swirling the solution, 3 ml of $AgNO_3$. (Immediate white precipitate, presence of ferrocyanide. Note 3.) If a large precipitate results, add $AgNO_3$, in 0.5-ml portions, until no more precipitate forms (do not add a total of more than 5 ml). Filter the precipitate *at once*. As rapidly as a

clear filtrate is collected, transfer it to a 200-ml flask containing 50 to 75 mg of $Na_2S_2O_8$ (sodium peroxysulfate) dissolved in 5 ml of water. Wash the precipitate with 10 ml of water.

Immediately acidify the filtrate with HNO_3 and add 0.5 to 2 ml of $AgNO_3$. (Reddish-brown precipitate, presence of ferricyanide.)

Notes:

1. This can frequently be accomplished by transferring only the top layer of the asbestos filter with the precipitate and then pouring the hot NaOH through the remaining asbestos into the flask; after being boiled, the mixture is passed through the same filter.

2. As explained in the discussion, after the ammonium salts and ammonia are added to the solution, the subsequent precipitation, filtration, and acidification should be carried out as rapidly as possible. For this reason, the filter is made available even though ferrocyanide may be absent.

3. If much ferricyanide is present, a local reddish-brown precipitate will be formed where the silver nitrate enters the solution. For this reason, the solution should be swirled as the silver nitrate is added and then shaken vigorously. Should this reddish precipitate not dissolve, add 2 to 5 ml more NH_4OH before filtering the mixture.

If much ferricyanide is present and the solution is allowed to stand for more than 5 min., it will slowly become turbid, because of the reduction of the ferricyanide and the consequent precipitation of silver ferrocyanide.

A white precipitate separating from an ammonia solution upon addition of silver nitrate is a distinctive test for ferrocyanide. Silver cyanide, chloride, bromide, and thiocyanate are relatively soluble in ammonia solutions of this concentration; silver sulfide is insoluble and the iodide is only slightly soluble, but these are distinctively colored.

A further confirmatory test may be made by mixing equal volumes of HCl and $Fe(NO_3)_3$ solution and adding this dropwise to the precipitate on the filter; a blue color indicates the presence of ferrocyanide in the precipitate.

Ferricyanide is an effective oxidizing agent, especially in alkaline solutions, being reduced by most of the common inorganic reducing agents and by many organic substances; because of this, a test for ferrocyanide will almost invariably be obtained if large amounts of ferricyanide were present in the original material.

P. 133. Estimation of Ferrocyanide

Discussion. The presence or absence of ferricyanide has been determined by its color in P. 132. However, it has not been possible to determine if smaller amounts of ferrocyanide are present with ferricyanide; therefore, before any estimations are made, the solution is diluted to a known volume and a small portion is tested for ferrocyanide with ferric nitrate. The addition of a ferric salt

to a solution containing ferrocyanide results in the formation of the characteristic blue compound, $Fe_4(Fe(CN)_6)_3$, known as Prussian blue. Ferric salts do not cause a precipitate with ferricyanide but form a soluble compound which imparts a brownish color to the solution. As ferrous salts cause a blue precipitate with ferricyanide,[1] the ferric salt should be free from any ferrous compounds; ferrous salts form with ferrocyanide a white precipitate of ferrous ferrocyanide, changing in the presence of potassium ion to potassium ferrous ferrocyanide, $K_2Fe(Fe(CN)_6)$.

Ferrocyanide is estimated by titration with permanganate. The reaction taking place can be represented as follows:

$$5Fe(CN)_6^{\equiv} + MnO_4^- + 8H^+ = 5Fe(CN)_6^{=} + Mn^{++} + 4H_2O.$$

This titration must be carried out in a relatively large volume of a solution which must be approximately 1 n. in sulfuric or hydrochloric acid, or the reaction will be complicated by the formation of a precipitate of potassium manganous ferrocyanide, which is so insoluble that the oxidation of the precipitated ferrocyanide proceeds very slowly. Because of the yellowish color of the ferricyanide formed, the end-point is not as sharp as it is with most permanganate titrations; this is overcome by titrating in a large volume and by using a comparison solution containing ferricyanide. Under these conditions, the titration can be carried out quite precisely, and, because of the high equivalent weight and the ease with which it can be purified by recrystallization, potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$, has been suggested as a primary standard[2] for permanganate solutions.

Procedure 133: ESTIMATION OF FERROCYANIDE. Neutralize the NaOH filtrate (from P. 132) with 18 n. sulfuric acid, add 1 ml in excess, and cool (Note 1). If there is uncertainty as to the presence of ferrocyanide, transfer the solution to a 100-ml volumetric flask, dilute it to the mark, and mix it thoroughly. Pipet 10 ml of the resulting solution into a test tube, add 1 ml of 1 n. $Fe(NO_3)_3$ (Note 2), and let the mixture stand for 5 min. (Blue precipitate or coloration, presence of ferrocyanide.)

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[1] This compound is called Turnbull's blue but has been found to be substantially the same as Prussian blue; the ferrous iron is oxidized to the ferric state and the ferricyanide is reduced, apparently because of the relative solubilities of the compounds involved.

[2] Gintl, *Z. anal. Chem.*, **13**, 124 (1874); Müller and Lauterbach, *ibid.*, **61**, 398 (1922); Kolthoff, *Rec. Trav. Chem.*, **41**, 343 (1922).

If ferrocyanide is absent, treat the solution by P. 134.

If ferrocyanide is present, pipet 10 to 50 ml (Note 3) of the solution into a 500-ml flask and add 200 ml of water and 30 ml of H_2SO_4. Titrate the solution with standard 0.1 n. permanganate solution until the color changes from a light greenish-yellow to yellowish-pink (Note 4). From the volume of permanganate used, calculate the amount of ferrocyanide present.

Treat the remainder of the solution by P. 134 to estimate ferricyanide.

Notes:

1. If ferricyanide is absent, this solution should be treated directly by the next paragraph to estimate ferrocyanide.

2. The ferric nitrate solution should be free of ferrous iron, as otherwise a blue precipitate would result if ferricyanide were present.

Even 0.5 mg of ferrocyanide in the original solution will give a blue or blue-green color to the solution within 5 min.; however, with such small quantities, the color develops slowly. On longer standing, a coagulated precipitate will usually collect in the bottom of the tube.

3. The amount of solution to be taken here will depend upon the amounts of the two substances thought to be present. If, in the test for ferrocyanide, only a small precipitate is obtained (corresponding to 10 mg or less), it will be more expedient to compare this with known precipitates produced under similar conditions and to use all of the remaining solution for the volumetric estimation of ferricyanide. It is to be noted that because of the high equivalent weight of the complex cyanides, only small volumes of permanganate (or of thiosulfate in P. 134) will be required.

4. This end-point can be observed more precisely by the use of a reference standard prepared by the addition of approximately the same amount of ferricyanide to the same volume of water and acid as are present in the titrated solution.

P. 134. Estimation of Ferricyanide

Discussion. As would be predicted from their molal potentials, the reaction between ferricyanide and iodide to give iodine and ferrocyanide,

$$2Fe(CN)_6^{\equiv} + 3I^- = 2Fe(CN)_6^{\equiv\equiv} + I_3^-,$$

reaches an equilibrium with the four substances present in measurable amounts. Therefore, in order for the reaction to be used as the basis for a quantitative method for the estimation of ferricyanide, it is necessary to displace it by lowering the concentration of one or both of the products. This is accomplished by precipitating the

ferrocyanide as a zinc salt—in the presence of potassion ion, probably $K_2Zn_3(Fe(CN)_6)_2$—and reducing the tri-iodide to iodide by titrating with thiosulfate.

Procedure 134: ESTIMATION OF FERRICYANIDE. Pipet 25 to 50 ml (Note 3, P. 133) of the diluted solution (from P. 133) from the volumetric flask into a 200-ml flask. Slowly add 1 g of sodium bicarbonate to the solution, neutralize with HCl, and add a 5-ml excess. Swirl the solution (Note 1). Add 3 g of KI, swirl the solution until this is dissolved, let the solution stand for 1 min. in a stoppered flask, and then add 1.5 g of zinc sulfate. (Liberation of iodine, and formation of white precipitate, presence of ferricyanide.) Titrate the solution with 0.1 n. thiosulfate until the iodine color becomes indistinct, add 5 ml of starch indicator, and then add the thiosulfate slowly until the blue color just disappears (Note 2). From the volume of thiosulfate used, calculate the weight of ferricyanide present.

Notes:

1. The bicarbonate is added in order to furnish carbon dioxide to sweep air out of the solution upon acidification and thus reduce the "oxygen error" (oxidation of iodide by dissolved oxygen) in the titration. The solution should be swirled until all the carbon dioxide is expelled before the KI is added; otherwise, iodine vapor is likely to be lost through the escape of carbon dioxide bubbles.

2. A permanently bluish-colored precipitate or solution indicates the presence of iron; if the reagents are free of this element, a colorless solution and a white precipitate will be obtained.

TABULAR OUTLINE XV

The Analysis of the Halide Group

Filtrate from the Precipitation of Ferro- and Ferricyanide (P. 131)
Add $AgNO_3$. (P. 141)

Precipitate: The Halide Group
AgI, AgSCN, AgBr, AgCl ($Ag_2C_2O_4$, $AgIO_3$, $AgBrO_3$)
Boil with Na_2CO_3. (P. 141)

Filtrate:
Remaining acidic constituents
(To P. 151)

Residue: AgI, AgSCN, AgBr, AgCl, Ag_2O
Boil with $(NH_4)_2S$ *and* NH_4OH. (P. 142)

Filtrate:
$C_2O_4^{=}$, IO_3^-, BrO_3^-
Na^+, $CO_3^=$
(To Oxy-Halogen and Phosphate Groups)

Residue:
Ag_2S
Discard.

Filtrate: I^-, SCN^-, Br^-, Cl^-, $(NH_4)^+HS^-$, NH_4OH
Acidify with $HClO_4$; *boil out* H_2S.
Add $Fe_2(SO_4)_3$ *and* CCl_4. (P. 143)

CCl_4 layer:
I_2
Add water.
Titrate with $Na_2S_2O_3$.
(P. 144)

Aqueous layer: $Fe{\cdot}Fe(SCN)_6$ (red color), Br^-, Cl^-, Fe^{+++}, Fe^{++}
Add $NaHSO_4$, Na_2SO_4 *and* $NaNO_3$.
Boil 5 to 7 min. (P. 145)

Expelled gases:
HCN, I_2 (that not removed by the CCl_4), NO

Solution: Br^-, Cl^-, Fe^{+++}, HSO_4^-, $SO_4^=$, NO_3^-, Na^+
Add H_2SO_4, $KMnO_4$, *and* CCl_4.
(P. 146)

CCl_4 layer:
Br_2
Add water and KI.
(I_3^-, Br^-)
Titrate with $Na_2S_2O_3$.
I^-, Br^-, $S_4O_6^=$
(P. 147)

Aqueous layer:
Cl^-, Fe^{+++}, MnO_4^-, Mn^{++}, MnO_2, H^+, HSO_4^-, NO_3^-, Na^+
Add $NaNO_2$.
(MnO_4^-, MnO_2, reduced to Mn^{++})
Add $AgNO_3$.
Precipitate: AgCl
(P. 148)
Estimate chloride by P. 27.

The Analysis of the Halide Group

P. 141. Precipitation of the Halide Group

Discussion. By addition of silver nitrate to the perchloric acid solution from the precipitation of ferrocyanide and ferricyanide, the anions chloride, bromide, iodide, and thiocyanate are precipitated; these are termed the Halide Group. Thiocyanate shows a marked similarity to iodide in both its metathetical and its oxidation-reduction reactions and is thus included in this group. In addition to these anions, iodate is quite completely precipitated; if an excess of 5 ml of silver nitrate is added in the procedure below, bromate precipitates when more than approximately 100 mg are present and oxalate precipitates when more than 50 mg are present. Because these latter constituents would unduly complicate the subsequent analysis of this group, the precipitate is treated with sodium carbonate solution, whereby they are metathesized, the silver being precipitated as a mixture of carbonate and oxide and the iodate, bromate, and oxalate passing into solution; the Halide Group constituents are not appreciably metathesized, less than 0.2 mg of chloride, the most soluble of the group, passing into solution.

Sulfide, cyanide, and the complex cyanides of iron would likewise be precipitated by silver ion from the acid solution; therefore, the previous removal of these constituents is an advantage. Phosphate, arsenate, arsenite, and borate all form silver salts which are insoluble in a neutral solution but, being the salts of weak acids, are readily soluble in perchloric (and other highly ionized) acid solutions. Sulfide and cyanide are also salts of extremely weak acids, but they are precipitated by silver ion from acid solutions because of (1) the extreme insolubility of silver sulfide and (2) the fact that cyanide forms with silver the very stable ion $Ag(CN)_2^-$, which is very little dissociated into cyanide and silver ions. The solubility product of silver cyanide is usually more conveniently expressed in terms of this ion, thus: $[Ag^+][Ag(CN)_2^-] = K_{s.p.}$

The sodium carbonate solution containing the iodate, bromate, and oxalate is acidified and the oxy-halogen ions are reduced to the corresponding halides with sulfite. These are then precipitated with silver nitrate, and the precipitates are united with any subsequent Oxy-Halogen Group precipitate (P. 161). The oxalate in the filtrate is precipitated by addition of calcium ion and by making the solution

ammoniacal. The resulting precipitate of calcium oxalate is collected on the same filter with the remainder of the oxalate which is later precipitated in P. 166.

Procedure 141: PRECIPITATION OF THE HALIDE GROUP. To the filtrate from the precipitation of the Ferrocyanide Group (P. 131) add 1 to 10 ml of 1 n. $AgNO_3$. (White or yellowish precipitate, presence of the Halide Group. Note 1.)

Filter the precipitate on an asbestos (chloride-free) filter and wash it with two 3-ml portions of 0.6 n. HNO_3, adding these washings to the filtrate. Wash the precipitate with 20 ml of 0.6 n. HNO_3. Discard the washings, or, if oxidizing constituents are present, neutralize them with NaOH and add them to the Na_2CO_3 solution to be used as directed in the second paragraph below (Note 2). Treat the filtrate by. P. 151.

If oxalate, iodate, or bromate are known to be absent, treat the precipitate by P. 142.

If oxalate, iodate, or bromate may be present, transfer the asbestos filter with the precipitate to a beaker with the aid of 25 ml of 3 n. Na_2CO_3, add 0.2 ml of $AgNO_3$ (Note 3), and heat the mixture to boiling for 5 min., disintegrating the precipitate with the flattened end of a stirring rod (Note 4). Filter the mixture through a thin asbestos filter and wash the residue with 20 ml of hot water, collecting this wash water with the filtrate. Treat the residue by P. 142 (Note 5).

Make the filtrate acid with 6 n. HNO_3 (*Caution*: A vigorous evolution of CO_2 occurs) and add 1 ml in excess. Add solid $NaHSO_3$, 10 to 50 mg at a time, until any color which appears in the solution is bleached or until the odor of SO_2 can be detected above the solution (Note 6). Pass a rapid stream of air or CO_2 through the cold solution until the odor of SO_2 is no longer evident (Note 7). Add 0.5 to 5 ml of $AgNO_3$ and gently boil the solution for 2 to 3 min. (Note 8). Cool the mixture to room temperature and add 5 ml of 16 n. HNO_3. (Yellowish precipitate, presence of iodate or bromate.) Filter out the precipitate on an asbestos filter, wash it with 0.6 n. HNO_3, and combine it with any precipitate obtained in P. 151.

To the filtrate add 10 ml of $Ca(NO_3)_2$, slowly add 15 n. NH_4OH until it is alkaline, and then add 2 ml in excess

(Note 9). Let the solution stand for 10 min. (White precipitate, presence of oxalate.)

Reserve the mixture until P. 166 is carried out, and then filter the precipitate on the filter used for the precipitate obtained in that procedure. Wash and treat the combined precipitates as directed in that procedure. Discard the filtrate.

Notes:

1. The color of the halide precipitates has been stated in Note 3, P. 114. Silver iodate, bromate, and oxalate form as white crystalline or granular precipitates. No more than 1 ml of $AgNO_3$ should be added if no precipitate is obtained, as otherwise small amounts of bromate or oxalate may cause a precipitate. The behavior of thiosulfate with silver ion has been discussed in P. 114, Note 1. The precipitation of the black silver sulfide, with the attendant color changes, serves as a sensitive detection of thiosulfate, and no complications are introduced into the analysis of the Halide Group by the presence of the Ag_2S.

2. Silver iodate and bromate are appreciably soluble in the 0.6 n. HNO_3; therefore, if oxidizing agents are present, this wash solution is combined with the Na_2CO_3 solution which is to be used to remove the remainder of the iodate and bromate from the precipitate.

3. It has been found that, unless a small amount of silver is added to the sodium carbonate solution, silver chloride, if present alone, is appreciably metathesized. Under the conditions given, less than 0.2 mg of chloride passes into the solution. The Na_2CO_3 should be free from ammonia compounds.

4. It is necessary that the precipitate be disintegrated in order for effective metathesis to take place in the time specified. With large amounts of iodate or bromate, the metathesis is not complete with one treatment with sodium carbonate; thus, with 250 mg each of iodate and bromate present, 10 to 30 mg and 5 to 10 mg, respectively, of these constituents remained in the precipitate. Accordingly, if these anions are thought to be present and a more complete metathesis is desired, the treatment with sodium carbonate should be repeated. Silver oxalate is completely metathesized, but, if large quantities of oxalate are present, some reduction of silver to the metallic form may occur. It is to be noted that oxalate will be present only if more than 50 mg were present in the solution from which the group precipitation was made.

5. As this silver precipitate of the Halide Group constituents becomes somewhat inert on standing, it should be treated at once by P. 142; otherwise an incomplete metathesis may be obtained there.

6. With an insufficient amount of $NaHSO_3$, both iodate and bromate would be reduced to iodine and bromine, respectively; with an excess, the reduction proceeds to the halide ion. No more $NaHSO_3$ should be added than is necessary to remove any iodine or bromine color and produce the first detectable smell of SO_2 above the solution. A large excess of the sulfite might lead later to reduction of the silver ion present.

7. The solution is not heated, and the SO_2 is removed by a stream of air or CO_2, in order to prevent possible oxidation of iodide by the nitrate present. The SO_2 must be removed or it might cause partial reduction of the silver ion to metallic silver or of the concentrated nitric acid later added; this additional acid is added to redissolve any silver oxalate which may have been precipitated. Air may be bubbled through the solution from a compressed-air line or by a water aspirator, as was done in P. 121 and P. 124; CO_2 from a tank is equally satisfactory.

8. Unless a permanent precipitate forms with the first 0.5 ml of silver nitrate, no more should be added, or silver oxalate may be precipitated; an excess of the silver nitrate should be avoided by noting when further addition fails to produce a precipitate.

9. The calcium nitrate is added and the solution is then made ammoniacal, because by this order a more crystalline and easily filtered calcium oxalate precipitate is obtained. For the same reason it is an advantage to let the precipitate stand until the remainder of the oxalate is precipitated in P. 166; both precipitates can then be collected on the same filter.

P. 142. Metathesis of the Silver Halide Group Precipitate by Sulfide

Discussion. After the Halide Group anions have been separated in the form of their insoluble silver salts, a method for their solution and separation from the silver has to be considered. If thiocyanate were not present, this could be accomplished by treatment with a solution of a powerful reducing agent, such as zinc in an acid solution, or by fusion with an alkaline flux, such as sodium carbonate; however, by such a process, thiocyanate would be converted into other compounds. Upon being treated with zinc in an acid solution, thiocyanate is decomposed into hydrogen sulfide and hydrocyanic acid, and efforts were made to develop a process based on this reaction, but it was found that, although the silver from all of the Halide Group precipitates was completely reduced to the metallic state, the decomposition of the thiocyanate thus set free was not complete within a reasonable time, nor was the conversion to sulfide and cyanide quantitative, as other products (COS and compounds with offensive odors) were also formed.

Use was therefore made of the fact that silver sulfide is much less soluble than any of the Halide Group precipitates, so that, if they are treated with an alkaline sulfide, metathesis to silver sulfide takes place, the halide passing into solution. In the procedure below, the group precipitate is first treated with ammonium hydroxide, in order to dissolve it insofar as possible before adding the sulfide and thus avoid incomplete metathesis because of enclosure of the precipitate in a layer of sulfide; for the same reason, the ammonium sulfide is then added slowly and the residue is con-

tinuously broken up. In ammonia solutions, silver chloride is readily soluble, silver thiocyanate and bromide dissolve to a considerable extent, and silver iodide is only slightly soluble.

The metathesis must take place in an alkaline solution, because in acid solutions the sulfide ion concentration is so low that the metathesis of iodide may be incomplete. After the silver sulfide precipitate is filtered out, the solution is evaporated in order to remove the ammonium sulfide; this takes place because of the hydrolysis of this salt into ammonia and hydrogen sulfide, which are both volatile products.

Procedure 142: METATHESIS OF THE SILVER HALIDE GROUP PRECIPITATE BY SULFIDE. Transfer the Halide Group precipitate (from P. 141) to a flask with the aid of 10 to 15 ml of 15 n. NH_4OH and add dropwise 5 to 15 ml of $(NH_4)_2S$ reagent, shaking the mixture and disintegrating the precipitate thoroughly with the flattened end of a stirring rod during this addition (Note 1). Boil the mixture gently for 5 min. (hood). Filter out the residue and wash it with 5 to 25 ml of hot water, collecting the washings with the filtrate. (Discard the precipitate. Note 2.) Evaporate the filtrate to 5 to 10 ml, cool it, add 3 ml 9 n. $HClO_4$, and filter out any precipitate (Note 3). Wash the precipitate with 2 to 3 ml of water, collect the solution in a small short-stem separating funnel, and treat it by P. 143.

Notes:

1. In order to obtain a complete metathesis, the following precautions are necessary: (1) As much of the precipitate as possible should be first dissolved in the NH_4OH; (2) the $(NH_4)_2S$ should be a freshly prepared colorless reagent of full strength (the so-called "ammonium polysulfide" reagent frequently used for separating the Copper and Tin Groups is not suitable, as the sulfur and thiosulfate which it contains cause trouble in subsequent operations); (3) the sulfide reagent should be added slowly and gradually; and (4) the precipitate should be completely broken up and disintegrated during the process.

If a colorless ammonium sulfide solution is not available, proceed as follows:

> Transfer the Halide Group precipitate to a flask with the aid of 15 ml of 15 n. NH_4OH, and saturate the solution with H_2S. Add 5 ml of 15 n. NH_4OH and disintegrate the precipitate thoroughly with the flattened end of a stirring rod. Treat the mixture by the procedure above, beginning with the second sentence.

2. If iodide is thought to be present in large amounts and a quantitative

estimation is desired, the sulfide residue should be boiled with 6 n. HNO_3 for 5 to 10 min., filtered, and again treated with NH_4OH and $(NH_4)_2S$. The hot HNO_3 dissolves the silver sulfide, but not the silver iodide; this smaller residue is then completely metathesized by the second treatment with sulfide.

3. A precipitate may result when the solution is boiled or acidified, owing to the presence of disulfide, S_2^-, and of thiosulfate, $S_2O_3^-$, in the $(NH_4)_2S$ reagent or to its formation by oxidation in the hot solution. This sulfur should be filtered out, as it is troublesome during the subsequent extractions of any iodine present by carbon tetrachloride.

$HClO_4$ is used, rather than HNO_3, in order to avoid possible oxidation of thiocyanate or iodide by the nitric acid.

P. 143. Detection and Separation of Iodide and Detection of Thiocyanate

General discussion. *The Separation of the Constituents of the Halide Group.* The separation of the constituents included in the Halide Group (iodide, thiocyanate, bromide, and chloride) presents certain difficulties, and various methods have been proposed for the systematic analysis of this group.[1]

Most methods for the qualitative (and quantitative) separation of iodide, bromide, and chloride are based upon the difference in the ease of oxidation of these anions to the elementary substance. An inspection of their respective potentials indicates that it should be possible, by suitable selection of the oxidizing agent, to oxidize iodide to iodine without the formation of an appreciable amount of bromine. Among the oxidizing agents which have been used for this purpose are nitrite, peroxide, peroxysulfate, permanganate, and dichromate, in solutions of controlled acidity, and ferric iron. The equations for the reactions involved are as follows:

$$2I^- + 2H^+ + 2HNO_2 = 2NO + I_2 + 2H_2O.$$

$$2I^- + 2H^+ + H_2O_2 = I_2 + 2H_2O.$$

$$2I^- + S_2O_8^= = 2SO_4^= + I_2.$$

$$10I^- + 2MnO_4^- + 16H^+ = 5I_2 + 2Mn^{++} + 8H_2O.$$

$$6I^- + Cr_2O_7^= + 14H^+ = 3I_2 + 2Cr^{+++} + 7H_2O.$$

$$2I^- + 2Fe^{+++} = I_2 + 2Fe^{++}.$$

[1] Noyes, *Qualitative Chemical Analysis*, 9th Ed., Macmillan, 1922; McAlpine and Soule, *Prescott and Johnson's Qualitative Chemical Analysis*, Van Nostrand, 1933; Curtman and Wikoff, *J. Am. Chem. Soc.*, **37**, 298 (1915); Curtman and Schneiderman, *Rec. trav. Chem.*, **54**, 158 (1935); Heisig and Heisig, *J. Ind. Eng. Chem., Anal. Ed.*, **7**, 249 (1935).

However, the situation is more complicated when thiocyanate is included, as it is oxidized by most of the agents listed above, the final products being hydrocyanic acid and sulfate. The hydrocyanic acid is troublesome, as in its presence iodide and bromide may be oxidized to iodine cyanide (ICN) and bromine cyanide (BrCN), respectively, and thus escape detection. Of the above oxidizing agents, nitrous acid is especially effective in the detection of iodide, as it oxidizes the iodide rapidly and completely without oxidizing bromide under a fairly wide range of concentrations of acid and nitrite; it cannot be used here because it reacts rapidly with thiocyanate. Peroxide was eliminated because at the acidity at which iodide will be completely oxidized at a practical rate, oxidation of bromide was appreciable and catalytic decomposition of the peroxide was troublesome. Permanganate rapidly oxidizes thiocyanate, and dichromate oxidizes iodide somewhat slowly at acidities which prevent an appreciable oxidation of bromide.

Ferric iron is peculiarly fitted for the oxidation of iodide for the following reasons: (1) It oxidizes iodide without action on bromide; (2) the reaction is not critical with respect to the acid concentration; (3) an excess of ferric iron to a certain extent stabilizes the thiocyanate against oxidation because of the formation of the complex molecule $Fe \cdot Fe(SCN)_6$; and (4) the color of this compound provides a means for the detection of thiocyanate. The reaction between ferric iron and iodide has been used in P. 53 for the quantitative estimation of iron, and a discussion of the factors affecting the reaction will be found in the discussion and notes of that procedure. The characteristics of the reaction as used here, where an excess of ferric iron is added to the iodide, may be summarized briefly: An equilibrium is reached and the rate of the oxidation is so slow as to be somewhat troublesome, but, by repeated extractions with carbon tetrachloride, a practically complete oxidation and separation of the iodide can be obtained. The methods for the removal (and determination) of thiocyanate and the separation of bromide are discussed in P. 145 and P. 146.

The Extraction of Iodine from Aqueous Solutions by Means of Organic Solvents. The law of physical equilibrium states that, when the same substance is distributed and has reached an equilibrium between two phases, the ratio of the concentrations (more properly, the activities) in the two phases will have a constant value (at a given temperature), thus:

$$\frac{C_1}{C_2} = K.$$

Therefore, when an aqueous solution containing iodine is shaken with certain organic solvents, such as CCl_4, CS_2, $CHCl_3$ (chloroform), or $CHBr_3$ (bromoform), the iodine passes into the non-aqueous phase until the equilibrium ratio (called in the case of the partition of a solute between two solvents "the distribution ratio") characteristic of the particular substances involved is established. There are shown in Table XXXI the values of these ratios for the distribution of iodine and bromine between the solvents mentioned above and water. It is to be noted that in all cases the value of this ratio is much greater than 1, so that relatively efficient extractions can be made of the iodine.

TABLE XXXI

THE DISTRIBUTION RATIOS AT 25°C. FOR THE EQUILIBRIUM OF BROMINE AND IODINE BETWEEN VARIOUS SOLVENTS AND WATER

	CCl_4	CS_2	$CHCl_3$	$CHBr_3$
Br_2	27	76		64
I_2	87	586	130	467

Of these solvents, carbon tetrachloride has the least favorable ratio for the extraction of the halides from aqueous solutions; however, it is less volatile and therefore easier to handle than carbon disulfide or chloroform, it presents no fire hazard, and it is cheaper and more readily available than bromoform. The color of iodine when dissolved in these solvents is much more intense than it is in water; therefore, because of the concentration of the iodine in the organic solvent and of the intensity of the color therein, a very delicate test is provided. Under the conditions of this procedure, when iodide is present alone, 0.04 mg can be detected if bromoform is used, and 0.05 mg if carbon tetrachloride is used.

Ferric ion also reacts with thiocyanate to give the intensely colored compound $Fe \cdot Fe(SCN)_6$, which (after removal of the iodine from the aqueous solution) provides a sensitive test for the presence of thiocyanate. Iodine is reduced by thiocyanate, but the rate of this reaction is so slow under the conditions of this procedure that 0.5 mg of either iodide or thiocyanate can be detected in the presence of 250 mg of the other.

Procedure 143: DETECTION AND SEPARATION OF IODIDE AND DETECTION OF THIOCYANATE. Add to the cold solution (from P. 142) in a separating funnel 3 ml of CCl_4 (Note 1) and 5 ml of 1 f. $Fe_2(SO_4)_3$. Shake the solution intermittently for 2 to 5 min. (Purple to violet color in the

CCl_4, presence of iodide, Note 2; pink to red color in the aqueous layer, presence of thiocyanate.)

If iodide is present, add 7 ml of CCl_4 and again shake intermittently for 1 to 3 min. Draw off the CCl_4 layer into a 200-ml flask provided with a clean rubber stopper. Add successive 5-ml portions of CCl_4, shaking the mixture and collecting the CCl_4 with the first portion, until the CCl_4 remains colorless (Note 3). (Pink to red color in the aqueous layer, presence of thiocyanate.)

Treat the aqueous solution by P. 145 (Note 4); treat the CCl_4 extracts by P. 144.

Notes:

1. Experiments have shown that by the substitution throughout this procedure of $CHBr_3$ for the CCl_4, a more sensitive detection of iodine can be obtained and that the extraction of large amounts of iodine from the aqueous solution can be made more rapidly and with a smaller total volume of the solvent. The use of the $CHBr_3$ is not specified because it may not be readily available, because it is more expensive, and because it forms a more stable emulsion when shaken with the aqueous solution.

2. If thiocyanate is present in large amounts, the red color of the ferric thiocyanate compound will make it difficult to detect the presence of a small amount of iodine in the CCl_4. In this case separate the CCl_4 layer from the aqueous layer, wash it with 1 to 2 ml of water, again separate it, collect it in a small test tube (70 mm by 9 mm), and look lengthwise through the test tube against a white background. Especially when such a tube is being used for the detection of bromide (as in P. 146), it is advantageous to compare the solution being tested with a similar tube containing pure CCl_4.

If the ammonium sulfide solution used in P. 142 has stood for considerable time, it has been found that reducing compounds are formed which may prevent the appearance of an iodine color within the specified time when small amounts of iodide (1 mg or less) are present. In this case the detection can be made certain by immersing the separating funnel in a beaker of water at approximately 50°C. for 2 to 3 min.

3. Any iodine remaining in the aqueous solution is volatilized in the next procedure and thus will not interfere with the subsequent detection of bromide or chloride. Therefore, if a quantitative estimation of the iodide is not desired, it is necessary to remove the iodine only until the presence or absence of thiocyanate can be observed in the aqueous layer.

As the reaction between iodide and ferric iron proceeds somewhat slowly, it is advantageous to allow some time between successive shakings of the mixture. The two layers should be adequately mixed but not shaken so hard or continuously as to cause the formation of an emulsion.

4. Even in the absence of both iodide and thiocyanate, the aqueous solution should be treated by P. 145 in order to oxidize the reducing constituents, such as thiosulfate, remaining from the ammonium sulfide (P. 142). These would reduce large amounts of permanganate in P. 146 which would tend to give a troublesome precipitate of MnO_2.

P. 144. Estimation of Iodide

Discussion. The estimation of iodide is easily and rapidly made by adding water containing iodide to the carbon tetrachloride solution of the iodine obtained in P. 142 and titrating the mixture with a standard thiosulfate solution. The iodide, because of the formation of the tri-iodide ion, causes more of the iodine to pass into the aqueous phase until an equilibrium between the two phases is established. Upon titration with thiosulfate, the concentration of the iodine in the aqueous phase is lowered and the equilibrium again shifts. This process is continued until all the iodine is extracted from the carbon tetrachloride. The end-point is taken upon the disappearance of the iodine color from the carbon tetrachloride layer, or starch may be added and the disappearance of the blue color in the aqueous phase may be taken as the end-point. It is necessary that the mixture be vigorously shaken in order to establish equilibrium rapidly between the two phases. The general discussion preceding the preparation and use of standard iodine solutions (P. X) should be consulted.

Procedure 144: ESTIMATION OF IODIDE. Add 50 ml of water containing 1 g of KI to the CCl_4 extracts from P. 143 (Note 1) and titrate the mixture with standard 0.1 n. $Na_2S_2O_3$, shaking vigorously, until the two layers are colorless (Note 2). From the volume of thiosulfate used, calculate the amount of iodide present.

Notes:

1. Care should be taken that none of the aqueous solution containing $Fe_2(SO_4)_3$ has remained with the CCl_4 layers; the ferric ion would be reduced by iodide, causing erroneous values for the iodine present.

2. The end-point can be readily obtained by observing the disappearance of the color from the CCl_4 layer. If desired, when the color in the CCl_4 becomes uncertain, starch indicator solution can be added to the aqueous layer and the titration can be continued to the disappearance of the blue color.

P. 145. Elimination of Thiocyanate (and Iodide)

Discussion. Iodide having been detected and partially or completely removed from the solution, various methods for the determination and removal of thiocyanate were investigated. As this anion had already been detected (by the ferric thiocyanate color), efforts were made to estimate and oxidize it by titration with per-

manganate. It is known that the titration of thiocyanate by permanganate in an acid solution, based upon the reaction

$$5SCN^- + 6MnO_4^- + 18H^+ = 5HSO_4^- + 5HCN + 6Mn^{++} + 4H_2O,$$

is not a precise process (oxidation by the oxygen of the air being induced and side reactions occurring), but it was found that, in the absence of bromide, estimations could be made which were within 2 to 5 per cent of the amount present. However, when bromide was present, bromine cyanide was formed,

$$5HCN + 5Br^- + 2MnO_4^- + 11H^+ = 5BrCN + 2Mn^{++} + 8H_2O,$$

and this resulted not only in errors in the titration but also in subsequent failure to detect small amounts of bromide. Moreover, if this compound was later reduced, it caused the formation of a precipitate upon subsequent addition of silver nitrate for the detection of chloride.

An investigation was made of the separation of thiocyanate by precipitating it as cuprous thiocyanate; this is commonly done by the addition of a cupric salt and a reducing agent such as sulfur dioxide. Difficulty was experienced in obtaining complete reduction of the ferric iron in the presence of thiocyanate, and, unless this was obtained, the precipitation of the thiocyanate was incomplete. Complete precipitation was obtained by first neutralizing the solution with sodium hydroxide, filtering out the ferric and ferrous hydroxides resulting, just acidifying the filtrate, adding cupric nitrate, and saturating with sulfur dioxide. However, when considerable amounts of bromide were present, difficulty was experienced in attaining conditions under which the precipitation of thiocyanate was complete without causing the precipitation of cuprous bromide. In fact, this separation appeared to be possible only because of the pronounced tendency of cuprous bromide to supersaturate cold solutions; when such solutions were heated, precipitation occurred.

The method given below was adopted as a result of investigations[2] showing that, by proper adjustment of the acidity of the solution, thiocyanate could be oxidized by nitrate ion and the resulting hydrogen cyanide could be expelled without appreciable oxidation, loss of bromide, or formation of bromine cyanide. Iodide, if not previously removed, is also oxidized and volatilized.

[2] Unpublished work by D. K. Beavon and Erwin Baumgarten.

An incidental advantage of this method is that any reducing compounds introduced into the analysis by the ammonium sulfide in P. 142 and any ferrous iron present are oxidized, thus reducing the amount of permanganate which has to be added later for the oxidation of bromide; in this way the formation of a precipitate of manganese dioxide (which causes that procedure to be somewhat troublesome) usually can be avoided. In order to avoid oxidation of bromide, the hydrogen ion concentration of the solution should be closely controlled; because of this and because considerable amounts of acid are used in the oxidation reaction, a buffering action is provided by the use of sulfate and hydrosulfate (see P. 61 for a discussion of the buffering action thus obtained). Similarly, sodium nitrate is added in considerable excess in order that the oxidizing potential be maintained fairly constant even when large amounts of thiocyanate are oxidized. Experiments have shown that 0.5 mg of bromide can be detected in the presence of 250 mg of thiocyanate and that, with 250 mg of bromide alone present, only about 2 mg were lost after boiling for 10 min.; however, with 125 mg each of thiocyanate and bromide, as much as 25 to 30 mg of bromide may be lost.

An extensive study of the reaction was made in order to ascertain if the hydrogen cyanide evolved could be collected and an estimation of the amount of cyanide present could be made thereby. It was found that the thiocyanate was not quantitatively converted to cyanide, and that the fraction so converted was dependent upon (1) the acidity of the solution, (2) the amount of ferric iron in the solution, and (3) the amount of thiocyanate present. Under the conditions of this procedure, with 250 mg of thiocyanate, it was found that the yield of cyanide was approximately 80 per cent of the theoretical amount; with 150 mg, 90 per cent; and, with 50 mg, 95 per cent. With a given amount of thiocyanate the yield is constant to within 2 to 5 per cent, so that, by constructing a curve from these data, the amount of thiocyanate can be approximately calculated from the amount of cyanide collected. A procedure for the collection and estimation of the evolved hydrogen cyanide is included in Note 2 of this procedure.

Procedure 145: ELIMINATION OF THIOCYANATE (AND IODIDE). Transfer the aqueous solution (from P. 143) to a 200-ml flask, add 3 g of Na_2SO_4, 10 ml of 6 f. $NaHSO_4$, and 3 g of $NaNO_3$, and dilute it to 50 ml (Note 1). Heat the solution just to boiling for 5 min., swirling it continuously

(Notes 2, 3); do not allow the solution to concentrate by evaporation. If the solution has not become practically colorless (Note 4), add to it 5 to 10 ml of water (depending upon the amount which has evaporated), and boil it vigorously for 2 min. more. Cool the solution to room temperature, add to it 10 ml of H_2SO_4, and treat it by P. 146.

Notes:

1. It is necessary that the volume of the solution and the amount of sulfate and nitrate be properly adjusted, so that complete elimination of thiocyanate without loss of bromide can be obtained.

2. If it is desired to estimate the HCN evolved, before heating the solution transfer it to a distilling flask fitted with a safety tube and side arm (as described in P. 41 and P. 42). Pass the outlet tube of the distilling flask through a two-hole stopper into a large test tube (1 in. by 7 in.) containing 20 ml of 1 n. NaOH and 5 ml of NH_4OH. The second hole of the stopper is fitted with a glass tube carrying rubber tubing which is connected to a water aspirator. An ebullition tube (described in P. 42) should be provided in the distilling flask. By means of the aspirator, draw air through the solution at such a rate that the liquid is prevented from rising in the safety tube and boil it as directed above. Transfer the receiving solution to a 200-ml flask, add 2 drops of 1 n. KI and 1 ml of NH_4OH, and titrate with standard 0.1 n. $AgNO_3$ to the first permanent yellowish opalescence (see P. 23). From the amount of cyanide found present and the data given in the discussion, an approximate estimate of the amount of thiocyanate present can be made.

3. If no thiocyanate was found present in P. 143, the solution should be boiled for only 1 to 2 min. This is sufficient to oxidize any reducing agents introduced by the ammonium sulfide reagent and to prevent having to use a large volume of permanganate in oxidizing the bromide in P. 146.

If much bromide is present, a permanent yellow color (due to ferric bromide) will persist in the solution; however, it is still possible to note when the more brownish-colored products of the reaction are no longer present.

P. 146. Detection and Separation of Bromide

Discussion. In the procedure below, bromide is separated from chloride by oxidation with permanganate and the bromine thus formed is extracted with carbon tetrachloride. The possibility of carrying out this separation would be predicted from the difference in the potentials of the two elements, but these would indicate that, in order to avoid oxidation of chloride, care would be required in the adjustment of the hydrogen ion concentration if permanganate were used as the oxidizing agent. It would also be predicted from the permanganate and the hydrogen ion concentrations obtaining in the

procedure below (approximately 2×10^{-4} and 0.2 to 0.5 m., respectively) that substantially all of the chloride would be oxidized. That this does not occur to an appreciable extent is due to the slow rate at which permanganate oxidizes chloride in cold solutions.

As is explained in the discussion of permanganate titrations (pp. 53–59), if the hydrogen ion concentration is not sufficiently high, a precipitate of manganese dioxide will be obtained.

Procedure 146: DETECTION AND SEPARATION OF BROMIDE. Transfer the solution from P. 145 to a short-stem separating funnel, add to it 3 ml CCl_4 (Note 1) and, dropwise, 0.1 f. $KMnO_4$ until a perceptible pink color remains, and then 2 drops in excess (Note 2). Shake the solution intermittently for 1 to 2 min. (Yellow to orange color in the CCl_4, presence of bromide. Note 3.)

If bromide is present, add 5 to 20 ml more CCl_4 and again shake it (Note 4). Draw off the CCl_4 layer into a 200-ml flask containing 1 g of KI dissolved in 50 ml of water (Note 5). Add successive 5-ml portions of CCl_4 to the aqueous layer, shaking the mixture and collecting the CCl_4 with the first portion, until the carbon tetrachloride added remains colorless. If the aqueous solution becomes colorless at any time, again add $KMnO_4$ until 2 drops in excess are present.

Treat the CCl_4 extracts by P. 147. Treat the aqueous solution by P. 148.

Notes:

1. Before the $KMnO_4$ is added, the mixture should be shaken and the CCl_4 should be examined to see that no iodine has remained in the solution.

2. Frequently CCl_4 contains reducing compounds which cause a slow reduction of permanganate; for this reason, if the permanganate color fades, more should be added and the 2-drop excess should be maintained.

3. See Note 2, P. 143, in regard to examining the CCl_4 layer to detect small amounts of bromine.

4. If an estimation of the amount of bromide (and in P. 148 of chloride) is not desired, the removal of the bromine can be more rapidly accomplished, after removing the first CCl_4 extraction, by diluting the solution with 50 ml of water and boiling it gently for 2 to 3 min., adding more $KMnO_4$ if the color fades. Under these conditions the bromide is more rapidly oxidized and expelled from the solution, while only a small fraction of any chloride present will be lost.

It is also possible to titrate separately (by P. 147) each carbon tetrachloride layer until the amount of bromine extracted by the last portion is found to be so small that the bromine remaining in the aqueous layer can be volatilized by boiling as suggested above.

5. Extreme care should be taken that the carbon tetrachloride layers be free of the aqueous layer containing permanganate, as this would also oxidize iodide.

P. 147. Estimation of Bromide

Discussion. In P. 146 the carbon tetrachloride solutions containing the bromine were added to an aqueous solution containing an excess of iodide in order to reduce the more volatile bromine to bromide, thus liberating an equivalent amount of iodine, which not only is less volatile but also is more stably held in the solution because of the formation of the tri-iodide ion. This iodine is titrated with thiosulfate as was done in the estimation of iodide.

Procedure 147: ESTIMATION OF BROMIDE. Titrate the mixture containing the CCl_4 extracts immediately with standard 0.1 n. $Na_2S_2O_3$, shaking vigorously, until the two layers are colorless (see Notes to P. 144). From the volume of thiosulfate used, calculate the amount of bromide present.

P. 148. Detection and Estimation of Chloride

Discussion. The solution from P. 146 will contain an excess of permanganate and frequently may contain a precipitate of manganese dioxide. These are both reduced by addition of nitrite so that a clear solution is available for the detection of chloride; this is done by the addition of silver ion, thus precipitating silver chloride. A standard silver nitrate solution is used so that the amount of chloride can be estimated by adding an excess of silver ion, coagulating the precipitate, and determining the excess of silver by a titration with standard thiocyanate solution. The ferric iron already present acts as the indicator. See P. VI and P. 27 for discussions and notes concerning the titration.

Procedure 148: DETECTION AND ESTIMATION OF CHLORIDE. Add chloride-free $NaNO_2$ solution 5 drops at a time, to the solution from which bromide has been extracted (P. 146), until the permanganate color is removed and any precipitate has dissolved (Note 1). Add 1 ml of standard 0.1 n. $AgNO_3$ solution. (White precipitate, presence of chloride. Note 2.) If chloride is found present, treat the solution as directed in the last two paragraphs of P. 27. From the

volume of standard $AgNO_3$ and KSCN used, calculate the amount of chloride present.

Notes:

1. A large excess of $NaNO_2$ should be avoided, as it may later cause a local precipitate of $AgNO_2$. This can be distinguished from AgCl, as it is more crystalline and readily dissolves on addition of HNO_3.

2. Chloride is a common impurity in reagents. Therefore, if only a small precipitate is obtained, the reagents used in the analysis should be used in making a blank; any precipitate so obtained should be compared with that obtained here.

The Analysis of the Oxy-Halogen Group

(See Tabular Outline XI)

P. 151. Precipitation of the Oxy-Halogen Group

Discussion. As was stated in P. 141, iodate is completely precipitated as silver iodate in that procedure and any bromate in excess of 100 mg is likely to be precipitated there. In this procedure the bromate remaining, and any chlorate, are reduced by the addition of a soluble nitrite and are precipitated as the corresponding halide silver salt. Nitrite is used as a reducing agent because it reacts rapidly with the oxy-halogen anions and because it does not introduce undesirable compounds into the analysis, as would sulfite or a metallic ion. Peroxide could be employed, but it does not react as rapidly with the ions to be reduced here; also, the 3 per cent solution of commerce frequently contains considerable amounts of chloride.

It is to be noted that some bromate will always be found here, so that, if an oxy-halogen precipitate is obtained in P. 141 and none is obtained in this procedure, the presence of iodate alone is confirmed. Perchlorate and periodate are not reduced in this procedure and therefore escape detection here (see P. 4 for a discussion of the oxidizing properties of perchloric acid); the existence of perbromic acid has not been proved. Although it is not reduced by nitrite under the conditions of this procedure, periodate is more reactive than perchlorate and is reduced by iodide ion in acid solutions; it therefore gives a test for oxidizing agents in P. 112. Sodium para-periodate ($Na_3H_2IO_6$) is so slightly soluble in alkaline solutions that not more than approximately 2.5 mg/ml will pass into the sodium carbonate solution; this will be partially precipitated with the Phosphate Group in P. 161 but will escape detection in the analysis of that group. Because neither perchlorate nor periodate would be detected in the course of this systematic analysis, separate procedures (P. 153 and P. 154) are provided for their detection and estimation.

Hypochlorite, a commonly occurring oxy-halogen anion, is decomposed by boiling alkaline solutions into chlorate and chloride. Therefore, if both chloride and chlorate are found present, this may be caused by the presence of hypochlorite in the original sample; its

presence should be confirmed by treating a portion of the original material by P. 152.

The Oxy-Halogen Group precipitate obtained in this procedure (combined with that obtained in P. 141) is treated by P. 142 and the subsequent procedures for the analysis of the Halide Group to identify and estimate the amount of the individual halides present.

Procedure 151: PRECIPITATION OF THE OXY-HALOGEN GROUP. If neither oxidizing constituents (P. 112) nor oxy-halogen acids (P. 114) have been found present, treat the solution (from P. 141) directly by P. 161 (Note 1).

If either of these groups of constituents have been found present, add to the solution from the Halide Group precipitation 2 ml of HNO_3 and 5 ml of chloride-free $NaNO_2$ (Note 2). (White or yellowish precipitate, presence of bromate or chlorate.) Filter out the precipitate on an asbestos filter and wash it with 5 to 10 ml of 0.6 n. HNO_3, collecting this solution with the filtrate. Treat the filtrate by P. 161.

Wash the precipitate with 10 ml of 0.6 n. HNO_3, combine it with any oxy-halogen precipitate obtained in P. 141, and treat the combined precipitates by P. 142 and the subsequent Halide Group procedures to detect and estimate the halogen elements present. If iodide is found by P. 143, the presence of iodate is indicated (see the discussion above). If bromide is found by P. 146, the presence of bromate is indicated. If chloride is found by P. 148, the presence of chlorate or hypochlorite is indicated. If chloride has been previously found, treat a portion of the original material by P. 152 to distinguish between chloride, chlorate, and hypochlorite. Treat a portion of the sodium carbonate solution (from P. 111) by P. 153 to detect and estimate perchlorate and by P. 154 to detect periodate.

Notes:

1. If in P. 112 the oxidizing constituents and in P. 114 the halogen oxy-acids have been found absent, none of the oxy-halogen anions can be present. Chlorate may not be detected in the test for oxidizing constituents but is detected in P. 114 as an oxy-halogen anion.

2. As nitrous acid is not a highly ionized acid, the addition of its salt causes a reduction in the hydrogen ion concentration of the solution. As this might cause the precipitation of silver oxalate or other silver salts of weak acids, additional HNO_3 is first added. The precipitate is later washed with dilute acid, and not water, for the same reason.

P. 152. Separation and Estimation of Hypochlorite

Discussion. As explained in P. 151, hypochlorite is decomposed by boiling alkaline solutions into chlorate and chloride and therefore would not be present after the sodium carbonate treatment. In case both chlorate and chloride have been found in the sodium carbonate solution, it is necessary to test an aqueous extract of the original material for hypochlorite. The method used here for the separation and estimation of hypochlorite depends upon the following facts: (1) Hypochlorous acid is a very weak acid ($K_A = 1.1 \times 10^{-8}$ at 25°C.) and is thus formed upon acidification of its salts with even weak acids; (2) hypochlorous acid forms stable esters with monohydroxy alcohols; and (3) these esters are much more soluble in organic solvents, such as carbon tetrachloride, than in water and can therefore be extracted from their aqueous solutions by such solvents. These facts have been studied as a commercial method for the preparation of pure hypochlorite solutions[1] and have been developed into the analytical method used in the procedure below.[2] In this method tertiary butyl alcohol is added to the acidified extract of the material and this solution is then shaken with carbon tetrachloride, with the result that the hypochlorite is extracted as the ester. Tertiary butyl alcohol was selected because it has been found that the tertiary alcohols are more stable with respect to oxidation than are the primary or secondary alcohols. Experiments have shown that, of the other oxidizing anions provided for in this system, none that could be present with hypochlorite is extracted by the carbon tetrachloride under these conditions, and that, therefore, after the carbon tetrachloride layer has been separated, the hypochlorite present can be detected and estimated by adding the carbon tetrachloride extract to a solution of a soluble iodide acidified with acetic acid.[3] The iodine set free indicates the presence of hypochlorite, and the amount present is estimated by titrating with a standard thiosulfate solution.

The results of a series of experiments on the detection of hypochlorite in the presence of various other constituents have shown that, under the conditions of the procedure below, as little as 0.58

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[1] Taylor, MacMullen, and Gammal, *J. Am. Chem. Soc.*, **47**, 395 (1925).

[2] Unpublished experiments by Erwin Baumgarten.

[3] Rupp, *Z. anal. Chem.*, **56**, 586 (1917), has shown that an iodometric estimation of hypochlorites can be made in the presence of chlorates if the solution is acidified with acetic acid; no appreciable reduction of the chlorate occurs in the time required for the titration of the iodine liberated by the hypochlorite.

mg of hypochlorite can be detected, and that nitrite is the only other oxidizing constituent which causes a positive test. As nitrite and hypochlorite are not compatible constituents, hypochlorite is absent if nitrite is found present in P. 182.

Two methods for estimating the hypochlorite were investigated. In the first, or direct, method, the carbon tetrachloride layer from the extraction was added to an aqueous potassium iodide solution acidified with acetic acid. This caused a quantitative reduction of the hypochlorite, and the resulting iodine was titrated with standard thiosulfate solution. In the second, or indirect, method, the aqueous solution (from the extraction) is acidified and treated with

TABLE XXXII

THE ESTIMATION OF HYPOCHLORITE

Expt.	ClO^- Taken (mg)	Other Constituents (mg)	Result of Hypochlorite Estimation			
			Direct Method		Indirect Method	
			ClO^- Found (mg)	Error (%)	ClO^- Found (mg)	Error (%)
1	57.8	.....	56.5	−2.2	57.7	−0.1[a]
2	23.0	MnO_4^-, 119	20.8	−9.6	23.1	+0.4
3	23.1	IO_3^-, 10	22.6	−2.2	23.0	−0.4
4	23.0	$Cr_2O_7^=$, 10	22.6	−1.7	..	.....
5	22.8	$Cr_2O_7^=$, 10	22.3	−2.2	22.7	−0.4
6	25.8	$AsO_4^{\equiv}$, 10	25.4	−1.6	.	. ...
7	26.4	ClO_3^-, 10	25.9	−1.9	26.5	+0.4
8	26.4	NO_3^-, 10	26.0	−1.5	26.5	+0.4
9	23.2	BrO_3^-, 25	22.6	−2.6	23.1	−0.4
10	22.9	ClO_3^-, 100	22.5	−1.8	22.8	−0.5
11	63.5	ClO_3^-, 100	62.4	−1.7	63.3	−0.3

[a] Less than one drop of thiosulfate was required to titrate the aqueous layer after the extraction.

iodide, and any iodine formed is titrated, so that any oxidizing agents remaining in the aqueous solution are determined. The total amount of oxidizing constituents originally present are estimated by similarly treating the same volume of the original solution as was used for the extraction with iodide and acid and titrating with thiosulfate. The total oxidizing equivalents originally present minus those remaining after the extraction are the number of equivalents of hypochlorite present. This method eliminates the errors caused in the direct hypochlorite determination by the volatilization of hypochlorous acid from the solutions during the extraction process or by the reduction of the hypochlorite by impurities commonly

present in the alcohol. It is apparent that both methods can be used on the solutions from one extraction. The results of tests of these methods are shown in Table XXXII.

Procedure 152: SEPARATION AND ESTIMATION OF HYPOCHLORITE. Weigh out 0.2 to 0.4 g of the original material into a small flask, add 5 ml of water, and thoroughly disintegrate the solid particles with the flattened end of a stirring rod (Note 1). Filter the mixture through a paper filter and collect the filtrate in a separating funnel. Mix 4 ml of 3 n. $NaC_2H_3O_2$ with 2 ml of $HC_2H_3O_2$ and rapidly wash the residue and filter with this solution. Collect this with the water extract in the separating funnel.

Add to the prepared solution 10 ml of CCl_4 to which has been added 0.5 ml of tertiary butyl alcohol (Note 2). Stopper the funnel, cool the mixture, shake it intermittently for 30 sec., and allow it to stand until the two layers separate. Draw off the carbon tetrachloride layer into 50 ml of water containing 5 ml of $HC_2H_3O_2$ and 2 g of KI (Note 3). (Iodine color in the solution, presence of hypochlorite.) If it is desired to estimate the amount of hypochlorite present, repeat the extraction with two additional portions of the carbon tetrachloride–tertiary butyl alcohol mixture. Add these to the iodide solution and titrate it with 0.1 n. $Na_2S_2O_3$ until the iodine color is indistinct. Then add 5 ml of starch and again titrate to the disappearance of the blue color. From the volume of thiosulfate used, calculate the amount of hypochlorite present (Note 4).

Notes:

1. If a quantitative estimation is desired or if the percentage of hypochlorite in the solid material is thought to be small, a larger sample and larger amounts of the carbon tetrachloride–tertiary butyl alcohol extracting medium should be used.

If the material to be tested is a solution, take from 10 to 100 ml, depending upon the amount of hypochlorite thought to be present.

2. As both carbon tetrachloride and the tertiary butyl alcohol may contain reducing substances, the purest available materials should be used. If a considerable number of analyses are to be made, an adaquate volume of the carbon tetrachloride–tertiary butyl alcohol solution should be provided as a reagent.

3. If a very sensitive test for small amounts of hypochlorite is desired, the carbon tetrachloride layer should be collected in a second separating funnel containing 5 ml of water, the mixture shaken, the layers allowed to

separate, and the carbon tetrachloride layer then drawn off into the iodide solution. By this step it is made certain that any of the aqueous solution, which may contain other oxidizing agents that would oxidize the iodide, is removed from the carbon tetrachloride layer.

4. If a more precise estimation of the hypochlorite is desired, proceed as follows:

Prepare a solution of the original material as directed in the first paragraph of the above procedure and dilute this to a definite volume in a volumetric flask. Pipet out one portion, treat it by the procedure above, and add the *aqueous* layer to 50 ml of water to which has been added 2 g of KI and 10 ml of H_2SO_4. Let the mixture stand closed for 5 min. and titrate any iodine resulting with 0.1 n. $Na_2S_2O_3$, as directed above.

Pipet out another portion of the original solution, add it directly to the same volume of water, KI, and H_2SO_4, close the flask, and let it stand for 5 min. Again titrate the iodine resulting. From the difference in the volume of standard thiosulfate required to titrate the original solution and that required to titrate the aqueous layer after the hypochlorite has been extracted, the amount of hypochlorite present can be calculated.

As hypochlorite solutions are unstable, they should not be allowed to stand any longer than is necessary to carry out the required operations. It was found that the concentration of a hypochlorite solution, acidified with acetic acid–acetate solution, decreased 3.6 per cent upon standing for 40 min. in the dark; the decomposition is more rapid in sunlight. The above procedure is not satisfactory in the presence of arsenate, as arsenate reacts incompletely with the iodide in the time given.

P. 153. Detection and Estimation of Perchlorate

Discussion. This procedure is based upon experiments showing that perchloric acid is reduced by ferrous sulfate in fuming sulfuric acid and that the products of the reduction, mainly chlorine, can be distilled and collected in an alkaline sulfite solution.[4] Upon acidifying this solution and boiling out the excess of sulfite, the chloride present can be precipitated with a standard silver nitrate solution.

There are certain anions which would interfere with this procedure, as, upon being heated with fuming sulfuric acid, they would yield volatile products that would be collected in the receiving solution and give a precipitate with silver ion. The halides, oxy-halogens, thiocyanate, cyanide, and complex cyanides behave in this manner, and they have to be eliminated before this procedure is applied. This is done by first acidifying the sodium carbonate solution, adding sulfite (to reduce any oxy-halogens present), and then adding silver nitrate and filtering out any resulting precipitate.

[4] Unpublished experiments by F. C. Ingalls.

Manganous sulfate was investigated as a reducing agent. It was found that 0.5 mg of perchlorate could be detected by the purple color which it produced upon being heated with a mixture of sulfuric and phosphoric acids containing manganous sulfate. However, nitrate caused the same color, and it was found that manganous sulfate, even in the presence of phosphoric acid, did not cause the complete reduction of perchloric acid and was therefore not suitable for the quantitative estimation of perchlorate.

Procedure 153: DETECTION AND ESTIMATION OF PERCHLORATE. *Detection.* If no test for the Halogen and Cyanide Groups or the oxidizing anions was obtained in P. 114 or P. 112, pipet 10 ml of the sodium carbonate solution into a 250-ml distilling flask and treat it as directed in the second and subsequent paragraphs below (Note 1).

If the Halogen and Cyanide Groups or the oxidizing anions were found present in P. 114 or P. 112, pipet 10 ml of the sodium carbonate solution into a 100-ml conical flask (Note 1), make it just acid with H_2SO_4, and add solid $NaHSO_3$, 50 mg at a time, until the odor of SO_2 is detectable above the solution. Heat the mixture almost to boiling and add $AgNO_3$, 0.25 ml at a time, until further addition causes no more precipitation (in no case adding more than 10 ml). Heat the mixture until the precipitate is coagulated and the odor of SO_2 is no longer apparent. Filter out the precipitate and wash it with 3 to 5 ml of water, collecting the wash water with the filtrate in a 250-ml distilling flask. Discard the precipitate.

Insert the side tube of the distilling flask through a two-hole stopper almost to the bottom of a 100-ml round-bottom receiving flask (see Fig. 29) to which has been added 0.5 g of $NaHSO_3$, 5 ml of 6 n. NaOH, and 40 ml of water. Add to the distilling flask 2.5 to 5 g of anhydrous $FeSO_4$ (Note 2). By means of a short tube in the second hole of the stopper, connect the receiving flask to an aspirator and close the distilling flask with a stopper carrying a thistle tube extending to the bottom of the flask. Draw a slow current of air through the flasks by means of the aspirator and add slowly through the thistle tube 15 to 20 ml of 36 n. H_2SO_4.

While maintaining a slow current of air through the apparatus, heat the mixture in the distilling flask until the sulfuric acid fumes freely (Note 3).

Remove the receiving solution, transfer it to a 200-ml flask, make it just acid with HNO_3, add 5 ml in excess, and then boil it until the odor of SO_2 is no longer detectable. Add to the solution exactly 1.00 ml of standard 0.1 n. $AgNO_3$. (White precipitate, presence of perchlorate. Note 4.)

Treat the receiving solution as directed below.

Estimation. If perchlorate is present and an estimation of the amount is desired, treat the mixture by the last two paragraphs of P. 27.

Notes:

1. If organic matter has been found present in P. 3, add 5 ml of 16 n. HNO_3 to the Na_2CO_3 solution, evaporate it *almost* to dryness on a water bath, add 5 ml of water, and treat it as directed above. This preliminary treatment with HNO_3 prevents the danger of an explosive reaction between perchloric acid and any organic matter.

2. The amount of the $FeSO_4$ to be added should be adjusted to the amount of perchlorate and of other oxidizing agents thought to be present, any previous information regarding the material and the results of the analyses already carried out being taken into consideration. The more $FeSO_4$ there is added, the greater the tendency of the material to "bump" during the subsequent boiling. If the anhydrous salt is not available, the hydrated material ($FeSO_4 \cdot 7H_2O$) may be used.

Only the best grade of ferrous salt available should be used, as otherwise an appreciable amount of chloride may be introduced into the analysis; if the presence of chloride in the ferrous sulfate is suspected, a blank should be made.

The salt can be expeditiously introduced into the flask by rolling a strip of paper into a tube slightly smaller in diameter than the neck of the distilling flask and pouring the crystals through it.

3. It is necessary that the sulfuric acid be caused to fume in order to decompose all the perchloric acid and expel the chlorine. The bulb should fill with dense white fumes.

Bumping of the solution is minimized by maintaining a continuous flow of air through the solution and by applying the flame toward the side of the flask (but not above the level of the solution), where there is a thinner layer of solution.

4. As chloride is commonly present in reagents, the detection of a small amount of perchlorate should be confirmed by carrying out a blank analysis.

P. 154. Detection of Periodate

Discussion. The presence of periodate would be indicated in the test for oxidizing constituents in P. 112 but would not be detected in any of the procedures of the systematic analysis. Therefore, this procedure is provided for the case that oxidizing constitu-

ents have been found present and a specific identification of periodate is desired. In making this detection, iodide and iodate are removed by precipitation with silver nitrate in an acid solution, the excess silver is removed by precipitation with sodium chloride, the solution is made 6 n. in hydrochloric acid, and an excess of ferrous iron is added. Periodate is reduced by ferrous iron to free iodine; by shaking the solution with carbon tetrachloride, a more sensitive test for iodine is obtained. As iodide and iodate have been removed previously, the presence of free iodine shows the presence of periodate; hypoiodite is unstable and rapidly decomposes to iodide and iodate. Under the conditions of the procedure below, 0.1 mg of periodate can be readily detected when present alone; when phosphate is present, the sensitivity is reduced to 0.2 mg, probably because of partial reduction of the iodine to iodide.

Procedure 154: DETECTION OF PERIODATE. If oxidizing constituents have been found present in P. 112, acidify 5 ml of the sodium carbonate solution with 9 n. $HClO_4$ (Note 1), add 1 ml in excess, and then add 1 n. $AgNO_3$, 0.5 ml at a time, as long as a precipitate continues to form. Filter out and discard the precipitate, collecting the filtrate in a ground-glass-stoppered flask. Add 1 n. NaCl to the filtrate, 1 ml at a time, until no more precipitate forms. Stopper the flask and shake the mixture vigorously after each addition. Again filter out and discard the precipitate (Note 2).

Add to the filtrate a volume of 12 n. HCl equal to that of the solution (Note 3). Cool the solution, immediately add 1 g of solid $FeSO_4$ (or 2.5 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) and 2 ml of CCl_4, and shake the mixture intermittently for 5 min. (Purple color in the CCl_4, presence of periodate.)

Notes:

1. $HClO_4$ is used for acidifying the solution instead of HNO_3, as the latter acid tends to oxidize ferrous iron; however, some nitrate is introduced with the silver nitrate, so that, to avoid this oxidation, the solution should be kept cold after the ferrous sulfate is added.

2. The excess silver is removed because silver ion is reduced to metallic silver by ferrous salts; also, the detection of the iodine color is a more distinctive test than the precipitation of silver iodide.

3. The solution is made approximately 6 n. in HCl, as the rate at which periodate reacts with ferrous iron is much slower at lower acid concentrations. Ferrous iron is used for the reduction because it reduces the periodate only to free iodine—not to iodide.

If a crystalline precipitate (NaCl) is formed, add 5 ml of 6 n. HCl.

TABULAR OUTLINE XVI

The Analysis of the Phosphate Group

Filtrate from Oxy-Halogen Group Precipitation:
(Contains remaining anions, Cd^{++}, Ag^{+}, $HC_2H_3O_2$, HNO_2, $H^+NO_3^-$)
Neutralize with NaOH; add $HC_2H_3O_2$.
Add $AgNO_3$. (P. 161)

Precipitate: Ag_3AsO_4, Ag_3PO_4, Ag_3AsO_3, $Ag_2C_2O_4$, Ag *Treat with HCl.* (P. 162)	Filtrate: *Treat by P. 171.*

Residue: AgCl, Ag *Discard.*	Filtrate: H_3AsO_4, H_3PO_4, H_3AsO_3, AsO^+, $H_2C_2O_4$, H^+Cl^- *Add excess of* NH_4OH.

Add $Mg(NO_3)_2$. (P. 162)

Precipitate: $Mg(NH_4)AsO_4 \cdot 6H_2O$, $Mg(NH_4)PO_4 \cdot 6H_2O$ *Dissolve in HCl, add KI.* (H_3PO_4, AsO^+, $AsCl_3$, I_3^-, I_2, H^+Cl^-) *Titrate with* $Na_2S_2O_3$. (H_3PO_4, AsO^+, $AsCl_3$, I^-, $S_4O_6^=$, H^+Cl^-) *Saturate with* H_2S. (P. 163)	Filtrate: $HAsO_2^-$, $C_2O_4^=$, $Mg^{++}(NO_3^-)_2$, NH_4^+, NH_4OH *Add* H_2O_2, *heat.* (P. 165)

Precipitate: $MgNH_4AsO_4 \cdot 6H_2O$ *Treat by P. 89.*	Filtrate: $C_2O_4^=$, $Mg^{++}(NO_3^-)_2$, NH_4^+, NH_4OH

Add $Ca(NO_3)_2$. (P. 166)

Precipitate: As_2S_3 *Discard.*	Filtrate: H_3PO_4, I^-, $S_4O_6^=$, H^+Cl^- *Add excess* NH_4OH.

Add $Mg(NO_3)_2$.
Precipitate: $MgNH_4PO_4 \cdot 6H_2O$ (P. 164)

Precipitate: $CaC_2O_4 \cdot H_2O$ *Treat by P. 87.*	Filtrate: *Discard.*

The Analysis of the Phosphate Group

P. 161. Precipitation of the Phosphate Group

Discussion. The Ferrocyanide, Halide, and Oxy-Halogen Group precipitations have been made in solutions approximately 0.5 n. or greater in nitric and perchloric acids in order to prevent the precipitation of the cadmium and silver salts of certain weak acids. In this procedure the hydrogen ion concentration of the solution is reduced to, and fixed at, a *p*H of about 5.5 (by neutralizing the solution containing acetic acid with sodium hydroxide, then adding a known amount of acetic acid, and thus obtaining a solution with a known ratio of acetate to acetic acid). Under these conditions phosphate (if present in amounts greater than 1 to 2 mg), arsenate, arsenite, and oxalate are precipitated as silver salts. Phosphite, if present, is rapidly oxidized under these conditions by silver ion to phosphate and thus causes a precipitate of silver phosphate; the black precipitate of finely divided silver which is formed gives a sensitive indication of the presence of phosphite.

Chromate, if present as such, would be precipitated as silver chromate under the conditions of this procedure; however, this constituent is reduced to the chromic state by the nitrite added in P. 151. Chromic hydroxide is not precipitated at this *p*H from an acetate-acetic acid solution unless it is present in very large amounts.

Procedure 161: PRECIPITATION OF THE PHOSPHATE GROUP. To the filtrate from the Oxy-Halogen Group precipitation (P. 151), or the solution from P. 121, add NaOH until the solution is just neutral (Note 1) to litmus, and then add just 0.5 ml of $HC_2H_3O_2$ and 1 to 5 ml of $AgNO_3$ (Note 2). Heat the mixture to 80° to 90°C. (Precipitate, presence of Phosphate Group. Notes 3, 4.)

Filter out the precipitate on a paper filter and wash it with 10 to 20 ml of hot water. Treat the precipitate by P. 162. Treat the filtrate by P. 171.

Notes:

1. The NaOH can be added rapidly until the first permanent precipitate of silver oxide or Phosphate Group constituents is produced.

Under no conditions should the solution be alkaline to litmus, as then a

large precipitate of silver oxide is usually formed which is very slow to redissolve.

If they are available, "Nitrazine" (sodium dinitrophenyl-azo-napthol disulfonate) test papers are much more satisfactory for making this adjustment of the acid concentration. By their use the *p*H can be reduced to 5.5 without first having to make the solution neutral or alkaline; this, as mentioned above, frequently causes a troublesome precipitate of silver oxide. In using these papers, the sodium hydroxide is added to the acid solution until, upon wetting a small strip of the paper, a color is produced which matches that corresponding to a *p*H of 5.5 on the color chart provided with the papers. In making the final adjustment, the color should be compared only after the strip has been wet for at least 45 sec. and not longer than 2 min.[1] Other indicator test papers (P. 3, Note 6) may be used, but they are not as suitable for the adjustment of the hydrogen ion concentration to the particular range desired in this procedure as is the Nitrazine.

2. There frequently results at this point a crystalline precipitate of silver acetate. This dissolves when the solution is heated and should not be mistaken for a Phosphate Group precipitate. Only 1 ml of the $AgNO_3$ should be added until it is seen that a permanent precipitate is being produced.

3. The color of the precipitate may indicate the constituents present. Silver phosphate is yellow, silver arsenate is reddish-brown, silver arsenite is yellow, and silver oxalate is white. A black precipitate on neutralization of the solution indicates phosphite; if large amounts of arsenite are present, a small amount of it may be oxidized by the silver ion.

Frequently a small dark precipitate is obtained at this point which is apparently caused by organic material previously introduced into the analysis. In order to confirm the presence of the Phosphate Group, and to avoid the analysis of that group in its absence, proceed as follows:

> Pour dropwise through the precipitate 4 ml of cold 3 n. HNO_3 and then 15 ml of water and collect the clear solution in a small flask. Make the solution just neutral to litmus with NaOH and then add 5 drops of $HC_2H_3O_2$—the solution should react slightly acid to litmus. Add 1 ml of 3 n. $NaC_2H_3O_2$, heat the solution to 60° to 80°C., and add 1 ml of 1 n. $AgNO_3$. (Precipitate, presence of the Phosphate Group.)

As much as 0.5 mg of any of the constituents of the Phosphate Group will give a precipitate under the above conditions. The volume should be between 20 and 25 ml, or a precipitate of silver acetate will form; this is readily soluble in the hot solution.

4. Under the conditions of the above procedure, 0.5 mg of any of the constituents except phosphate will give an easily recognized precipitate; 1 to 2 mg of phosphate may remain undetected. This constituent will have been tested for in the basic analysis.

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[1] More detailed information concerning this indicator will be supplied by E. R. Squibb and Sons, from whom the indicator can be obtained either in an alcoholic solution or as the test papers.

P. 162. Separation of Phosphate and Arsenate from Arsenite and Oxalate

Discussion. Before proceeding with the analysis of this group, it is necessary that the precipitate of the silver salts be brought into solution. This might be accomplished by the use of ammonium hydroxide, as the subsequent separations of this group are carried out in ammoniacal solutions. However, it was found that the silver salts dissolved rather slowly and that excessive amounts of concentrated ammonia solutions were required; any metallic silver present was not dissolved by ammonia and had to be filtered out. By the use of hydrochloric acid, a dual solvent action is obtained; first, the anions of the silver salts are converted into the un-ionized acids, and, second, the silver ion is precipitated as silver chloride, which is then filtered out with any metallic silver that may be present. Experiments showed that the process gave a satisfactory solution of the precipitates, and it is used below.

The hydrochloric acid solution is neutralized, and then an excess of ammonium hydroxide and of a soluble magnesium salt is added. Under these conditions phosphate is precipitated as magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$) and arsenate as the analogous magnesium ammonium arsenate ($MgNH_4AsO_4 \cdot 6H_2O$). The quantitative precipitation of these compounds requires a close adjustment of the hydroxyl ion concentration of the solution. They are appreciably soluble in water because of their hydrolysis, as indicated by the equation

$$MgNH_4PO_{4(s)} + H_2O = Mg^{++} + NH_4OH + HPO_4^{=},$$

so that it is evident that the presence of an excess of the products on the right should decrease this solubility. In addition, the solubility product of this salt has the form $[Mg^{++}][NH_4^{+}][PO_4^{=}] = K$, indicating the desirability of increasing the concentration of the ammonium ion. However, the hydroxyl ion concentration of the solution is controlled by the ratio of ammonium ion to ammonium hydroxide present, as shown by the equation

$$[OH^{-}] = K_B \frac{[NH_4OH]}{[NH_4^{+}]}.$$

Therefore, increasing the ammonium ion would decrease the hydroxyl

ion, and this would result in increased hydrolysis of the phosphate ion, as follows:

$$PO_4^{\equiv} + HOH = HPO_4^{=} + OH^-$$

and

$$HPO_4^{=} + HOH = H_2PO_4^- + OH^-.$$

(It can be shown that all of these ions are present in appreciable concentrations in the saturated solution.) However, the hydroxyl ion concentration cannot be unduly raised, or the solubility product of magnesium hydroxide will be exceeded and precipitation of this compound will occur. It is thus seen that the minimum solubility of these compounds will be obtained in a solution with a high concentration of magnesium ion and a hydroxyl ion concentration fixed just below the value causing precipitation of magnesium hydroxide by means of a fixed ratio of ammonium hydroxide and ammonium ion, these constituents being present in relatively high concentrations (thus making possible a high ammonium ion concentration without unduly decreasing the hydroxyl ion concentration).

In the present procedure the conditions are not adjusted for this minimum solubility, because it is desired to avoid the possibility of precipitating arsenite (as $Mg_3(AsO_3)_2$). Experimentally it has been shown that, under the conditions given below, less than 1 mg of phosphate or arsenate will give a precipitate in 5 to 10 min.; 250 mg of arsenite will not cause a precipitate within 30 min. but may do so on longer standing.

A consideration of the ionization constants for ammonium hydroxide and either phosphoric or arsenic acid shows that in an ammoniacal solution containing considerable ammonium salts the molal concentration of either the phosphate or the arsenate ion has to be extremely small; this fact is probably responsible to a considerable extent for the tendency of magnesium ammonium phosphate and arsenate solutions to supersaturate and to reach their equilibrium solubility only slowly.

The presence of oxalate increases the solubility of magnesium salts because of the formation of un-ionized or complex compounds; for this reason it is essential that sufficient magnesium be added to be equivalent not only to the phosphates and arsenates but also to the oxalate which may be present (see P. 86 and P. 88 in regard to the properties of magnesium oxalate).

Procedure 162: PRECIPITATION OF PHOSPHATE AND ARSENATE. Dissolve the silver precipitate (P. 161) by pouring repeatedly through it 20 ml of 3 n. HCl. Wash

the filter with 5 ml of 0.12 n. HCl. Discard the residue (Note 1).

Make the solution alkaline with NH_4OH and add 10 ml in excess (Note 2). Add to the solution 20 ml of $Mg(NO_3)_2$ reagent (Note 3) and let it stand for at least 10 min., but not longer than 30 min., frequently shaking it vigorously (Note 4). (White precipitate, presence of phosphate or arsenate. Note 5.) Wash the precipitate with 10 ml of 0.12 n. NH_4OH and treat it by P. 163. Treat the filtrate by P. 165.

Notes:

1. If phosphite has been present, the silver chloride residue will contain some metallic silver. This can be made more apparent by pouring dilute ammonia through the precipitate; a black residue remains.

2. If chromate has been present in the original material, it will have been reduced to chromic ion and may be partly precipitated (as chromic hydroxide) in P. 161; this will be dissolved by the HCl and then precipitated by the NH_4OH. Therefore, any precipitate produced at this place should be filtered from the solution before the magnesium salt is added.

3. The magnesium nitrate reagent contains $Mg(NO_3)_2$, NH_4OH, and NH_4NO_3. For its preparation, see the Appendix.

4. The mixture should not be allowed to stand for longer than 30 min., or a precipitate of arsenite may be produced when large amounts are present. Arsenite is also slowly oxidized on standing in alkaline solutions; for this reason small amounts of arsenate are nearly always found when large amounts of arsenite are present.

5. If the basic analysis has been previously carried out and no arsenic has been found present, any precipitate found here must be due to phosphate (or phosphite in the original material). Distinction between arsenate and arsenite is not made in the basic analysis.

P. 163. Detection and Estimation of Arsenate

Discussion. The precipitates of $MgNH_4PO_4 \cdot 6H_2O$ and $MgNH_4AsO_4 \cdot 6H_2O$ from P. 162 are dissolved in hydrochloric acid, and then an excess of a soluble iodide is added. Under the conditions thus obtained arsenate oxides iodide, and an equivalent amount of iodine is liberated (see the discussion of P. 89); phosphate is not reduced. Therefore, the formation of iodine indicates the presence of arsenate, and the amount present can be estimated by titrating the iodine with a standard thiosulfate solution. As phosphate has probably been detected in the basic analysis, it will usually not be necessary to proceed further. If, however, it is desired to confirm further the presence of arsenic, this can be done by saturating the solution with hydrogen sulfide, thus quantitatively precipitating the arsenic as

the trisulfide. It is an advantage that the arsenic has been reduced to the tripositive condition, as the precipitation with hydrogen sulfide would take place very slowly from a solution of arsenic acid (see the discussion of P. 11). After removing the arsenic, a more sensitive test for phosphate can be made in the filtrate by again precipitating it as the magnesium ammonium salt.

In case only a small precipitate is obtained, and phosphate has been tested for in the basic analysis, a confirmatory test for arsenate can be made by treating the precipitate directly with silver nitrate. Magnesium ammonium arsenate will be metathesized to silver arsenate, and the precipitate will turn a brick-red color.

Procedure 163: DETECTION AND ESTIMATION OF ARSENATE. Treat the precipitate (from P. 162) as directed in the first two paragraphs of P. 89, "Estimation of Magnesium" (Note 1). (Iodine color upon adding the KI, presence of arsenate.) Do not add an excess of $Na_2S_2O_3$ (Note 2). Saturate the solution with H_2S. (Yellow precipitate, presence of arsenate.) Filter out the precipitate and wash it with 5 to 10 ml of 0.6 n. HCl. Discard the precipitate. Treat the filtrate by P. 164.

Notes:

1. As stated in the discussion, if only a qualitative test for the presence of arsenate is desired, it can be made as follows:

Add 2 drops of $HC_2H_3O_2$ to 1 ml of $AgNO_3$ and pour this dropwise over the precipitate. (Brownish-red precipitate, presence of arsenate.)

The $HC_2H_3O_2$ is added to increase the solubility of the magnesium salt and thus facilitate the metathesis of the magnesium ammonium arsenate to the silver compound.

2. Thiosulfate in an acid solution is decomposed into sulfur and sulfurous acid. Sulfurous acid reacts with H_2S to give sulfur. The sulfur thus formed would tend to obscure a small precipitate of arsenious sulfide.

P. 164. Detection of Phosphate

Discussion. After titrating any iodine produced in P. 163 with thiosulfate, it would have been possible to make the solution alkaline with ammonium hydroxide and test for phosphate by addition of a magnesium salt. This was not done because (1) it was desired to obtain a distinctive confirmatory test for arsenic (by precipitation of the sulfide), (2) a more complete precipitation of phosphate can be provided for if arsenite is not present, and (3) any oxidation of the

arsenite in the ammoniacal solution would cause a test for phosphate to be obtained.

The solution from the arsenious sulfide precipitation is evaporated to remove the hydrogen sulfide and to reduce the volume so that a quicker, more sensitive test for phosphate can be made. As arsenite is absent, the solution is made more alkaline than for the precipitation in P. 162, and 0.5 mg of phosphate will give a detectable precipitate in 5 min.

As phosphate is usually estimated in the basic analysis (P. 54), a procedure for that purpose is not included here.

Procedure 164: PRECIPITATION OF PHOSPHATE. Boil the filtrate (from P. 163) until the H_2S is expelled and the volume is approximately 15 ml. Filter out and discard any precipitate (Note 1). Make the solution alkaline with 6 n. NH_4OH and add 5 ml of 15 n. NH_4OH in excess. Add 10 ml of $Mg(NO_3)_2$ reagent and let the solution stand with frequent shaking for at least 10 min. (White precipitate, presence of phosphate. Note 2.)

Notes:

1. A precipitate of sulfur (caused by the oxidation of H_2S by the oxygen of the air) may be produced on boiling the solution. After the H_2S has been removed, it is also likely that the oxygen of the air will cause some oxidation of the iodide in the hot acid solution. The iodine color will disappear when the solution is made alkaline with ammonia, the iodine being converted into iodide and iodate by hydroxyl ion.

2. If a small white precipitate is obtained and it is desired to confirm the presence of phosphate, proceed as follows:

Dissolve the precipitate by pouring through the filter 5 ml of 6 n. HNO_3 and 5 ml of water. Add to the solution 5 ml of $(NH_4)_2MoO_4$ reagent. Heat the mixture to 40° to 60°C. and let it stand for 10 min. (Yellow precipitate, presence of phosphate.) (See P. 54, Note 1, for a discussion of this confirmatory test.)

P. 165. Detection of Arsenite

Discussion. By adding an excess of hydrogen peroxide to the filtrate from the arsenate and phosphate precipitation (P. 162), any arsenite present is oxidized to arsenate and precipitates as magnesium ammonium arsenate; under these conditions, oxalate is not oxidized by peroxide. The oxidation could be effected by either peroxide or nitrite without introducing undesirable constituents into the solution; however, it was found that the former is more

rapid in its action. The general principles of the precipitation have been discussed in P. 162.

Procedure 165: PRECIPITATION OF ARSENITE. Add to the filtrate (from P. 162) 5 ml of 3 per cent H_2O_2, heat it almost to boiling, then cool it to room temperature, and let it stand for at least 10 min., shaking it frequently (Note 1). (White precipitate, presence of arsenite.)

Wash the precipitate with 10 ml of 0.12 n. NH_4OH. Treat the precipitate by the first two paragraphs of P. 89, "Estimation of Magnesium," in order to estimate the amount of arsenite present.

Treat the filtrate by P. 166.

Note:

1. The solution is heated to increase the rate at which the oxidation takes place; it is then cooled in order to decrease the solubility of the precipitate.

P. 166. Precipitation of Oxalate

Discussion. By acidifying the ammoniacal filtrate (from P. 165) and adding a soluble calcium salt, oxalate is precipitated as calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$). Calcium oxalate is less soluble in an ammoniacal solution, but the formation of a precipitate in such a solution is not as distinctive a test for oxalate and the precipitate is more likely to be difficult to filter. This precipitation has been used in P. 86 and P. 87 for the precipitation and estimation of calcium, and reference should be made to the discussion and notes of these procedures. As discussed there, magnesium forms unionized or complex compounds with oxalate, and the presence of the magnesium salt added in P. 162 not only increases the solubility of calcium oxalate in the solution but also causes the precipitation of the oxalate to take place very slowly; because of this, alcohol is added to the solution.

Procedure 166: PRECIPITATION OF OXALATE. Boil the filtrate from P. 165 for 5 min., make it just acid with $HC_2H_3O_2$, and add to it, dropwise, shaking continuously, 10 ml of $Ca(NO_3)_2$ solution. Cool the solution to room temperature, add 30 ml of 95 per cent C_2H_5OH, and let it stand for at least 15 min., shaking it frequently (Note 1). (White precipitate, presence of oxalate.)

Filter and wash the precipitate as directed in P. 86. Combine this precipitate with any oxalate precipitate obtained in P. 141 and treat it by the first paragraph of P. 87, "Estimation of Calcium," in order to estimate the amount of oxalate present.

Discard the filtrate.

Note:

1. If time is available, and the detection of very small amounts of oxalate (less than 1 to 2 mg) is desired, the solution should be allowed to stand for several hours or longer.

Unless the solution is hot and the calcium is added very slowly, a finely divided precipitate will be obtained that will pass through the filter.

The Detection and Estimation of Sulfate and of Fluoride

(See Tabular Outline XI)

P. 171. Precipitation of Sulfate

Discussion. Sulfate and fluoride are not separated as a group but are precipitated singly. By making the filtrate from the Phosphate Group precipitation acid with nitric acid and adding barium nitrate, precipitation of the sulfate as the barium salt is effected. Barium fluoride is relatively soluble and is also the salt of a weak acid. Nitrates are avoided when making a barium sulfate precipitation for a quantitative gravimetric determination (because barium nitrate is carried down with the precipitate to a much greater extent than is barium chloride), but are used here instead of chlorides because of the presence of silver ion in the solution.

Barium sulfate can be obtained as a more coarsely crystalline and readily filterable precipitate if it is caused to separate from a hot acid solution; this is not done here because of the danger of volatilizing hydrogen fluoride from such a solution.

If present in large quantities, the sulfates of barium, strontium, and lead would not be completely metathesized by the sodium carbonate treatment in P. 111. If sulfate is detected and these basic constituents have been found present in the basic analysis, it is advisable that a portion of the sample of the original material be fused with sodium carbonate and a more complete estimation of sulfate be made in the filtrate from the fusion (see Note 4 below).

Procedure 171: PRECIPITATION OF SULFATE. Add to the filtrate from the Phosphate Group precipitation (P. 161) 5 ml of HNO_3 (Note 1) and, dropwise, 1 ml of 0.5 n. $Ba(NO_3)_2$. Let the mixture stand for 5 min. (Note 2). (White precipitate, presence of sulfate. Note 3.) If considerable precipitate is obtained, add the $Ba(NO_3)_2$, dropwise, in 1-ml portions, until precipitation ceases (do not add more than 10 ml). Stir the solution and let the precipitate produced by one portion settle, so that the effect of the next can be observed.

Filter the precipitate on a dense paper filter or, if it is

desired to weigh the precipitate, on a previously weighed sintered-glass filter (Notes 4, 5). Treat the filtrate by P. 172 (Note 6).

If the precipitate is to be weighed, wash the precipitate with hot water until a 5-ml portion of the wash water gives no precipitate with a drop of sulfuric acid. Then treat the precipitate and crucible as directed in P. XVIII *D*.

Notes:

1. If chromium (as chromate) has been found present in the basic analysis, or if the solution is at all greenish in color, it should be made alkaline with ammonia, then 2 to 5 ml in excess should be added (to dissolve any cadmium or silver salts), and the precipitate of chromic hydroxide should be filtered out, washed, and discarded.

2. The $Ba(NO_3)_2$ is added dropwise in order to avoid the formation of a finely divided precipitate that would be difficult to filter. Only a small volume of the $Ba(NO_3)_2$ is added at first in order to avoid possible precipitation of sulfite or fluoride; if a large amount of sulfate is found present, sulfite and fluoride cannot be present in large quantities and therefore a larger excess of barium ion is permissible.

3. Peroxysulfate ($S_2O_8^-$), if present in the original material, would cause a precipitate of barium sulfate. This compound decomposes in boiling alkaline solutions,

$$2S_2O_8^- + 4OH^- = 4SO_4^- + 2H_2O + O_2.$$

Any remaining after the sodium carbonate treatment would be reduced by the nitrite added in P. 151.

4. If barium, strontium, or lead have been found present in the analysis for the basic constituents, a 0.2-g sample of the material should be fused with Na_2CO_3, as directed in the first two paragraphs of P. 8, using 100 ml instead of 30 ml of water. Acidify the filtrate with HCl, add a few drops in excess, and precipitate the sulfate with an excess of $Ba(NO_3)_2$ (or, if available, preferably $BaCl_2$).

5. Before being used, the crucible should have been treated as directed in P XVIII *D* and weighed.

If a sintered-glass crucible is not available, a Gooch-type asbestos filter can be substituted. In this case, it is recommended that the Gooch crucible be prepared and washed with alcohol as recommended in P. XVIII *D* but that, instead of using the vacuum desiccator, the crucible be placed in an oven at 110°C. for 20 min. and then allowed to cool in an ordinary desiccator before being weighed.

6. If thiosulfate was present in the original material, that which was not decomposed into sulfur and sulfurous acid in P. 124 or P. 131 would be converted into silver sulfide and sulfuric acid in P. 141. Therefore, thiosulfate would cause a precipitate of barium sulfate in this procedure. Furthermore, the sulfurous acid formed from the thiosulfate subsequent to the discontinuation of the current of air in P. 124 would largely remain in the solution. It would not cause a precipitate of barium sulfite in the strongly acid

solution of the above procedure but would tend to be oxidized in the less acid solution used for the precipitation of fluoride (P. 172) and would cause the formation of a barium sulfate precipitate, which might be mistaken for calcium fluoride. Because of this possibility, if thiosulfate has been present, the filtrate, before proceeding with the fluoride detection, should be treated as follows:

Add to the filtrate from the barium sulfate precipitate 2 ml of $NaNO_2$, heat the mixture to 60° to 80°C., and allow it to stand for 10 min. If considerable precipitate forms, add 1 to 2 ml more $Ba(NO_3)_2$. Filter out, wash, and discard the precipitate. Treat the filtrate by P. 172.

Nitrite is used as the oxidizing agent for the sulfurous acid because it reacts rapidly, is readily available, and introduces no undesirable constituents into the solution, as would chlorine, bromine, permanganate, or chromate, which are commonly used for the purpose; peroxide could be used but it often contains chloride.

P. 172. Precipitation of Fluoride

Discussion. Fluoride is detected by the precipitation of calcium fluoride from a very slightly acid solution. The precipitate would be less soluble in an alkaline solution but separates in a gelatinous form that is very difficult to filter, and the test might be obscured by the formation of barium or calcium carbonates through absorption of carbon dioxide from the air.

The gravimetric quantitative determination of fluoride is most frequently made by weighing the calcium fluoride precipitate. The precipitate is so difficult to filter that usually it is precipitated from an alkaline solution containing carbonate, so that the precipitate consists of a mixture of calcium carbonate and fluoride which is readily filtered. This mixed precipitate is ignited and treated with acetic acid, which extracts the calcium carbonate. The calcium fluoride (which is insoluble in the acetic acid) has been converted into a denser form by the ignition and now can be readily collected on a filter, washed, and weighed. This procedure is not applicable here, as it is desired primarily to detect the presence of fluoride and as the other basic ions introduced into the solution would make an unwieldy precipitate to handle. By making the precipitation from a very slightly acid solution and by prolonged boiling, the precipitate can be retained on a dense filter paper, especially if paper pulp is added to the solution.

Procedure 172: PRECIPITATION OF FLUORIDE. Add 5 to 15 ml of $Ca(NO_3)_2$ to the filtrate from the sulfate precipitation, and make it just alkaline with NH_4OH and then just

acid with $HC_2H_3O_2$. Heat the mixture to boiling and let it stand for 10 min. (White precipitate, presence of fluoride.)

If fluoride is present, heat the mixture almost to boiling until the precipitate appears to be coagulated (Note 1). Filter through a dense paper filter and wash the precipitate with hot water (Note 2). Discard the washings and filtrate. Transfer the precipitate to a previously weighed porcelain (or platinum) crucible, burn the paper as directed in the fourth paragraph of P. 7, and then heat the crucible and precipitate with a Bunsen or similar burner (Note 3) for 10 min. Let the crucible cool in a desiccator and weigh it.

Notes:

1. By prolonged heating of the solution, the precipitate is usually aggregated so that it can be retained on a dense paper filter. Paper pulp added to the solution is quite effective in aiding the coagulation and in retaining the precipitate. This can be purchased in tablet form or can be prepared by tearing a rapid-filtering quantitative paper into small bits and violently shaking it with water in a test tube until it is disintegrated.

2. If a small precipitate is obtained, or if it is desired only to confirm the presence of fluoride, proceed as follows:

Dry the filter and precipitate, roll the filter, and burn it while holding it suspended by means of a platinum wire. Collect the residue in a porcelain crucible and again heat it until all the carbon is burned off. Add to the crucible 3 to 4 times as much finely ground quartz powder (do not use precipitated silica) as there is residue, and intimately mix these substances. By means of a small strip of dry glazed paper, transfer this mixture to the bottom of a small test tube (6 to 8 mm in diameter and 80 to 100 mm in length). Add to the mixture, by means of a dropper or small pipet, about twice the volume of 36 n. H_2SO_4 as there is solid. Fit the test tube with a stopper carrying a piece of glass tubing which has been wet on the inside so that a ring of water adheres to (but does not close) the lower end. Adjust the tubing so that this end extends to within 10 to 15 mm of the material in the bottom. Gently heat the mixture in the bottom of the tube with a small flame (do not cause the H_2SO_4 to fume) for 2 to 3 min. (White precipitate or residue in the water, presence of fluoride.)

This test involves three reactions: First, the formation of HF from CaF_2 by the more highly ionized and less volatile H_2SO_4; second, the reaction of the HF with the quartz to form SiF_4,

$$4HF + SiO_2 = SiF_4 + 2H_2O;$$

and third, the hydrolysis of the SiF_4 upon coming in contact with the water on the tube,

$$3SiF_4 + 3H_2O = H_2SiO_{3(s)} + 2H_2SiF_6.$$

It is necessary to use quartz and not precipitated silica, as the SiF_4 tends to react with an excess of the amorphous variety as follows:

$$SiF_4 + SiO_2 = 2SiOF_2.$$

Experiments have shown that 0.3 mg of fluoride in the ignited residue will give an easily observable precipitate in the water.[1]

3. Although CaF_2 does not melt until the temperature reaches 1360°C., appreciable loss may be observed if the material is heated to a high temperature with moist paper. This loss is not due to reduction but apparently to loss of fluorine because of hydrolysis of the CaF_2 in the presence of water vapor. For this reason, the paper should be burned off at as low a temperature as possible.

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[1] For a more detailed discussion of this test and its applications, see Daniel, *Z. anorg. Chem.*, **38**, 299 (1904), or Treadwell-Hall, *Analytical Chemistry*, Vol I, Qualitative, 9th Ed., 1937, p. 437.

The Analysis of the Sodium Carbonate Solution for Nitrate, Nitrite, Borate, and Acetate

P. 181. Detection and Estimation of Nitrate and Nitrite

Discussion. The method used here for the detection and estimation of nitrate and nitrite depends upon the fact that these substances are reduced to ammonia by aluminum metal in an alkaline solution; zinc metal causes the same reduction but is slower in its action. If it is available, Devarda's alloy (Cu, 50 per cent; Al, 45 per cent; and Zn 5 per cent) may be used to advantage; it reacts as rapidly as does aluminum, seems to cause less bumping, and introduces less aluminum into the solution. The distillation of ammonia from alkaline solutions and its estimation in the distillate have been discussed in P. 96, "Detection and Estimation of Ammonia."

Other nitrogen compounds which will evolve ammonia under the conditions of this experiment are cyanide, ferrocyanide, ferricyanide, and thiocyanate; these, if present, are therefore precipitated and removed by previous addition of silver sulfate to the sodium carbonate solution.

Procedure 181: DETECTION AND ESTIMATION OF NITRATE AND NITRITE. Pipet 10 ml of the Na_2CO_3 solution (from P. 111) into a 300-ml Kjeldahl flask (Notes 1, 2), add 25 ml of water and 5 ml of NaOH, and boil the solution as long as any ammonia is evolved (Note 3). Set up a condenser as directed in P. 96, "Estimation of Ammonia," and a receiving flask containing 25 ml of water to which has been added 1 ml of K_2HgI_4 reagent (Note 4). Also have available a second flask containing 25 ml of water and 2 drops of methyl red indicator and into which has been pipeted 5 ml of 0.2 n. standard acid. Cool the solution in the distilling flask, add to it 1 g of coarse, clean aluminum turnings (Note 5), immediately insert the glass wool (if a spray trap is not attached to the condenser), and connect the distilling flask to the condenser (Note 6, P. 96). Heat the flask (if necessary) so that a steady evolution of gas is maintained. If the reaction in the flask becomes so vigorous as to cause froth-

TABULAR OUTLINE XVII

The Analysis of the Sodium Carbonate Solution for Nitrate, Nitrite, Borate, and Acetate

Analyze separate portions of the sodium carbonate solution for the indicated acidic constituents.

Nitrate and Nitrite	Nitrite	Borate	Acetate
Distill with NaOH and Al. *Collect NH_3 in an excess of standard HCl.* (P. 181) Distillate: NH_4Cl, excess HCl — Residual solution: *Discard.* *Add K_2HgI_4 reagent to portion.* ($Hg_2NH_2I_3$, red-brown precipitate, presence of nitrate and/or nitrite.) *Titrate excess acid with standard NaOH.* (P. 181)	*Add $NaClO_3$, acidify with HNO_3.* (NO_3^- from NO_2^-; Cl^- from ClO_3^-) *Add $AgNO_3$.* (AgCl, presence of nitrite.) *Neutralize with $NaHCO_3$, add K_2CrO_4, and titrate with $AgNO_3$.* ($AgCl$, Ag_2CrO_4) (P. 182)	*Add 12 n. HCl, and C_2H_5OH.* *Add turmeric reagent.* (Pink to orange-red color, presence of borate.) (P. 183)	*Add C_2H_5OH and concentrated H_2SO_4.* *Warm.* ($C_2H_5 \cdot C_2H_3O_2$, detected by its odor, presence of acetate.) (P. 184)

ing, remove the flame, taking care, however, that the receiving solution is not sucked back into the condenser (Note 7, P. 96). Continue the distillation for 5 min. or until an orange or reddish precipitate begins to form in the receiving solution. (Orange or reddish precipitate, presence of nitrate or nitrite.)

If nitrate or nitrite is found present, *immediately* replace the flask containing the K_2HgI_4 reagent with the one containing the standard acid and continue the distillation until about 15 ml of distillate have been collected. If the pink color of the receiving solution changes to yellow, pipet in 5 ml more of the standard acid, repeating this process as often as necessary.

Lower the receiving flask until the end of the adapter is just above the solution, remove the flame from the distilling flask, disconnect the adapter from the condenser, and wash the solution adhering to it into the receiving flask.

Cool the solution in the receiving flask and titrate it with standard 0.2 n. NaOH until a change from red to yellow is obtained (Note 8, P. 96). From the volumes of standard HCl and NaOH, the total number of equivalents of nitrate and nitrite present can be estimated.

Notes:

1. If no oxidizing agents were found present in P. 112, the absence of nitrite is shown but nitrate may be present. Therefore, if a positive reaction is obtained by applying the following test, which is used by A. A. Noyes[1] for the detection of oxidizing constituents, the presence of nitrate is indicated.

Pipet 2 ml of the sodium carbonate solution (from P. 111) into a test tube containing 5 ml of 12 n. HCl to which solid $MnCl_2 \cdot 4H_2O$ has been added until a small amount of solid is present. Slowly heat the mixture to 80° to 90°C. (Dark brown color, presence of oxidizing constituents.)

This test is given by all of the constituents included in P. 112 and also by chlorate and nitrate. Therefore, if the test in P. 112 was negative even after adding 5 ml of 12 n. HCl, a positive reaction here indicates the presence of nitrate.

The so-called "brown-ring test" for nitrates and nitrites can be made as follows:

Pipet 2 ml of the sodium carbonate solution (from P. 111) into a test tube and slowly add to it 1 ml of 6 n. H_2SO_4. Cool the solution

[1] Noyes, *Qualitative Analysis*, 9th Ed., Macmillan, 1922, p. 142.

with tap water and, while keeping it cool, add 5 ml of 36 n. H_2SO_4. Saturate 5 ml of water with $FeSO_4 \cdot 7H_2O$ and by means of a dropper carefully add this to the sulfuric acid solution. Incline the test tube and carefully flow the $FeSO_4$ onto the surface of the sulfuric acid so that the two layers do not mix. Allow the test tube to stand for 5 min. (Brown or pink color between the two layers, presence of nitrate or nitrite.)

In this test the ferrous iron reduces the nitrate and forms a colored complex ion, $FeNO^{++}$, with the nitric oxide. Nitrous acid will give the test even with very dilute acids. Cyanide, ferrocyanide, ferricyanide, thiocyanate, chromate, and iodate interfere, in that they give various colored products; they may be removed by adding 0.5 to 1 g of Ag_2SO_4 to the sodium carbonate solution, vigorously shaking the mixture, and filtering out the resulting residue. Under the conditions of the test above, 0.7 mg of nitrate or nitrite will give a perceptible brownish ring; the color is more distinctly visible against a white background.

2. If cyanide, ferrocyanide, ferricyanide, or thiocyanate have been found present (or may be present), proceed as follows:

Pipet the sodium carbonate solution into a small flask, add 0.5 to 1.5 g of nitrate-free Ag_2SO_4 (the amount depending upon the equivalents of the above constituents which may be present), warm the mixture, and vigorously shake it for 2 to 3 min. Filter out the residue, collecting the filtrate in the Kjeldahl flask.

By this procedure the constituents mentioned above are precipitated as the silver salts, and any excess silver sulfate is metathesized to the carbonate.

3. It is essential that all of the ammonia not expelled by boiling the sodium carbonate solution be removed before a test for nitrates or nitrites is made. Ammonia can be detected by inserting a stopper carrying a tube with a piece of litmus paper as directed in P. 96, "Detection of Ammonia."

4. If a qualitative detection of nitrate and nitrite has been made (see Note 1 above), the test with K_2HgI_4 reagent should be omitted and distillation should be made directly into the standard acid.

5. The aluminum turnings should be clean and free from nitride. For the detection of very small amounts of nitrate or nitrite, a blank should be run with the same amount of sodium hydroxide, carbonate, and aluminum as is used in the procedure. If available, 2 g of Devarda's alloy can be substituted for the aluminum (see the discussion above); the reaction proceeds somewhat more smoothly with this material.

P. 182. Detection and Estimation of Nitrite

Discussion. The detection and estimation of nitrous acid is made in this procedure by causing it to react with an excess of chlorate. Any chloride thus produced is detected and estimated by a titration with standard silver nitrate solution, chromate being used as indicator. (For a discussion of this titration, see P. 95.) Any chloride or other anions forming insoluble silver salts are removed

by first treating the sodium carbonate solution of the sample with an excess of silver carbonate.

This method for estimating nitrite is used here because of the ease and rapidity with which it can be carried out. It is subject to errors, ranging from 1 to 5 per cent, because the reaction between nitrite and chlorate is not instantaneous, and, in a solution of the acidity which is required for this reaction, either loss of nitric oxide or oxidation of this compound by the oxygen in the air may take place.[2]

A procedure for use if only a rapid qualitative test for nitrite is desired is provided in Note 1 below. It is based upon the following reaction which takes place between nitrous acid and thiourea in weakly acid solutions:[3]

$$HNO_2 + CS(NH_2)_2 = N_2 + SCN^- + H^+ + 2H_2O.$$

The thiocyanate formed is detected by the formation of the characteristic red color upon the addition of a ferric salt.

Procedure 182: DETECTION AND ESTIMATION OF NITRITE. Pipet 5 ml of the Na_2CO_3 solution (from P. 111) into a 200-ml flask (Notes 1, 2), add 10 ml of 1 f. $NaClO_3$ solution, and dilute the mixture to a volume of approximately 100 ml. Acidify the solution with HNO_3, swirling it continuously, add 1 ml in excess, and let it stand for 5 min. Add 0.2 ml of standard 0.1 n. $AgNO_3$. (White precipitate, presence of nitrite.)

If nitrite is present, make the solution neutral to litmus with 1 f. $NaHCO_3$ (this should require approximately 6 ml) and add 2 ml in excess. Add 3 drops of 3 n. K_2CrO_4 and titrate with the standard $AgNO_3$ to the appearance of the first perceptible brownish or reddish color in the solution or in the precipitate (see P. 95). From the volume of $AgNO_3$ used, calculate the amount of nitrite present (Note 3).

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[2] For a critical study and bibliography of various methods for determining nitrite, see Cool and Yoe, *J. Ind. Eng. Chem., Anal. Ed.*, **5**, 112 (1933).

[3] In strongly acid solution the reaction proceeds as follows:

$$2CS(NH_2)_2 + 2HNO_2 = C_2S_2N_4H_6 + 2NO + 2H_2O.$$

See Werner, *J. Chem. Soc.*, **101**, 2180 (1912), and Coade and Werner, *ibid.*, **103**, 1221 (1913), for a study of these reactions and their use as a means for the gasometric determination of nitrite.

Notes:

1. If only a qualitative detection of the presence of nitrite is desired, proceed as follows:

Pipet 2 ml of the Na_2CO_3 solution into a test tube. (If thiocyanate or iodide have been found present in P. 143, add 0.2 g of Ag_2CO_3, shake the mixture vigorously for 30 sec., and filter out the residue.) Add 2 ml of a 1 f. solution of thiourea and, slowly, 2 ml of $HC_2H_3O_2$. Let the solution stand for 3 min. Add 2 ml of H_2SO_4 and 1 ml of 1 f. $Fe_2(SO_4)_3$. (Red color, presence of nitrite.)

Thiocyanate and iodide give colored compounds with ferric iron; they are removed by the silver carbonate. Under the conditions of the above test, 0.05 mg of nitrite will cause a perceptible red color with the ferric sulfate. In case of doubt, the solution should be compared with one prepared in the same way from 1 ml of 3 n. Na_2CO_3 and 1 ml of water.

2. If in P. 114 any constituents of the Halogen or Cyanide Groups have been found present, the sodium carbonate solution should be shaken vigorously with 0.5 g of silver carbonate for 30 sec., the residue should be filtered out, and the solution should be collected in the 200-ml flask.

3. From the total number of equivalents of nitrate and nitrite found in P. 181 and the equivalents of nitrite found in this procedure, an estimation can be made as to whether or not a significant amount of nitrate is present. Tests for traces of nitrate in the presence of nitrites are of doubtful value, as nitrite is readily oxidized to nitrate and as nitrate is formed upon acidifying nitrite solutions.

P. 183. Detection of Borate

Discussion. The detection of borate depends upon the property which boric acid possesses of changing the yellow coloring material (curcumin) present in the extract from turmeric root into an isomeric orange-red compound (rosocyanine).[4] Ferric iron causes a similar red color with curcumin, but this would have been removed by the carbonate treatment. As strong oxidizing agents prevent the color change, they must be reduced before applying the test. Iodides would be likely to liberate iodine (oxidation by oxygen in strongly acid solution), which would mask the color. The test for borate is frequently made by means of "turmeric paper," which is immersed in an acid solution of the material being tested and then dried; if borate is present, a reddish-brown stain is produced which turns a gray or dark blue, depending upon the amount of borate present. This method is not used, as it gives very little quantitative information.

The brownish-red color produced by the turmeric and borate in a

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[4] Clark and Jackson, *Am. Chem. J.*, **39**, 696 (1908).

solution containing concentrated hydrochloric acid and alcohol has been used by Noyes[5] for the detection of borate. Schafer,[6] in a study of the colorimetric estimation of borate by this method, has found that the color is most intense in strong hydrochloric acid but that for a colorimetric estimation a more dilute solution is preferable. The method as given below will detect 0.2 mg of borate, and a rough estimation of larger amounts can be made.

Procedure 183: DETECTION OF BORATE. Pipet 5 ml of the sodium carbonate solution (from P. 111) into a test tube (Note 1). Add (slowly until the carbonate is neutralized) 10 ml of 12 n. HCl and then 10 ml of 95 per cent C_2H_5OH (Note 2). Add just 1 ml of turmeric reagent (Note 3) and allow the tube to stand for 5 min. (Pink to orange-red color, presence of borate. Note 4.)

If borate is found present, add to 3 test tubes successively 0.5, 5, and 50 mg of borate in 2.5 ml of water (Note 5) and 2.5 ml of 3 n. Na_2CO_3. Treat each of the solutions as directed above, beginning with the addition of the acid, and, after 5 min., compare the color observed in the procedure above with that in the standard tubes.

Notes:

1. If oxidizing agents or iodide have been found present, proceed as follows: Pipet the 5 ml of the sodium carbonate solution into a small flask, acidify it with H_2SO_4, and add 2 ml in excess. Then add 1 ml of 12 n. HCl, and evaporate the solution until the sulfuric acid begins to fume. Cool, dilute (care) with 5 ml of water, filter out any precipitate, and treat as directed above.

The hydrochloric acid will reduce oxidizing agents in the hot sulfuric acid and, with any hydriodic acid (present from iodides), will be volatilized from the fuming sulfuric acid. Large amounts of iodide might cause reduction of the sulfuric acid, but the resulting iodine will be volatilized.

2. On adding the alcohol, a precipitate of sodium chloride may result; in this case cool the mixture, allow the salt to settle, and then decant the solution into another test tube.

3. The turmeric reagent is a half-saturated alcoholic solution of turmeric extract. As the volume of the solution added should be measured very closely, it is convenient not to have too concentrated a solution. Acetic acid solutions of the turmeric extract may be used, but they appear not to be as stable as the diluted alcoholic solution.

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[5] Noyes, *Qualitative Analysis*, 9th Ed., Macmillan, 1922, p. 160.
[6] Schafer, *Z. anal. Chem.*, **110**, 11 (1937).

4. As the turmeric reagent has a fairly intense yellow color, the decision as to the presence of small amounts of borate should not be made without a comparison solution. This should be made as follows:

Pipet 2.5 ml of 3 n. Na_2CO_3 into a test tube, and add 2.5 ml of water, 10 ml of 12 n. HCl, 10 ml of 95 per cent C_2H_5OH, and 1 ml of turmeric reagent.

The tube being tested should be compared with the blank thus prepared. Even with small amounts of borate the color usually begins to appear within 2 min. and is substantially constant within 5 min. after the addition of the turmeric reagent. The color is influenced by the concentration of the HCl and of the alcohol; therefore it is advisable to conform to the specified conditions. If the solutions are allowed to stand, the tubes should be corked, as otherwise the color fades, presumably because of oxidation.

5. The volume of solution should be kept constant; if a stock solution of borate is not available, 5 ml of the test solution (10 mg/ml) should be evaporated to 2.5 ml.

Because of the slow development of the color, this estimation is not conveniently made by adding borate to a solution containing alcohol, acid, and turmeric in the proper amounts until the color obtained matches that in the sample tube.

P. 184. Detection of Acetate

Discussion. Although acetic acid is an organic acid, it is so commonly used in inorganic chemistry that a procedure for its detection is provided. Acetate is so soluble and so stable with respect to oxidation that no very characteristic reactions of these types are available for the detection of this anion; in other than very small amounts it is readily identified by its odor above solutions made strongly acid. The test used here is based upon the reaction which takes place in a dehydrating medium, such as a concentrated sulfuric acid solution, between acetic acid and ethyl alcohol to produce an ester which has a distinctive and easily recognizable odor; the use of other alcohols has been suggested. The reaction, when ethyl alcohol is used, can be represented as follows:

$$HC_2H_3O_2 + C_2H_5OH = \underset{\text{(ethyl acetate)}}{C_2H_5 \cdot C_2H_3O_2} + H_2O.$$

The estimation of acetate is usually carried out by distilling the material with either sulfuric or phosphoric acid and collecting the acetic acid in an excess of standard base; the excess of base is then titrated with standard acid, a suitable indicator being used. Reference books on organic analysis should be consulted for the details of the procedure.

Procedure 184: DETECTION OF ACETATE. Pipet 2 ml of the sodium carbonate solution into a 25-ml round-bottom flask, evaporate it almost to dryness, and cool the residual mixture (Note 1). Add 0.2 ml of 95 per cent C_2H_5OH and 1 ml of 36 n. H_2SO_4. Immerse the flask in a beaker of boiling water and note the odor of the escaping vapors. (Odor of ethyl acetate, presence of acetate. Note 2.)

Notes:

1. As little as 5 mg of acetate can be detected by adding 2 ml of 6 n. H_2SO_4 to the sodium carbonate solution, heating the solution to boiling, and noting the characteristic odor of acetic acid above the hot solution.

2. Ethyl acetate is readily available, and its characteristic odor should be identified before making this test. Comparison solutions of sulfuric acid and ethyl alcohol, and of ethyl acetate, should be used so as not to be misled by the odor of the alcohol. As little as 1 mg of acetate can be detected by this test, 10 mg give a very pronounced odor, and with as much as 50 mg a strong odor of acetic acid is also obtained.

TABULAR OUTLINE XVIII

The Analysis of the Residue from the Sodium Carbonate Treatment

Residue from the Sodium Carbonate Treatment:
(Carbonates, oxides, and unchanged material)
Transfer to a distilling flask, add Zn and 18 n. H_2SO_4.
(Gases evolved: CO_2, H_2S, HCN)
Distill into a solution containing NaOH, NH_4OH, and $AgNO_3$. (P. 191)

Distillate:
$CO_3^=$, Ag_2S, $Ag(CN)_2^-$, CN^-
Treat by P. 122 and P. 123.

Residual solution:
Distill until the H_2SO_4 fumes.
(Gases evolved: HCl, HBr, I_2, HF; also HCN)
Collect in NaOH and Na_2SO_3. (P. 192)

Distillate:
Cl^-, Br^-, I^-, F^-, CN^- in NaOH and Na_2SO_3
Add HNO_3 and $AgNO_3$. (P. 192)

Residual solution:
H_3BO_3 in H_2SO_4
Add CH_3OH, distill into HCl solution. (P. 193)

Precipitate:
AgCl, AgBr, AgI, AgCN
Analyze by P. 142–148.

Filtrate:
HF, $AgNO_3$
Add NH_4OH and $Ca(NO_3)_2$.
Precipitate:
CaF_2

Distillate:
$(CH_3O)_3B$
Add extract of turmeric in CH_3OH.
(Yellow to orange color, presence of borate.)

Residual solution:
Discard.

The Analysis of the Residue from the Sodium Carbonate Treatment

General discussion. The sodium carbonate treatment of the sample (P. 111) may leave certain insoluble acidic constituents in the residue. This may be due, in the case of many natural substances or high-temperature products, to a slow rate of metathesis, or it may be that the solubility relations are such that no appreciable metathesis can take place. The latter is the case with most sulfides, with the silver halides, with certain complex iron cyanides, and with certain phosphates and arsenates (the last two will have been detected in the analysis for the basic constituents and will not be again tested for here).

The constituents which are tested for in this residue are sulfide, the halides, cyanide (which may be derived from a complex cyanide), fluoride, and borate. These constituents, together with sulfate and carbonate, include all of those which are likely to be found in natural substances or high-temperature products; therefore, if the material for analysis is of such origin, the acidic analysis can be much simplified by treating a weighed portion of it directly by the procedures given below for the analysis of the sodium carbonate residue, by P. 201 for the detection of carbonate, and by Note 4, P. 171, for the detection of sulfate.

P. 191. Detection of Sulfide and Cyanide in the Sodium Carbonate Residue

Discussion. In this procedure the residue from the sodium carbonate treatment is distilled with sulfuric acid in the presence of metallic zinc, and the hydrogen sulfide and hydrogen cyanide evolved are collected in an alkaline receiving solution. The procedure is based upon these facts: (1) The sulfides of the elements of the Ammonium Sulfide Group are dissolved and the hydrogen sulfide is expelled by being heated with a solution of a strong acid; (2) most simple and complex cyanides are decomposed by being boiled with 6 to 8 n. sulfuric acid; and (3) the elements of the Hydrogen Sulfide Group (whose sulfides and cyanides may be more insoluble in acids) are reduced to the metal by metallic zinc in acid solutions, and, therefore, these compounds are dissolved by such treatment.

Silver cyanide and thiocyanate and many complex cyanides are

not completely decomposed by the sodium carbonate treatment. Silver cyanide and thiocyanate would be decomposed by the treatment with acid and zinc (metallic silver being precipitated); the thiocyanate would be decomposed into various compounds, mainly cyanide and sulfide (see the discussion of P. 142), by the action of the acid and zinc. The complex iron cyanides would be at least partly decomposed, so that hydrogen cyanide would also be evolved from the solution.

The hydrogen sulfide and cyanide are collected and the solution is analyzed as was done in the procedures for the separation and estimation of sulfide and cyanide in the sodium carbonate solution (P. 121 to P. 123).

If the material is known to be a natural substance or a high-temperature product, it is likely to be resistant to attack by the sodium carbonate treatment of P. 111, and therefore it would be more expeditious to treat it directly by the procedure below (see Note 3).

Procedure 191: DETECTION AND ESTIMATION OF SULFIDE AND CYANIDE IN THE SODIUM CARBONATE RESIDUE. If a sample of the material has been treated by P. 111, transfer the well-washed residue from that procedure to a 200-ml distilling flask with the aid of 5 ml of water (Note 3). Add about 1 g of zinc metal (granular or shot) and close the flask with a stopper carrying a safety tube extending to the bottom of the flask (as directed in P. 42). Insert the side arm into a 200-ml flask containing 50 ml of water, 10 ml of 6 n. NaOH, 5 ml of 6 n. NH_4OH (Note 8, P. 121), and exactly 2.00 ml of standard 0.1 n. $AgNO_3$. Add 10 ml of 18 n. H_2SO_4 by means of a dropper through the safety tube and then gently boil the mixture for 4 to 5 min. (Brown or black precipitate in the receiving vessel, presence of sulfide.)

If sulfide is present, add 5 ml of water through the safety tube and boil the mixture until about 5 ml have distilled (Note 1). Treat the distillate by P. 122 to P. 123. Treat the residual solution by P. 192.

If sulfide is absent, pipet 5 ml of the receiving solution into a test tube containing 2.00 ml of standard 0.1 n. $AgNO_3$. Add 5 ml of HNO_3 (Note 7, P. 121). (White precipitate, presence of cyanide. Note 2.) If cyanide is absent, treat the residual solution by P. 192 and discard the distillates.

If cyanide is present, make the mixture alkaline with ammonia and return it to the receiving flask. Add 5 ml of water to the distilling flask and distill the mixture until 5 ml have been collected in the distillate. Treat the distillate by P. 123. Treat the residual solution by P. 192.

Notes:

1. The mixture should not be allowed to concentrate, or any halogen acids present may begin to pass into the receiving vessel.
2. If thiocyanate were present, it would decompose, as stated above, and give a test for both sulfide and cyanide. Thiocyanate usually would appear here only if originally present as silver thiocyanate; other thiocyanates would be at least partially decomposed by the treatment with sodium carbonate. Therefore, if both sulfide and cyanide are found present in considerable amounts, a decision as to what constituents may be present will be aided by consideration of the results of the analysis of the basic constituents.
3. If the original material is a natural substance or a high-temperature product (see the discussion above), proceed as follows:

Weigh out 0.5 g of the finely ground sample (P. 1) and transfer it to a 200-ml distilling flask. Add 5 ml of water and proceed as directed in the procedure above, beginning with the second sentence.

P. 192. Detection of the Halides in the Sodium Carbonate Residue

Discussion. In this procedure the sulfuric acid solution from the procedure for the detection of sulfide and cyanide is evaporated until the sulfuric acid is caused to fume. By so doing, the volatile acids are distilled and collected in a receiving solution. The effect of fuming insoluble compounds of volatile acids with a high-boiling-point acid (such as sulfuric, phosphoric, or perchloric) has been discussed in P. 7. It should be pointed out that such compounds as the insoluble silver halides (in which the anion is combined with a readily reducible cation) would have been dissolved in P. 191 above. However, these halogen acids are so highly ionized that they would not be distilled from the solution until the high temperature and dehydrating action of the hot concentrated sulfuric acid became effective. Hydrofluoric acid is not volatilized in P. 191, even though it is not a highly ionized acid, the ionization constant for the equilibrium

$$HF = H^+ + F^-$$

having the value 7.4×10^{-4}. In addition, there is a second equilibrium,

$$HF + F^- = HF_2^-,$$

for which the constant has the value 4.7. There is no evidence for the existence in solutions of the molecule H_2F_2.[1] However, the partial pressure of hydrogen fluoride gas above dilute solutions is so very small that no appreciable volatilization occurs until the sulfuric acid becomes hot and concentrated.

Hydrogen fluoride is at least partially polymerized in the gaseous state; there is still some uncertainty as to the exact molecular species and equilibria existing at various temperatures and pressures. Fluoride would appear in the sodium carbonate residue usually as calcium fluoride, and this would be only slowly attacked by the dilute acid used in P. 191.

Hydriodic acid is oxidized by the action of hot sulfuric acid; however, the iodine formed is distilled over and changed to iodide and iodate by the alkaline solution used in the receiving vessel. Upon acidifying this solution, any iodide present is reduced by means of sulfite.

Certain complex cyanides may not be completely decomposed by the treatment with dilute acid in P. 191, and therefore cyanide may appear in this distillate, as all complex cyanides are decomposed by the fuming acid.

The iodide, bromide, chloride, and any cyanide collected in the distillate are detected by precipitation with silver nitrate in an acid solution. This precipitate of the silver salts is then treated by the procedures for the analysis of the Halide Group for the detection of the individual constituents; cyanide is converted to thiocyanate in the ammonium sulfide metathesis of P. 142. Fluoride is detected in the filtrate by precipitation as calcium fluoride.

Procedure 192: DETECTION OF THE HALIDES IN THE SODIUM CARBONATE RESIDUE. Insert the side arm of the distilling flask containing the sulfuric acid mixture from P. 191 into a 200-ml flask containing 50 ml of water and 2 ml of NaOH. Distill the mixture until the sulfuric acid has fumed (Notes 1, 2) for 2 to 3 min. Treat the distillate as directed below. Treat the residual H_2SO_4 solution by P. 193.

Remove the receiving solution, make it just acid with

[1] Pick, Nernst's *Festschrifte*, 1912, p. 360; Davies and Hudleston, *J. Chem. Soc.*, **125**, 260 (1924); Wynne-Jones and Hudleston, *ibid.*, **125**, 1031 (1924); Anthony and Hudleston, *ibid.*, **127**, 1122 (1925); Jehn and Hudleston, *ibid.* **125**, 1451 (1924); Simons, *Chem. Rev.*, **8**, 213 (1931); Yost and Hatcher, *J. Chem. Ed.*, **10**, 330 (1933).

HNO_3, and, if any iodine or bromine color is formed, add saturated $NaHSO_3$ solution dropwise until the solution is decolorized; avoid an excess of the $NaHSO_3$ (Note 3). Filter out and reject any precipitate (Note 4). Add 2 ml of HNO_3 and 1 ml of $AgNO_3$. (White or yellowish precipitate, presence of the halides. Note 5.) Add $AgNO_3$, 1 ml at a time, until no more precipitate is produced. Filter out the precipitate, wash it with hot water, and treat it by P. 142 to P. 148.

Treat the filtrate by P. 172 to detect and estimate fluoride.

Notes:

1. If the mixture tends to "bump" badly, connect the distilling flask to the receiving flask by means of a two-hole stopper and draw a steady current of air through the two vessels with an aspirator during the distillation.

2. The H_2SO_4 will not fume until approximately 5 ml of the original solution (including the 10 ml of 18 n. H_2SO_4) remain in the flask; at this point, even though the liquid in the flask is heated until it boils, the vapors condense and run down the sides of the flask in viscous streams, and very few bubbles pass into the receiving vessel. Complete expulsion of fluoride is aided by actually boiling the sulfuric acid and by repeatedly removing the flame just long enough to allow air to be sucked into the flask through the safety tube, and then again heating the liquid to boiling.

3. The distillate should be cold before being acidified, in order to minimize the loss of HCN from the solution.

4. SiF_4, resulting from HF and a silicate, may distill over from the concentrated acid. This would be hydrolyzed to silicic acid in the receiving vessel (see Note 2, P. 173), and should be removed before testing for the halides.

5. A dark precipitate of Ag_2S will be formed if sulfide has not been completely expelled in P. 191; certain reducing substances may also reduce the concentrated sulfuric acid to sulfide. Therefore, if a dark precipitate is produced, it is necessary to filter it out and treat it by P. 142 to P. 148 to detect the halides. However, a qualitative test for all of these constituents except iodide can be made by pouring 5 ml of NH_4OH through the precipitate and making this filtrate acid with HNO_3.

P. 193. Detection of Borate in the Sodium Carbonate Residue

Discussion. Boric acid, although an extremely weak acid, is not sufficiently volatile to be quantitatively removed either with the sulfides and cyanides or with the halides. Some boric acid may be distilled with the steam that passes over in P. 191 and P. 192, but only a small fraction of the total amount is lost. Upon the addition of methyl alcohol to the sulfuric acid solution containing boric acid,

the volatile trimethyl borate $(CH_3O)_3B$, is formed and this compound can be distilled with the excess alcohol. The methyl borate and alcohol are condensed in cold water, in which the methyl borate largely hydrolyzes to boric acid and methyl alcohol. The boric acid in this solution is then detected by the color which it gives with turmeric extract, as was done in P. 183.

Procedure 193: DETECTION OF BORATE IN THE SODIUM CARBONATE RESIDUE. Cool the residual mixture (from P. 192) in the distilling flask to room temperature or below, and add, in small portions, 12 ml of CH_3OH, gently swirling the solution after each addition. Place an ebullition tube (Note 3, P. 42) in the distilling flask and insert the side arm of the tube in a test tube immersed in a beaker of cold water. Add 5 ml of water to the test tube and slowly heat the distilling flask until 10 ml of the alcohol have distilled (Note 1). Remove the distillate, cool it, add 10 ml of 12 n. HCl and 1 ml of turmeric reagent (Note 3, P. 183), and allow it to stand for 5 min. (Pink to orange-red color, presence of borate. Note 4, P. 183.)

If borate is found present, proceed as directed in the last paragraph of P. 183 to estimate the amount.

Note:

1. As it is desirable that a definite volume of the alcohol be collected, the receiving test tube should be measured or marked with a china-marking pencil, so that just 10 ml will be collected.

The Analysis of the Original Material for Carbonate

P. 201. Detection and Estimation of Carbonate

Discussion. The detection of carbonate is based upon the fact that, upon being heated with a strong acid, all carbonates are decomposed with evolution of carbon dioxide, which, upon being absorbed in a barium hydroxide solution, causes a precipitate of barium carbonate. This test for carbonate obviously cannot be made on the solution prepared by using sodium carbonate (P. 111), and therefore a portion of the original sample is utilized.

An approximate estimation of the amount of carbonate present is made by filtering out the precipitate of barium carbonate, dissolving it in an excess of standard acid, and titrating the excess with a solution of a standard base. Reference books on quantitative analysis should be consulted in regard to methods for the more accurate estimation of the carbon dioxide in various materials.

Procedure 201: DETECTION AND ESTIMATION OF CARBONATE. Weigh into a small porcelain "boat" 0.5 to 2 g, depending upon the amount of carbonate thought to be present (Notes 1, 2), of the sample of the original material.

Set up a distilling flask similar to that used for the distillation of arsenic (P. 42) and fit the upper end of the safety tube with a short piece of rubber tubing so that a small funnel or a soda-lime tube can be attached (Note 3). Provide as the receiving vessel a 200-ml round-bottom flask fitted with a two-hole rubber stopper. Insert the side arm of the distilling flask through one hole of the stopper, add to the distilling flask 25 ml of water, and boil it vigorously for 3 to 5 min. In a flask similarly boil 25 ml of 3 n. HCl (Note 4). Remove the receiving vessel, add to it 50 ml of clear saturated $Ba(OH)_2$ solution, and temporarily plug the holes of the stopper. Open the distilling flask just long enough to slide in the porcelain boat containing the sample, immediately close the flask, clamp it into place, apply a small flame, and insert the side arm through one of the holes of the rubber stopper of the receiving vessel so that it reaches almost to the bottom of the $Ba(OH)_2$ solution.

Attach a small funnel to the safety tube and pour the hot 3 n. HCl into the distilling flask at such a rate that a steady stream of bubbles passes into the $Ba(OH)_2$ solution (Notes 5, 6). When all the acid has been added, close the stopcock of the separating funnel and distill over 5 to 10 ml of the solution. (White precipitate in the $Ba(OH)_2$ solution, presence of carbonate. Note 7.) While continuing to heat the solution, withdraw and close the receiving solution. Discard the residual solution.

If an estimation of the carbonate present is desired, prepare a rapid-filtering asbestos (or sintered-glass) filter, pass the $Ba(OH)_2$ solution through it (keeping the flask closed when not pouring), and immediately wash the precipitate with boiling water until the wash solution is neutral to litmus. Discard the filtrate and washings (Note 2). Transfer the precipitate (Note 8) to a 400-ml flask, add 25 ml of water, and add standard 0.2 n. HCl from a buret until the precipitate is dissolved. Heat the mixture almost to boiling, cool it to room temperature (see the discussion and last paragraph of P. XVII), add 2 drops of methyl orange indicator solution (see the last paragraph of Note 7, P. XVII), and titrate with standard 0.2 n. NaOH until the color of the solution matches that given by 2 drops of the indicator in the same volume of water. From the volumes of standard acid and base used, calculate the amount of carbonate present.

Notes:

1. The presence of carbonate will usually be detected in the preliminary tests of P. 3 (Note 7), and the amount of effervescence noted there gives a rough estimate of the amount present. A quick qualitative test can be made by transferring 0.2 to 0.5 g of the sample to a test tube, adding 2 ml of HCl, and inserting in the tube a drop of $Ba(OH)_2$ solution held in a loop of platinum wire. Bubble formation in the acid and an immediate white precipitate on the surface of the drop indicates the presence of carbonate. If no reaction takes place, the mixture should be gently warmed.

The so-called "boat" is a container 60 to 100 mm in length, 7 to 20 mm in width, and 8 to 12 mm in depth. Boats of this type are made of various materials, such as alundum, nickel, and platinum; they are designed to facilitate inserting materials into tubes for various combustion methods of analysis.

2. A detection and estimation of sulfide can be combined with this procedure for carbonate by adding metallic zinc to the sample and then testing the filtrate from the barium carbonate precipitate for sulfide. The results

obtained from treating the sodium carbonate solution and residue separately (as in P. 121 and P. 191) are more reliable, as most sulfides would remain in the carbonate residue, and most oxidizing agents, which would oxidize sulfide in an acid solution, are carried into the sodium carbonate solution (P. 111). Also, substances such as sulfite and thiosulfate, which in acid solutions containing metallic zinc would cause an evolution of hydrogen sulfide, are likely to pass into the carbonate solution. If for some special reason it is desired to combine the sulfide test with the one above, proceed as follows:

> Add 1 g of metallic zinc (granular or shot) to the sample in the boat, and proceed with the distillation as directed above. Collect the filtrate and washings from the barium carbonate precipitate in a 200-ml flask, and add 1 g of solid NH_4NO_3 and just 2.00 ml of standard 0.1 n. $AgNO_3$. (Brown to black precipitate, presence of sulfide.) Treat the mixture by P. 122.

Upon the addition of the ammonium nitrate, an amount of ammonium hydroxide equivalent to the excess barium hydroxide present is formed. The precipitation of the black silver sulfide in an ammoniacal solution is characteristic of sulfide. Reducing agents may give a dark precipitate of metallic silver in ammoniacal solutions, but the two precipitates are usually readily distinguished—in case of doubt, the confirmatory test of Note 3, P. 122, may be utilized.

3. A more accurate determination can be made by fitting the safety tube with a small calcium chloride tube filled with soda lime, connecting the second hole of the stopper in the receiving flask with a water aspirator by means of a short length of glass tubing, and drawing a slow stream of CO_2-free air through the apparatus during the subsequent operations. In this way, possible loss of CO_2 through the safety tube is minimized.

For more accurate work it would be advisable also to provide a second $Ba(OH)_2$ receiving solution, as the absorption of CO_2 by barium hydroxide solutions is not as efficient as the more concentrated potassium hydroxide solutions commonly used in quantitative methods.

4. The solutions used in the distillation are first boiled in order to free them of CO_2; also, in order to minimize absorption of CO_2 from the air by the barium hydroxide, the process should be carried out expeditiously and the barium hydroxide solution should be exposed to the air as little as possible.

Care must be taken in the subsequent distillation to keep the flame applied uniformly to the distilling flask and to remove the barium hydroxide solution before removing the flame in order to prevent solution from being sucked into the distilling flask.

The hydrochloric acid used should not be more concentrated than 3 n., so that it will not be distilled into the barium hydroxide solution in excessive quantities.

5. The flow of acid into the distilling flask should be so regulated that not more than 2 or 3 bubbles a second pass into the barium hydroxide; otherwise complete absorption might not be obtained.

6. If sulfite has been found present (P. 124), SO_2 would pass over into the distillate and might precipitate as barium sulfite, or be partially oxidized and precipitate as sulfate. This interference can be avoided by adding 10 ml of 3 per cent H_2O_2 to the distilling flask before the acid is introduced;

sulfite is oxidized to sulfate by peroxide.[1] If the peroxide is used, the test for sulfide suggested in Note 2 cannot be made.

7. If only a qualitative detection of carbonate is desired, the solution should be made just acid with $HC_2H_3O_2$; barium carbonate will dissolve with bubble formation.

8. The filter with the precipitate should be placed directly in the beaker and treated with the acid.

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[1] Curtman and Hart, *Chem. News*, **119**, 25, 39 (1919), have found that 1 mg of carbonate can be detected in the presence of 500 mg of sulfite by this means

APPENDIX

A Suggested Course of Instruction

The material outlined below indicates in general the arrangement and content of the year's course in analytical chemistry as it is given in the sophomore year at the California Institute of Technology. The time assigned to the course is 6 hours of laboratory, 2 hours of class, and 2 hours of preparation per week for 36 weeks. The topics indicated in the outline are the laboratory assignments; the classroom treatment follows closely the laboratory assignment and is to a large extent a development, by lectures, problems, and quizzes, of the principles involved in the laboratory work. All of the assignments included in the outline are not required of any one student, as the selection varies from year to year and as a broader range of methods is covered by allowing the student some option in his assignments. The topics indicated by an asterisk are those which may be omitted from shorter courses or may be made optional.

It is seen that the material given in the first part of the course follows the lines of the conventional instruction in quantitative analysis and provides the necessary training in precise quantitative technique. This work not only serves to develop the required skill in quantitative manipulation, which adds much to the effectiveness of the student in the second part of the course, but also permits a logical sequence to be followed in developing the principles in the classwork. However, although only the determinations of single constituents are being carried out in the laboratory, special emphasis is placed in the class discussions upon following the qualitative behavior of these constituents, upon their separation from other constituents, and upon the effect of other constituents upon the quantitative methods being used; in this way a constant review of the main outlines of the qualitative system is obtained. Where the scholastic year is divided into two semesters, this quantitative work can be condensed to provide material for the first semester and many of the single determinations listed below can be given as part of the systematic analysis of various materials in the second part of the course. It has been found desirable to require the student to consult other references and the original literature early in the course, and it is recommended that the following books be readily available in the library or preferably in the laboratory: Treadwell-Hall, *Analytical*

Chemistry, Vol. I, Qualitative, Wiley, 1937, and Vol. II, Quantitative, Wiley, 1935; Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929; Kolthoff and Furman, *Volumetric Analysis*, Vol. I, Theoretical Principles, and Vol. II, Practical Methods, Wiley, 1929; Kolthoff and Sandell, *Quantitative Inorganic Analysis*, Macmillan, 1936; as many of the modern elementary textbooks of quantitative analysis as are available; and a Chemical Handbook.

In beginning the second part of the course, the systematic qualitative and semi-quantitative analysis, it is recommended that in the laboratory this work be taken up by groups. If the time is limited, the more difficult and time-consuming separations should be omitted and only the simpler (although less exact) optional procedures which have been provided in many such cases should be covered. The student should first analyze a known solution containing the elements of the particular group being studied in amounts ranging from 1 to 200 mg; this solution can be prepared from the test solutions on the reagent shelf. In this preliminary work the student should be encouraged to carry out experiments with small amounts of the constituents to establish the sensitivity of the separations and confirmatory tests, and emphasis should be placed upon developing facility in judging the amount of a constituent from the size of its characteristic precipitates. Next, a solid material can be analyzed qualitatively for the various constituents of the group being studied and quantitatively for one or two specified constituents. Except for very advanced students, the complete analysis, qualitative and semi-quantitative, of complex substances should not be undertaken; the demands in technique and experience of such "marathon analyses" are beyond the ability and patience of most students. Also, a wider range of methods can usually be covered more effectively by a larger number of simpler analyses.

The nature of the classwork will be determined largely by the students' previous training in inorganic chemistry and qualitative analysis. The chemistry of the separations and estimations is given in the tabular outlines, and these should be so mastered that the student is able to construct similar tables for any combination of constituents presented to him by the instructor. If possible, the systematic analysis for the acidic constituents should be covered, as the principles involved there are more diversified than those found in the basic system. With more advanced classes the course can be conducted more in the nature of a critical study of the major separations, such as the various sulfide and hydroxide precipitations,

with the students being encouraged to look up topics in the original literature.

Part I. Quantitative Training.

1. Determination of Balance Characteristics, P. I, P. II, and P. III.
2. *Calibration of Weights, P. IV.
3. Preparation of a Silver Nitrate Solution, P. V.
   (a) Calibration of Flask, P. V, Note 8.
4. Preparation and Standardization of a Thiocyanate Solution, P. VI.
   (a) Calibration of Pipet, P. VI, Note 3, and Buret, P. VI, Note 6.
5. *Determination of Mercury, P. 45.
   (a) Titration of Mercuric Nitrate Solutions or Mercuric Oxide Mixtures.
6. Volumetric Determination of Chloride.
   (a) Analysis of Soluble Chloride Mixtures (Chromate and Adsorption Indicators), P. 95.
7. Gravimetric Determination of Chloride, P. XVIII, Optional Methods *A*, *B*, *C*, or *D*, as Desired.
8. Preparation of a Permanganate Solution, P. VII.
9. Standardization of a Permanganate Solution, P. VIII.
10. *Determination of Ferrocyanide, P. 133.
    (a) Titration of Potassium Ferrocyanide Solutions.
11. Determination of the Iron in an Acid-Soluble Ore, Zimmermann-Reinhardt Method, P. 53*A*, Note 2.
12. *Preparation and Standardization of a Ferrous Sulfate Solution, P. IX.
13. *Determination of Available Oxygen in Pyrolusite, P. 72, Note 3.
14. Preparation of an Iodine Solution, P. X.
15. Standardization of an Iodine Solution, P. XII.
16. *Determination of the Antimony in a Stibnite, P. 47, Note 6.
17. Preparation of a Thiosulfate Solution, P. XIII.
18. Standardization of a Thiosulfate Solution.[1]
    (a) Using Potassium Dichromate, P. XIV.
    (b) Using a Standard Iodine Solution, P. XIV, Note 5.
    (c) Using a Standard Permanganate Solution, P. XIV, Note 5.
    (d) Using Potassium Iodate, Problem 4, p. 521.
19. Determination of Copper in Brass, P. 28, or in Ores, P. 28, Note 4.
20. *Determination of Antimony in a Stibnite, Using the Iodine Monochloride End-Point, P. 47, Notes 6 and 2.
21. Preparation of a Sodium Hydroxide Solution, P. XV.
22. Standardization of a Sodium Hydroxide Solution.
    (a) Using Potassium Hydrophthalate, P. XVI.
    (b) Using Benzoic Acid, Problem 3, p. 525.
23. Preparation and Standardization of a Hydrochloric Acid Solution.[1]
    (a) Using Sodium Carbonate, P. XVII.

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*Optional experiment. See p. 505.

[1] Each student may select or be assigned any two methods and check the agreement of the methods.

(b) Using Sodium Tetraborate, P. XVII, Note 8.
(c) Using Potassium Iodate, Problem 6, p. 526.
(d) Using Sodium Oxalate, Problem 4, p. 526.

24. Determination of the Total Alkalinity of Soda Ash, Problem 12, p. 528.
25. Analysis of Glacial Acetic Acid, Problem 13, p. 528.
26. *Analysis of Mixtures or Solutions Containing as Possible Constituents Hydroxide, Carbonate, or Hydrocarbonate, Problems 8, 9, and 10, p. 527, and reference texts.[2]
27. *Analysis of Mixtures or Solutions Containing as Possible Constituents Phosphoric Acid, Dihydrogen Phosphate, Monohydrogen Phosphate, or Phosphate, Problem 11, p. 528, and reference texts.[2]
28. *Determination of Silica in a Soluble Silicate, P. 7, Note 11.
29. *Electrolytic Determination of Copper and Lead.[3]
30. *Electrometric Titrations.[3]
31. *Electrometric *p*H Determination.[3]

Part II. The Systematic Qualitative and Semi-Quantitative Analysis of Solutions and Solids for the Basic and Acidic Constituents.

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[2] These analyses are usually given as laboratory problems, with the student required to consult the literature, select his method, and turn in a critical discussion of this method (its relative advantages, sources of error, probable accuracy, and so forth) with his analysis.

[3] Procedures for these determinations are not given in this book.

Questions and Problems

Discussion. The following questions and problems are intended to develop and extend the material previously given rather than to aid in memorizing the detailed system of analysis or to drill in the use of certain formulas. In the stoichiometric problems, most of the methods for the estimation of the various constituents, both acidic and basic, have been covered in order that the student can become familiar with the principles of the methods, even though these particular methods have not been carried out in the laboratory. In a considerable number of stoichiometric problems involving determinations not given in the text, the methods are stated in such manipulative detail that they may be used as the basis for additional laboratory experiments. Rather extensive use has been made of problems involving the application of mass-action principles in order to give the student a more quantitative appreciation of the factors controlling chemical reactions than would be otherwise obtained. The liabilities and limitations involved in the use of concentrations in place of activities in mass-action expressions has been previously pointed out, as has the necessity, and value, of the use of approximate methods in solving mass-action expressions—these should be strongly emphasized by the instructor.

The subject of precision measures has been developed by means of problems; the instructor may omit or develop this treatment to suit the requirements of his class. The use of significant figures to show the limitations both of data and of method, experimental and theoretical, should be encouraged. Significant figures have been used below, except that repetition of zeros has occasionally been avoided by stating that an exact quantity has been measured; in such cases the usual precision of the measuring instrument is to be assumed.

Where *normal* concentrations are used, the *equivalent* value is determined by the reactions involved in the particular problem.

THE ANALYTICAL BALANCE

(See P. I to P. IV.)

1. Derive the relation $\tan \alpha = wL/DQ$, where α is the angle of rotation of the beam of a balance from its horizontal position, w is a small weight

applied to one side, L is the arm length, D is the distance from the point of support to the center of gravity, and Q is the weight of the beam system.

2. Derive the equation $S = LP/(QD - 2WD')$, which is given on p. 7 for the case in which the terminal knife edges are above the central knife edge.

3. What conclusions regarding the construction and condition of balances A and B can be drawn from the following observations? (a) Balance A has a sensitivity of 1.8 div./mg with no load, and 2.5 div./mg with a 20-g load. (b) Balance B has a sensitivity of 3.6 div./mg with a 1-g load, and 1.4 div./mg with a 50-g load.

4. Three balances and the accompanying sets of weights were tested by determining (a) the point of rest of the empty balance, (b) the point of rest with the weight marked "10" (g) on the left pan and the one marked "10*" on the right, and (c) the point of rest with these weights transposed. The data obtained were tabulated as follows:

Balance	Point of Rest		
	Empty Balance	10 on Left, 10* on Right	10* on Left, 10 on Right
C	9.8	10.7	8.6
D	10.2	11.2	9.2
E	9.9	10.6	10.6

What conclusions can be drawn regarding these balances and weights?

5. The distance from the central knife edge to the left terminal knife edge of a balance is 10.0003 cm and from the central knife edge to the right terminal knife edge 9.9998 cm. The apparent weight of a weighing bottle on the left pan is 24.7562 g. What is its correct weight? *Ans.* 24.7549 g.

6. In constructing a balance, the two terminal knife edges are mounted in the beam 8 cm apart. It is desired that the error of the balance not exceed 0.5 mg with a 50-g load (on each pan). What is the maximum distance from the center that the central knife edge can be placed? *Ans.* 0.00002 cm.

7. The point of rest of an unloaded balance was 9.8; with a weight of exactly 100 g on each pan, it was 6.4; when a 1-mg weight was added to the left pan, it became 8.9. Calculate the ratio of the arm lengths, L/R, of the balance. *Ans.* 0.999986.

8. A 10-mg rider is being used on a balance having its right arm calibrated in 12 equal divisions, the twelfth calibration being exactly above the terminal knife edge. With a crucible on the left pan, the original point of rest is restored when weights totaling 24.24 g are placed on the right pan and the rider position is read as 6.25. What is the crucible weight?

9. The specifications and characteristics of a balance are as follows: Weight of beam assembly, 420 g; beam length, 18 cm; pointer length, 20 cm; divisions on pointer scale, 0.1 cm; sensitivity, 4 div./mg; knife edges in same horizontal plane. Calculate the distance from the central knife edge to the center of gravity of the beam assembly.

10. A 100-ml volumetric flask is balanced by a tare and then filled to the

mark with water at 20°C. It requires 99.902 g of brass weights with a specific gravity of 8.3 to balance the water. What is the weight of the water (*in vacuo*)? (Assume that 1 l of air weighs 1.2 g.) What is the volume of the flask in milliliters? (See footnote, p. 30, for the definition of the liter.)

11. What would be the percentage error caused by not correcting for buoyancy when weighing out the following substances: (1) Sodium oxalate ($Na_2C_2O_4$), (2) benzoic acid (C_6H_5COOH), and (3) copper foil?

12. The data shown below were obtained in the calibration of a set of weights. Prepare a table similar to that of Table I, p. 18, and complete columns 5, 6, 7, and 8.

DATA OBTAINED IN THE CALIBRATION OF A SET OF WEIGHTS

Sensitivity of the Balance: 0.45 mg/div. for the Loads Applied

1	2	3	4	1	2	3	4
Face Value	Weights on Left Pan	Weights on Right Pan	Point of Rest	Face Value	Weights on Left Pan	Weights on Right Pan	Point of Rest
0.005							
rider	0.005	rider	10.0	1	0.5 + Σ	1	10.3
	rider	0.005	10.1		1	0.5 + Σ	9.5
0.01	0.005, rider	0.01	10.1	1*	1	1*	10.0
	0.01	0.005, rider	10.0		1*	1	9.8
0.01*	0.005, rider	0.01*	10.1	1**	1	1**	9.8
	0.01*	0.005, rider	10.2		1**	1	10.0
0.02	0.01, 0.01*	0.02	9.8	2	1, 1*	2	9.8
	0.02	0.01, 0.01*	10.2		2	1, 1*	9.8
0.05	0.02, + Σ[a]	0.05	10.2	5	2, 1, 1*, 1**	5	7.5
	0.05	0.02, + Σ	9.6		5	2, 1, 1*, 1**	11.7
0.1	0.05 + Σ	0.1	10.2	10	5 + Σ	10	9.4
	0.1	0.05 + Σ	9.7		10	5 + Σ	8.5
0.1*	0.05 + Σ	0.1*	10.2	10*	10	10*	7.4
	0.1*	0.05 + Σ	9.7		10*	10	10.2
0.2	0.1, 0.1*	0.2	10.2	20	10, 10*	20	10.2
	0.2	0.1, 0.1*	9.8		20	10, 10*	9.8
0.5	0.2 + Σ	0.5	10.0	50	20 + Σ	50	10.2
	0.5	0.2 + Σ	9.8		50	20 + Σ	9.6
				1	1 standard	1	10.0
					1	1 standard	9.6

[a] Σ indicates the sum of the smaller weights of the series.

ACCURACY, PRECISION, ERRORS, AND SIGNIFICANT FIGURES

(See Note 8, p. 11, in regard to significant figures.)

1. An object whose actual weight is 120.3142 g is weighed on various balances. Assuming that the weighing process is performed correctly to the limits of the instrument, how should the weight be recorded if the balance is sensitive (a) to only 1 mg; (b) to only 0.1 g? *Ans.* (a) 120.314 g; (b) 120.3 g.

How would this last weight be expressed in milligrams? *Ans.* 120,300 $\pm$ 100 mg, or 120.3×10^3 mg.

2. By the *accuracy* is meant the correctness of a measurement or result, the deviation from the true value; the *precision* expresses the reliability, and the reproducibility, of a measurement or series of measurements.

A volumetric method for determining chloride was tested by making analyses of specially purified sodium chloride. After correcting for all known *determinate* errors (that is, (1) instrumental errors, such as balance-arm inequality, (2) personal errors, such as peculiarities in reading rest points or burets, and (3) errors of method, such as the solubility of the precipitate), the following results were obtained, calculated as the per cent by weight of chlorine in the salt: (a) 60.56; (b) 60.53; (c) 60.60; (d) 60.64; (e) 60.62.

If only *indeterminate* errors (that is, purely accidental errors arising from andom causes which cannot be predicted or estimated) remain, they will obey the law of chance, and the following statements in regard to their magnitude and sign can be made:

1. Small errors occur more frequently than large ones.
2. Very large errors are rare.
3. Positive and negative errors are equally probable.

As positive and negative errors are equally probable, the most probable value for the quantity being measured will be the arithmetical mean of the series of measurements.

Calculate (a) the arithmetical mean; (b) the absolute error of this mean (in per cent); and (c) the relative error (expressed as parts per thousand and as per cent) of the above series of measurements. *Ans.* (a) 60.59; (b) -0.07 per cent; (c) 1.2 parts per thousand, or 0.12 per cent.

Notes: 1. These answers are measures of the accuracy of the above measurements. However, they are calculated from (1) the experimentally determined atomic weights, and (2) the assumption that the sodium chloride is absolutely pure; such experimental uncertainties always enter into attempts to calculate the accuracy of measurements.

2. In handling percentage values such as the above (which is frequently the case in quantitative analysis), care must be taken not to confuse the absolute error, which is the difference in the percentages, with the relative error when the latter (which is a ratio) is expressed as a percentage; also, it is seen that the relative values, rather than the absolute values, should be used in giving a measure of the merit of the analysis.

3. If the arithmetical mean of the deviations from the mean of the individual measurements of a series, taken without regard to sign, is calculated, the result will be a number called the *average deviation of a single observation or measurement*, which indicates how much, on the average, any single

measurement of the series will vary from the mean. This number, denoted by a.d., is frequently used, especially in analytical work, as a measure of the precision[1] of the single measurements of a series.

Calculate (a) the a.d. (average deviation of a single measurement) of the series of measurements given in Problem 2, and (b) the relative a.d., expressed as parts per thousand and as per cent. *Ans.* (a) 0.04 per cent; (b) 0.7 parts per thousand, or 0.07 per cent.

4. It can be shown that the arithmetical mean calculated from n equally reliable measurements is the $\sqrt{n}$ times as reliable as a single measurement. Therefore, if the uncertainty or average deviation of a single measurement of a series is a.d., the uncertainty attached to the mean of the series, called the *average deviation of the mean* and denoted by A.D., would be A.D. = a.d./$\sqrt{n}$.

Calculate (a) the A.D. (average deviation of the mean) of the series given in Problem 2, and (b) the relative A..D in parts per thousand and per cent. *Ans.* (a) 0.02 per cent; (b) 0.3 parts per thousand, or 0.03 per cent.

5. As the precision of the mean is increased only by the square root of the number of observations in a series, it is obvious that it is not practical to increase the precision of a series greatly by increasing the number of measurements.

A value is obtained from the mean of three measurements. How much more reliable would it be if (a) six and (b) nine measurements were made? *Ans.* (a) 1.4 times as reliable.

6. Frequently one measurement of a series will deviate widely from the others, and no explanation of the divergence can be found. If the series contains at least four measurements and if, upon computing the mean and the average deviation (omitting the doubtful observation) the deviation of the doubtful measurement from the mean is equal to or greater than four times the average deviation, the doubtful measurement should be discarded. It can be shown from the theory of probability that the chances are 993 in 1000 that the doubtful measurement has resulted from some mistake.[2]

Should any of the values given in Problem 2 be discarded?

7. An analyst was asked to determine the percentage of potassium in a certain substance. He carried out six determinations and obtained the following results: (1) 19.29; (2) 19.32; (3) 19.30; (4) 19.24; (5) 19.00; (6) 19.21.

(a) Should any determination be discarded? (b) What value should the analyst report? (c) What is the a.d. and the relative a.d.? (d) What is the A.D. and the relative A.D.? (e) The substance was potassium hydrophthalate, $KHC_8H_4O_4$. What is his absolute error and relative error? (f)

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[1] It is assumed that the *residual errors* (that is, errors remaining after the correction of the determinate errors—for example, errors in calibrations or in standards) are negligible in comparison with the *accidental errors*. Where this is not the case, the average deviation as calculated above is a deviation measure and not a true precision measure, since the residual errors may contribute a significant constant but indeterminate error to the measurement. For a more complete treatment of these topics, see Goodwin, *Precision of Measurements and Graphical Methods*, McGraw-Hill, 1920.

[2] Mellor, *Higher Mathematics for Students of Chemistry and Physics*, Longmans, Green, 1902, p. 533.

Why is the accuracy of the determination so much less than the precision? What assumptions are made in calculating the accuracy? *Ans.* (a) Yes, No. 5. (b) 19.27 per cent potassium. (c) 0.038 per cent; 0.20 per cent, or 2.0 parts per thousand. (d) 0.017 per cent; 0.9 part per thousand, or 0.09 per cent. (e) +0.13 per cent; 0.68 per cent, or 6.8 parts per thousand. (f) Probably because of some unsuspected determinate error, such as, for example, coprecipitation in a gravimetric determination. Correctness of atomic weights and purity of compound.

8. The data shown in the accompanying table were obtained by an analyst in carrying out the volumetric analysis of a low-grade iron ore: The container of the permanganate solution was labeled as follows: "25.01 ml of this $KMnO_4$ solution are equivalent to 0.1262 g of iron."

Determination	Weight of Sample (g)	Volume of $KMnO_4$ Used in Titration (ml)
1	1.2463	20.80
2	1.4324	23.91
3	1.1892	19.82
4	1.2279	20.30

(a) Should any analysis be discarded? (b) What percentage of iron should be reported? How many significant figures are justified? (c) What the a.d. and the relative a.d.? (d) Were any of the above measurements carried to an unnecessary precision?

9. The following weight values were reported (four measurements had been made in determining each value) with the accompanying precision indications:

$$W_1 = 12.461 \text{ g}, \pm 0.001 \text{ g}.$$
$$W_2 = 2.3861 \text{ g}, \text{A.D.} = 0.0001 \text{ g}.$$
$$W_3 = 0.0122 \text{ g}, \text{a.d.} = 0.4 \text{ mg}.$$

(a) Calculate the relative a.d. of each of the values, assuming that for W_1 the ± 0.001 represents the average deviation of the mean. (b) If these numbers were used in the formula

$$\frac{W_1 \times W_2}{W_3} = x,$$

how many significant figures should be used in the value of x? (c) If these numbers were used as

$$W_1 + W_2 + W_3 = \Sigma W,$$

how many significant figures should be used in the value of ΣW?

10. Where approximate methods of calculation do not introduce errors greater than the precision of the measurements involved, such approximate methods should always be used; they not only eliminate much tedious arithmetical work but frequently greatly reduce the chance of errors in the calculation. A large number of the cases where approximations are useful can be treated by the general formula

$$(1 \pm \delta)^m \approx 1 \pm m\delta,$$

where m is any number and δ is small in comparison with unity. The particular cases most often encountered are $1/(1 \pm \delta) \approx 1 \mp \delta$; $\sqrt{1 \pm \delta} \approx 1 \pm \frac{1}{2}\delta$; and $(1 \pm \delta)^2 \approx 1 \pm 2\delta$.

A solution which has been standardized at 20°C. is being used at 23°C. in a buret which was calibrated for use at 20°C. Calculate what factor should be applied to the volume readings thus obtained in order to convert them to a 20°C. basis.

Ans. $V_{20°} = V_{23°(\text{observed})} \times (1 + 0.000025)\,(23 - 20) \times \dfrac{(0.99757)}{(0.99823)}$.

$$V_{20°} \approx V_{23°(\text{observed})} \times (1 + 0.000075) \times \frac{(1 - 0.00243)}{(1 - 0.00177)}.$$

$$\approx V_{23°(\text{observed})} \times (1 + 0.000075 - 0.00243 + 0.00177).$$

$$\approx V_{23°(\text{observed})} \times 0.99942.$$

VOLUMETRIC METHODS OF ANALYSIS

Concentration Units

(See pp. 24–26.)

1. One gram (±0.01 g) of each of the following substances is taken to prepare a liter of solution: (1) $AgNO_3$, (2) KSCN, (3) $BaCl_2$, (4) $BaCl_2 \cdot 2H_2O$, (5) I_2, (6) $K_4Fe(CN)_6 \cdot 3H_2O$, (7) $Na_3AsO_4 \cdot 12H_2O$, (8) $KMnO_4$, (9) $K_2Cr_2O_7$, (10) $Na_2S_2O_3$.

(a) Calculate the formal concentration of each substance in the resulting solutions. (b) Assuming that each of the salts is completely ionized, calculate the molal concentration of the anion and cation in each case (neglect the hydrolysis of certain of these ions).

2. Calculate the formal concentration of H_2O in pure water at 20°C.

3. A solution containing 0.06003 g of $HC_2H_3O_2$ (acetic acid) is diluted to 1.500 l. What is the formal concentration of the acetic acid? It has been calculated from conductance measurements that the acetic acid in this solution is 15 per cent ionized. What is the molal concentration of the (a) $HC_2H_3O_2$, (b) H^+ and (c) $C_2H_3O_2^-$ in the solution? Calculate the ionization constant of acetic acid from the data given.

4. One tenth formal solutions of the overlined compounds shown below are prepared. State the normality of each of the solutions when used in the reaction indicated.

1. $AgNO_3 + \overline{KIO_3} = AgIO_{3(s)} + KNO_3$
2. $3AgNO_3 + \overline{FeCl_3} = 3AgCl_{(s)} + Fe(NO_3)_3$
3. $AgNO_3 + \overline{KSCN} = AgSCN_{(s)} + KNO_3$
4. $BaCl_2 + \overline{K_2CrO_4} = BaCrO_{4(s)} + 2KCl$
5. $\overline{K_2Cr_2O_7} + 2BaCl_2 + H_2O = 2BaCrO_{4(s)} + 2HCl + 2KCl$
6. $\overline{K_2CrO_4} + \overline{3FeCl_2} + 8HCl = CrCl_3 + 3FeCl_3 + 2KCl + 4H_2O$
7. $\overline{2FeCl_3} + \overline{SnCl_2} = 2FeCl_2 + SnCl_4$

8. $\overline{10FeSO_4} + \overline{2KMnO_4} + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

9. $\overline{2KMnO_4} + \overline{3MnSO_4} + 2H_2O = 5MnO_{2(s)} + K_2SO_4 + 2H_2SO_4$

10. $\overline{10KSCN} + \overline{12KMnO_4} + 13H_2SO_4 = 12MnSO_4 + 11K_2SO_4 + 10HCN + 8H_2O$

11. $\overline{KIO_3} + \overline{3SnCl_2} + 6HCl = KI + 3SnCl_4 + 3H_2O$

12. $\overline{KIO_3} + \overline{5KI} + 6HCl = 3I_2 + 3H_2O + 6KCl$

13. $\overline{KIO_3} + \overline{2KI} + 6HCl = 3ICl + 3KCl + 3H_2O$

14. $\overline{2Na_2S_2O_3} + \overline{I_2} = Na_2S_4O_6 + 2NaI$

15. $\overline{H_2SO_4} + \overline{Na_2CO_3} = Na_2SO_4 + H_2CO_3$

16. $H_2SO_4 + \overline{2Na_2CO_3} = 2NaHCO_3 + Na_2SO_4$

17. $\overline{H_3PO_4} + NaOH = NaH_2PO_4 + H_2O$

18. $\overline{H_3PO_4} + 2KOH = K_2HPO_4 + 2H_2O$

19. $\overline{H_2C_2O_4} + 2NaOH = Na_2C_2O_4 + 2H_2O$

Acid	Sp. Gr. $\left(\frac{20°}{4°}\right)$	Weight (%)
H_2SO_4	1.83	95
HNO_3	1.41	69
HCl	1.18	36
H_3PO_4	1.75	90

5. To the left are given data relating to the composition and specific gravity of some of the concentrated acids of commerce. Calculate the formal and normal concentrations of these acids.

6. Calculate the volume of each of these acids required to prepare 1 l of a 6 f. solution. What would be the normal concentration of each of these solutions? (Assume that the acid is converted to the neutral salt.)

The Calibration and Use of Volumetric Apparatus

(See P. V, Note 8.)

1. Explain the differences between the absolute density of water (in C.G.S. units) and the relative density.

2. What is the weight (*in vacuo*) of (a) 1 l of water and (b) 1000 cc of water, each at 4°C.? Calculate the ratio of the weight of the 1 l of water to the 1000 cc of water.

3. What is the weight (*in vacuo*) of 1 l of water at 20°C.?

4. Calculate to 0.01 g the difference in the weight of brass weights required to balance 1 l of water at 20°C. (a) in a vacuum and (b) in air with the barometric pressure 760 mm. What would be the percentage error caused by neglecting the buoyancy correction when weighing water in air under the above conditions?

5. It requires 24.925 g of weights to balance the water delivered by a 25-ml pipet at 20°C. What is the volume of the pipet in milliliters at that temperature? *Ans.* 24.991 ml.

6. What volume of water will this pipet deliver at 30°C.? *Ans.* 24.997 ml.

7. It is desired to calibrate a liter flask for use at 20°C. but the laboratory temperature at the time is 25°C. and the barometric pressure is 760 mm. Calculate to 0.01 g the apparent weight of water to be used for the desired calibration, the empty flask being balanced with a tare. *Ans.* 996.17 g.

8. You are calibrating a buret marked "20°C." for use at that temperature but find the laboratory temperature at the time of the calibration to be 25°C. and the barometric pressure to be 755 mm. Calculate the factor by which any apparent weight of water delivered by the buret can be converted to the desired volume.

9. A silver nitrate solution was prepared to be 0.10175 n. at 17°C. What is its normality at 24°C.?

10. A permanganate solution was standardized at 25°C. and found to be 0.09982 n. at that temperature. The solution was used without correction in a titration at 18°C. to determine the iron in an ore. What percentage error was thus introduced into the determination? *Ans.* 0.16 per cent, negative error.

Volumetric Precipitation Methods

(The principles relating to volumetric precipitation methods are discussed in P. V and P. VI; a list of the procedures utilizing methods of this type are given on p. 46.)

Stoichiometric Calculations

1. An analyst weighed out and dissolved 15.462 g of dry silver nitrate and then diluted the solution to the mark in a flask which had been found by calibration to contain 1001.40 ml. Calculate the normality of the solution.

2. The above silver nitrate solution was used for the standardization of a thiocyanate solution by the method of P. VI; 25.00 ml of the silver required 27.50 ml of the thiocyanate. Calculate the normality of the thiocyanate. What would be the result of attempting to carry out this titration in a neutral solution?

3. *The determination of the silver in an alloy.* A section of a clean silver coin weighing 0.3426 g was dissolved in 10 to 15 ml of 6 n. HNO_3, and the oxides of nitrogen were expelled by boiling. The solution was cooled, 3 ml of chloride-free 1 n. $Fe(NO_3)_3$ were added, and the solution was diluted to 50 ml and then titrated with the above thiocyanate solution as directed in P. VI, 34.70 ml being required. Calculate the percentage of silver in the coin. (*Note:* This titration of silver can be carried out in the presence of copper unless the ratio of copper to silver is greater 7 to 10.)

4. In carrying out the estimation of bismuth by P. 27, the BiOCl precipitate was dissolved in HNO_3, 12.00 ml of 0.1000 n. $AgNO_3$ were added, and 4.00 ml of 0.0500 n. KSCN were used for the final titration. Calculate

the milligrams of bismuth present. (*Note:* It is convenient to note that the volume in *milliliters* times the *normality* gives *milli-equivalents*, and also that *milli-equivalents* times the *gram-equivalent weight* gives *milligrams*. In solving the above problem by the use of equivalents, one should note that 1 *mole* of BiOCl gives 1 *equivalent* of chloride.)

What would be the effect on the above estimation of bismuth if the BiOCl precipitate contained by weight from 5 to 10 per cent of (a) $PbSO_4$; (b) $PbCl_2$; (c) AgCl?

5. A precipitate of pure sodium chloride was titrated with standard $AgNO_3$ as directed in the volumetric method of P. 95, chromate being used as indicator (the Mohr method). The titration required 12.62 ml of 0.1016 n. $AgNO_3$. Calculate the milligrams of sodium in the precipitate.

6. A mixed precipitate of sodium and potassium chlorides weighing 0.2076 g was dissolved and titrated by the Mohr method; 28.50 ml of 0.1055 n. $AgNO_3$ were used. Calculate the weight per cents of the two salts in the mixture.

7. A silver chloride precipitate was treated as directed in P. 23, 24.75 ml of 0.2024 f. KCN being used for the direct titration and 0.24 ml of 0.1020 f. $AgNO_3$ for the back-titration. Calculate the milligrams of silver present. Can this determination be classified as a volumetric precipitation process?

8. A thiocyanate solution was standardized by treating 0.4562 g of metallic mercury by the second and third paragraphs of P. 45. Calculate the normality of the thiocyanate if 42.56 ml were required for the titration. (See question to Problem 7.) Predict the probable effect of the presence of the following ions in the above titration in amounts approximately equivalent to that of the mercury: (a) Bromide; (b) iodate; (c) perchlorate; (d) phosphate; (e) unipositive silver; (f) bipositive lead.

9. A nickel chloride precipitate (from P. 64) was treated by P. 65, 0.10 ml of an exactly 0.1 n. $AgNO_3$ solution being added as directed. In dissolving the precipitate, 14.20 ml of a 0.1982 f. KCN solution were used, and then 0.08 ml of the silver nitrate was required to produce a permanent turbidity. Calculate the milligrams of nickel in the precipitate. (See question to Problem 7.)

10. The silver in various alloys is being determined by dissolving the alloys in HNO_3 and titrating with a standard KSCN solution (the Volhard titration). Calculate the sample weight of the alloy in order to have the buret reading in milliliters give directly the percentage of silver in the alloy when an exact 0.1 n. thiocyanate solution is used.

11. The mercury in cinnabar ores is being determined by titration with standard thiocyanate solutions. If a 1-g (± 1 mg) sample of the cinnabar is being taken, calculate what should be the normality of the thiocyanate in order that the buret reading in milliliters multiplied by 2 should give directly the percentage of mercury in an ore.

12. A 0.2350-g sample of a mixture of crude KCN and KSCN was dissolved in water and titrated with standard silver nitrate. The end-point was taken when no more precipitate formed on addition of the silver nitrate (see P. 22); 30.00 ml of 0.1000 f. solution were required. There was then added 1.00 ml of 1 n. KI and 5 ml of 6 n. NH_4OH, and the mixture was titrated with standard potassium cyanide solution until all of the precipitate dissolved, 40.00 ml of 0.1000 f. solution being used. Calculate the percentage of KCN and KSCN in the sample.

Applications of the Mass-Action Law

13. In the accompanying table are given the formal solubilities of certain salts at room temperature. Calculate solubility products for these salts, proceeding on the basis that they are completely ionized and assuming (a) that no significant hydrolysis of the ions occurs and (b) that the molal concentrations of the ions represent their activities. State in which cases these assumptions are least justified.

Salt	Formal Solubility
(a) $BaSO_4$	1×10^{-5}
(b) $BaCrO_4$	1.6×10^{-5}
(c) Ag_2CrO_4	8×10^{-5}
(d) $PbCl_2$	3.9×10^{-2}
(e) $ZnCO_3$	1.6×10^{-4}
(f) Ag_3PO_4	1.6×10^{-5}

14. Calculate the molal concentrations of the silver and the chloride ions when to 50.00 ml of 0.1000 n. chloride are added (a) 49.90, (b) 50.00, and (c) 50.10 ml of 0.1000 n. $AgNO_3$.

15. Calculate the volume of 0.10 n. $AgNO_3$ which would be required to saturate with silver chromate 100 ml of a solution containing 0.30 g of K_2CrO_4.

16. A soluble chloride is to be titrated with silver nitrate, with a soluble chromate being used as indicator. Calculate what should be the chromate ion concentration in order that silver chromate will precipitate when an amount of silver just equivalent to the chloride present has been added.

17. Repeat the calculation in Problem 16 for the case where a soluble iodide is to be titrated. Does the result of the calculation prove that a precise titration of iodide is impossible by this method? (*Note:* The titration of iodide or thiocyanate by the Mohr method is not satisfactory, because the adsorptive tendency of the precipitate makes the determination of the end-point uncertain.)

18. A soluble chloride is titrated with a standard silver nitrate solution, with chromate being used as indicator and 1 ml of a solution containing 50 g of K_2CrO_4 per liter having been added. Calculate the concentration of chloride ion in the titrated solution if the volume was 100 ml when Ag_2CrO_4 first precipitated.

19. In making an experiment to determine the "end-point error" of the Mohr titration, 2.0 ml of 1.0 n. K_2CrO_4 were diluted to 100 ml and then 0.010 n. $AgNO_3$ was added until the first perceptible precipitate was observed, 0.50 ml being required. Calculate the error (grams of chloride, plus or minus) in a determination made under the above conditions. *Ans.* 1.5×10^{-4} g, plus error.

20. (a) In making a determination of the KCN in a solution by the modified Liebig method, 2 ml of a KI solution (2 g of KI in 100 ml of solution) were added as indicator and the end-point was recognized when 0.10 mg of precipitate formed. The total amount of KCN present in the sample taken was 0.20 g. The volume of the solution at the end-point was 100 ml. Calculate the error (deviation in grams of KCN) in the determination. *Ans.* 6.7×10^{-5} g of KCN, minus error.

(b) Taking the results obtained in (a), calculate what would have to be the formal concentration of ammonia in the solution in order to obtain correct results. *Ans.* 3 f.

(See the footnote, p. 403, in regard to equilibrium expressions involving ammonia.)

Oxidation-Reduction Methods of Volumetric Analysis

Permanganate Methods

(A discussion of electronic reactions in general is given on pp. 47–53 and of permanganate methods on pp. 53–59. The standardization of permanganate solutions against sodium oxalate is given on pp. 61–65. The various applications of permanganate methods to this system of analysis are pointed out on p. 67.)

Stoichiometric Calculations

1. What weight of $KMnO_4$ should be taken to prepare a liter of 0.100 n. solution? (The titration is to be carried out in an acid solution.)

2. Manganous ion can be oxidized to manganese dioxide by permanganate in a neutral solution, and this reaction is the basis of the so-called Volhard titration of manganese. Calculate the weight of $KMnO_4$ to be taken to prepare a liter of 0.100 n. solution for use in the Volhard titration.

3. An approximately 0.1 n. $KMnO_4$ solution is to be standardized against sodium oxalate. Calculate the maximum and minimum limits to the weight of sample which should be taken. Explain.

4. A permanganate solution was standardized against ferrous ammonium sulfate crystals, 1.5684 g of the solid requiring 38.46 ml of the solution. Calculate the "iron titer" (see p. 64) of the solution.

5. (a) The cadmium sulfide precipitate resulting from the analysis of a 0.4762-g sample of an aluminum solder containing zinc, aluminum, and cadmium was treated by P. 30. The titration required 13.55 ml of a 0.06242 n. $KMnO_4$ solution. Calculate the percentage of cadmium in the solder.

(b) The zinc sulfide precipitate was treated by P. 62, 48.70 ml of a 0.2242 n. $KMnO_4$ solution being required for the titration. Calculate the percentage of zinc in the solder.

(c) Assuming that the constituents of the above alloy are known, prepare a tabular outline showing the most efficient procedure for obtaining the two sulfide precipitates.

6. The calcium oxalate precipitate from a 0.2250-g sample of a limestone was treated by the first paragraph of P. 87, 44.22 ml of 0.0982 n. $KMnO_4$ being used for the titration. Calculate the percentage of CaO in the sample. (*Note:* In the statement of analyses it is often conventional to report the elements as their oxides. This is advantageous, especially in silicate and carbonate rock analyses, as the sum of the basic and acid oxides, corrected by the oxygen equivalent of any non-oxygen anions, such as fluoride or sulfide, should give the total weight of the sample. For a discussion of the summation of the analytical results and of the statement of analyses, see Washington, *Chemical Analysis of Rocks*, 4th Ed., Wiley, 1930, pp. 23–28, or Hillebrand and Lundell, *Applied Inorganic Analysis*, Wiley, 1929, pp. 654–659.)

7. A permanganate solution was standardized against sodium oxalate, 0.2680 g of oxalate requiring 40.00 ml of the $KMnO_4$. This solution was then used in titrating a ferrocyanide solution (P. 133), 25.00 ml being required to titrate a 100-ml portion of the ferrocyanide. Calculate the weight of $K_4Fe(CN)_6 \cdot 3H_2O$ per liter required to prepare the ferrocyanide solution.

8. In determining the manganese in a steel by the Williams method, a 2.00-g sample was dissolved in nitric acid, an excess of solid $KClO_3$ was

slowly added, and the mixture was boiled until yellow fumes were no longer evolved (see P. 71). The precipitate was dissolved in a sulfuric acid solution into which had been pipeted 50.00 ml of 0.1014 f. ferrous sulfate solution. The resulting solution was titrated with 0.01042 f. $KMnO_4$, 20.27 ml being required. Calculate the percentage of manganese in the steel.

9. *The Volhard titration of bipositive manganese with permanganate.* Three 25.0-ml portions of a 0.0200 f. permanganate solution are pipeted into a flask containing an excess of concentrated HCl, and the solution is boiled, evaporated to fuming with an excess of sulfuric acid, cooled, and diluted. State the reactions taking place.

To the solution an excess of solid zinc oxide was added. Explain why this produces a buffered solution having a *p*H of approximately 6.

The mixture was heated to boiling and titrated with another portion of the original permanganate solution until a pink color was perceptible. Calculate how many milliliters would theoretically be required for the titration. (*Note:* In the above titration the precipitate which is formed tends to coprecipitate, either by adsorption or by formation of a manganous manganite, appreciable amounts of the manganous ion. By providing a high concentration of a zinc (or calcium) salt, selective coprecipitation of the latter is caused, and the manganese in the precipitate more nearly approaches the quadripositive state.)

Applications of the Mass-Action Law

10. In a titration of a certain reducing substance, 25 ml of 0.020 f. $KMnO^4$ were reduced to the bipositive state, and then 0.03 ml of the permanganate was added before the pink color was observed and the end-point was taken. Assuming that the final volume was 200 ml and the final hydrogen ion concentration was 1.0 m., calculate the potential set up in the solution. *Ans.* −1.42v.

11. If the titration in Problem 10 were carried out in a solution maintained 1.0 m. in chloride ion, calculate what would be the partial pressure of chlorine above the solution under equilibrium conditions. How are the results of this calculation to be reconciled with the conditions of P. 85 and P. 53*A*?

12. (a) A 0.010 f. solution of ferric perchlorate is shaken with an excess of solid silver until equilibrium is attained. Calculate the percentage of the iron not reduced. Perchlorate is not reduced.

(b) The process is repeated in a solution which is maintained 1.0 f. in HCl. Repeat the calculation.

Iodometric Methods

Stoichiometric Calculations

1. What is the normality (as a standard oxidizing agent) of a 0.1 f. KI_3 solution?

2. An iodine solution was standardized by the method given in P. XII; 0.2100 g of As_2O_3 required 40.20 ml of the iodine. Calculate the normality of the iodine.

3. A standard solution of potassium dichromate was prepared by weighing out 4.500 g of $K_2Cr_2O_7$ and diluting it to a liter. A 50.00-ml portion treated by P. XIV required 42.37 ml of a thiosulfate solution. Calculate the normality of the thiosulfate.

4. *The standardization of thiosulfate solutions against potassium iodate.* Potassium iodate can be purchased in a high state of purity or can be easily recrystallized and dried (160° to 180°C.). It is a satisfactory primary standard. In standardizing a thiosulfate solution, 0.1250 g of KIO_3 was weighed out into a flask and dissolved in 50 ml of water; 2 g of KI were dissolved in 10 ml of water and added to the iodate, followed by 2 ml of HCl. The mixture was then titrated with the thiosulfate, 41.02 ml being required. Calculate the normality of the thiosulfate. Calculate the percentage error introduced by an error of 0.2 mg in weighing the iodate. (*Note:* This method of standardizing a thiosulfate solution is highly recommended except for possible weighing error due to the low equivalent weight of the iodate. Because of this it is advisable to prepare a solution of the iodate as was done with the dichromate in P. XIV.)

5. In the analysis of an aluminum solder containing lead and cadmium, the lead sulfate precipitate (P. 24) from a 0.2280-g sample was treated by P. 25, 50.00 ml of the $K_2Cr_2O_7$ solution prepared in Problem 3 being added in carrying out the second paragraph, and 4.02 ml of the thiosulfate solution standardized in Problem 3 being used for the final titration. Calculate the percentage of lead in the sample. If the qualitative composition of this alloy were known, how would one most efficiently obtain the lead as chromate in order to carry out the above determination?

6. In the analysis of a 0.2042-g sample of a red brass containing copper and zinc, 27.02 ml of 0.1019 n. thiosulfate were used in P. 28. Calculate the percentage composition of the alloy. If the qualitative composition of the alloy were known, show by tabular outlines the most efficient method of carrying out an iodometric determination of the copper in (a) the red brass analyzed above; (b) a nickel coin (75 Cu, 25 Ni); (c) nickel silver (55 Cu, 18 Ni, 27 Zn); (d) ship-nail brass (64 Cu, 25 Zn, 8.5 Pb, 2.5 Sn); (e) Ampco metal (80–90 Cu, 8–10 Al, 6–7 Fe).

7. A 0.6612-g sample of a stibnite ore was treated as directed in P. 47, Note 6, 40.41 ml of a 0.1014 n. iodine solution being required for the titration. Calculate the percentage of antimony trisulfide in the ore. What would be the effect on this determination of the presence of arsenic in the ore?

8. In carrying out the analysis of a 0.2401-g sample of a solder containing lead and tin, 21.02 ml of a 0.1014 n. iodine solution were used in estimating the tin by P. 49. Calculate the percentage of tin present. Would it be permissible to simplify the analysis by treating the H_2S precipitate of P 11 directly by P. 49 if only an estimation of the tin was required?

9. *The iodometric determination of the iron in an ore.* A 0.4627-g sample of iron ore was boiled with hydrochloric acid until only a small residue remained. This was filtered out and treated in a platinum crucible with hydrofluoric acid, a few drops of sulfuric acid were added, the mixture was evaporated almost to dryness, and the residue was dissolved and added to the original hydrochloric acid solution. A 1 n. $KMnO_4$ solution was then added dropwise until a distinct pink color was obtained, the solution was evaporated to 4 to 5 ml, 20 ml of water were added, and the solution was treated by the last paragraph of P. 53, 41.62 ml of 0.1037 n. thiosulfate being used in the titration. Calculate the percentage of iron in the ore. Explain the process of treating the insoluble residue with hydrofluoric and sulfuric acids.

What is the purpose of the treatment with permanganate? What would be the effect on the results of the analysis if the ore contained appreciable amounts of the following minerals: (a) pyrolusite (MnO_2); (b) pyrite (FeS_2); (c) crocoite ($PbCrO_4$); (d) chalcopyrite ($CuFeS_2$); and (e) arsenopyrite (FeAsS)?

10. In an estimation of the cobalt in a magnet steel containing iron, cobalt, and chromium, the regular system of analysis was followed to P. 55. Then, as iron had been separated by P. 52 and zinc and nickel were known to be absent, the sulfide precipitate from P. 55 was dissolved in hydrochloric acid, with the aid of a little bromine water, and treated directly by the last paragraph of P. 66. A 1.026-g sample was taken and 18.72 ml of 0.0982 n. thiosulfate were used for the titration. Calculate the percentage of cobalt in the alloy.

11. A manganese dioxide precipitate from P. 71 was treated as directed in P. 72, 21.42 ml of 0.1179 n. $Na_2S_2O_3$ being used in the titration. Calculate the milligrams of manganese present.

12. A 1.000-g sample of a prepared "unknown" was analyzed for the basic constituents. The elements found present, the volumes of the standard solutions used in the estimations, and standardization data are given below. Calculate the percentage of each of these elements present in the unknown.

Cu:	$Na_2S_2O_3$,	20.41 ml	Co:	$Na_2S_2O_3$,	1.42 ml
As:	KI_3,	1.24 ml	Mn:	$Na_2S_2O_3$,	2.73 ml
Sb:	KI_3,	3.87 ml	Cr:	$Na_2S_2O_3$,	3.27 ml
Sn:	KI_3,	2.94 ml	Ba:	$Na_2S_2O_3$,	1.80 ml
Fe:	$Na_2S_2O_3$,	3.72 ml	Mg:	$Na_2S_2O_3$,	2.84 ml

Standardization Data:

A dichromate solution was prepared by weighing out 5.671 g of $K_2Cr_2O_7$ and diluting it to 1 l.

Four 25.00-ml portions of this solution were pipeted out and treated as directed in P. XIV, "The Standardization of a Thiosulfate Solution Against Potassium Dichromate." The volumes of thiosulfate used were as follows: Titration I, 30.09 ml; titration II, 30.71 ml; titration III, 30.12 ml; titration IV, 30.10 ml.

Four 25.00-ml portions of the KI_3 solution were pipeted and titrated with the $Na_2S_2O_3$ solution; the volumes were as follows: Titration I, 25.62 ml; titration II, 25.64 ml; titration III, 25.60 ml; titration IV, 25.65 ml.

13. A determination of the hydrazine (N_2H_4) in a solution was made by adding to the acid solution an excess of an iodate solution. The iodate oxidizes the hydrazine to nitrogen. After the completion of the reaction between the iodate and the hydrazine, an excess of potassium iodide was added and the solution was titrated with thiosulfate. The data obtained were as follows: Iodate used, 50.00 ml of 0.02000 f. KIO_3; iodide used, 3.0 g of solid KI; thiosulfate used, 20.00 ml of 0.1000 f. $Na_2S_2O_3$. Calculate the weight of hydrazine in the solution. *Ans.* 0.03205 g.

Applications of the Mass-Action Law

14. The solubility of iodine, I_2, in water at 25°C. is 0.00134 f.; its solubility in a 0.00500 f. potassium iodide solution is 0.00378 f. Calculate the formal solubility of iodine in a solution 0.100 f. in potassium iodide. *Ans.* 0.0501 f.

15. Calculate the formal concentrations of potassium iodide and iodine in a solution prepared by P. X. Calculate the molal concentration of iodine in such a solution. Calculate the partial pressure of iodine above such a solution. (The vapor pressure of solid iodine is 0.4 mm at 25°C.)

16. In carrying out a chromate determination, 50 ml of a 0.100 n. chromate solution were pipeted into a 600-ml flask, the flask was filled with CO_2, 3 g of solid KI and the proper amount of acid were added, and the solution was diluted to 100 ml and allowed to stand under CO_2 until the reaction was quantitatively complete and the iodine in the solution and in the space above the solution were in equilibrium. Just before beginning the titration, the CO_2 was inadvertently turned on and substantially all of the iodine in the vapor phase was swept away. Calculate the percentage error caused by this occurrence. (*Note*: Essential data will be found in Problems 14 and 15.)

17. In standardizing an approximately 0.1 n. iodine solution, 0.2-g samples of arsenious oxide were weighed out and dissolved in 10 ml of 6 n. NaOH, and the solution was diluted to 150 ml, treated as indicated below, and then titrated to a starch end-point. Predict the result of each titration, explaining in detail the basis for your prediction.

Sample I. The solution was made neutral to litmus with HCl.

Sample II. The solution was saturated with CO_2 gas.

Sample III. The solution was made neutral to litmus with HCl and saturated with CO_2 gas.

Sample IV. To the solution was added 10 ml of 6 f. H_3PO_4.

Sample V. The solution was made neutral to litmus, and 10 ml of 6 f. Na_3PO_4 were added.

Sample VI. The solution was made neutral to litmus, and 10 ml of 6 f. Na_2HPO_4 were added.

Sample VII. The solution was made neutral to litmus, 10 ml of 3 n. Na_2CO_3 were added, and the solution was then saturated with CO_2.

Sample VIII. To the solution was added 2.8 g of solid P_2O_5.

Sample IX. The solution was neutralized, and 10 ml of 6 f. Na_2HAsO_4 were added.

Sample X. The solution was made neutral to litmus, and 10 ml of a solution 6 f. in Na_2SO_3 and 0.6 f. in $NaHSO_3$ were added.

The Use of the Iodine Monochloride End-Point

(See pp. 85–88 for a discussion of this end-point and P. 47 for its application to the estimation of antimony.)

1. What weight of KIO_3 should be taken to prepare a solution which would be exactly 0.1 n. when used with the iodine monochloride end-point? What advantages do iodate solutions possess as standard oxidizing agents?

2. *The standardization of an iodate solution against arsenious oxide.* An iodate solution of unknown concentration was standardized as follows: 0.2014 g of As_2O_3 were weighed out, dissolved in 20 ml of cold 12 n. HCl, and transferred to a ground-glass-stoppered flask, 5 ml of CCl_4 were added, and the solution was titrated with the iodate solution until the iodine color which developed at the beginning of the titration was just removed, 41.07 ml of the iodate being required. Write the equations for the successive reactions taking place and calculate the normality and formality of the iodate solution.

3. A 0.5146-g sample of a stibnite material was treated first as directed in P. 47, Note 6, and then by the second and fourth paragraphs of Note 2 of that procedure. A 0.02487 f. KIO_3 solution was used for the titration, 35.46 ml being required. Calculate the percentage of Sb_2S_3 in the stibnite.

4. A dichromate solution was standardized as follows: A 25.00-ml portion was pipeted into a flask, and 5 ml of CCl_4 and 5 ml of 6 n. HCl and then 25.00 ml of 0.15000 f. KI were added. The solution was then titrated with 0.02500 f. KIO_3 (concentrated HCl being added so that the final solution was approximately 6 n. in HCl) until the CCl_4 showed no iodine color, 30.00 ml being required. Write the equations for the successive reactions taking place. Calculate the normality of the dichromate solution.

5. To 10.00 ml of a solution of As_2O_3 in 12 n. HCl were added 5 ml of CCl_4 and 5 ml of 0.1 f. ICl in 4 n. HCl. A color was produced in the CCl_4. The solution was then titrated with 0.04000 f. $KMnO_4$ until this color disappeared, 20.00 ml of the $KMnO_4$ solution being required. Write the equations for the successive reactions taking place. Calculate the weight of As_2O_3 in the original solution.

6. A 0.5000-g sample of a mixture of $KClO_4$ and $KMnO_4$ was added to 25.00 ml of 0.2000 f. KI and 25 ml of 12 n. HCl, and an iodine color resulted. This solution was then titrated with a 0.2000 n. $KMnO_4$ solution until the iodine color disappeared, 25.00 ml being used. Calculate the weight of $KMnO_4$ in the original sample.

Ionization Methods of Volumetric Analysis (Neutralization and Displacement Methods)

(A discussion of neutralization and displacement methods will be found on pp. 89–97. The applications of neutralization methods are listed on p. 109.)

1. In the preparation of a supply of constant-boiling hydrochloric acid, it was found that at 760 mm and 25°C. the density of the distillate was 1.09620. A gravimetric analysis of a 1.5694-g (air weight) sample of the distillate gave 1.2486 g of silver chloride. Calculate the normality of constant-boiling hydrochloric acid under the above conditions.

2. Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923), give the following table:

Composition of Constant-Boiling Hydrochloric Acid

Atmospheric Pressure During Distillation (mm of Hg)	Percentage by Weight of HCl in Distillate (vacuum weight)	Air Weight of Distillate Containing 1 mole of HCl
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.555

Calculate what weight of the acid (distilled at 740 mm) should be taken in order that just 40 ml of an exactly 0.1 n. NaOH solution may be used in a titration.

3. *The standardization of a base solution against benzoic acid.* A supply of pure benzoic acid ($C_6H_5 \cdot COOH$, $K_A = 6.6 \times 10^{-5}$) was just melted at 130° to 135°C. in a covered beaker, cooled,

broken up into particles of convenient size, and stored in a weighing bottle. A 0.6273-g sample was dissolved in 20 ml of alcohol in a 200-ml flask, the solution was diluted to 50 ml, 3 drops of phenolphthalein indicator were added, and the solution was titrated with a carbonate-free sodium hydroxide solution, 27.58 ml being used. A 20-ml portion of alcohol was diluted to 75 ml with carbon dioxide–free water and similarly titrated with the sodium hydroxide, 0.04 ml of the NaOH being used. Calculate the normality of the sodium hydroxide.

Approximately what error would have been introduced if the solid sodium hydroxide from which the solution just standardized had been prepared had contained 1 per cent by weight of Na_2CO_3?

How could the titration have been modified to give correctly the total alkalinity (carbonate and hydroxide) of the solution?

Which of the indicators shown in Fig. 16 could have been used to give results correct to within 0.2 per cent (assuming the alkali to be carbonate-free)?

4. *The standardization of an acid solution against sodium oxalate.* In the standardization of a hydrochloric acid solution, a 0.6824-g sample of sodium oxalate was weighed into a clean crucible and placed in an electric oven, and the temperature was gradually raised from 250° to 500°C. during an hour and then kept at that temperature for 30 min. Under these conditions, Na_2CO_3 is formed with evolution of CO. The crucible was cooled and transferred to a beaker, and the carbonate was dissolved in 50 ml of water and treated as directed in the last paragraph of P. XVII, 35.00 ml of the HCl being used. Calculate the normality of the HCl. How could the titration have been carried out if phenolphthalein were the only indicator available?

The heating of another sample of $Na_2C_2O_4$ was carried out in such manner that 1 per cent of the oxalate was converted to Na_2O. What error was caused in the standardization of the HCl?

5. A supply of borax was prepared, and a 1.2540-g sample was weighed out and titrated as directed in P. XVII, Note 8, 28.43 ml of an HCl solution being used. Calculate the normality of the HCl solution.

6. *The standardization of an acid solution against potassium iodate.*[3] To 100 ml of water were added 0.2542 g of KIO_3, 1 g of KI, 6 g of $Na_2S_2O_3 \cdot 5H_2O$, and 5 drops of methyl orange indicator solution. The solution was then titrated with a hydrochloric acid solution until the indicator changed, 35.21 ml being required. To 1 g of KI, 1 g of $Na_2S_2O_3 \cdot 5H_2O$, and 5 drops of indicator in 150 ml of water, acid was added until a similar color was obtained, 0.04 ml being required. Calculate the normality of the acid.

7. (a) A 0.800-g sample of a material containing both nitrates and ammonium salts was treated by P. 96, "Estimation of Ammonia"; 50.00 ml of 0.2014 n. HCl were used in the receiving flask and 28.72 ml of 0.1982 n. NaOH for the final titration. Calculate the percentage of NH_3 in the material.

(b) The residual solution was then treated by P. 181 (the test for nitrate or nitrite, with the K_2HgI_4 reagent being omitted), 50.00 ml of the standard

[3] See Kolthoff, *J. Am. Chem. Soc.*, **48**, 1447 (1926), for a comparison of potassium iodate, borax, and sodium carbonate as primary standards for acid solutions.

acid used above being initially added to the receiving vessel. The excess acid required 24.62 ml of the base. Calculate the percentage of nitrate (NO_3^-) present.

8. *The analysis of carbonate-hydrocarbonate mixtures.* A sample of technical sodium carbonate was analyzed for carbonate and hydrocarbonate as follows: A 2.10-g sample was dissolved and diluted to the mark in a 250-ml flask. A 50.00-ml portion was pipeted out and titrated as in the last paragraph of P. XVII, 37.80 ml of 0.2016 n. HCl being required. A second 50.00-ml portion was taken and 10.00 ml of 0.2021 n. NaOH were added. A 2-g portion of solid $BaCl_2 \cdot 2H_2O$ was then dissolved in water and added, and the mixture was titrated at once with the standard HCl, phenolphthalein being used as indicator, until the pink color disappeared, 8.62 ml of the acid being required. Calculate the percentages of Na_2CO_3 and $NaHCO_3$ in the material. (*Note*: More representative samples are obtained by weighing out large samples, diluting to volume, and taking an aliquot portion. The above method is also applicable to the analysis of mixtures of carbonate and hydroxide. The total alkalinity is determined as in the first step, the carbonate is then precipitated with barium chloride, and the hydroxide is titrated as in the second titration above.)

9. *The analysis of carbonate-hydrocarbonate mixtures.* In the analysis of a mixture of sodium carbonate and hydrocarbonate, a 5.00-g sample was dissolved and diluted to exactly 250 ml in a volumetric flask. A 50.00-ml portion was pipeted into a large flask and diluted to 200 ml, the solution was cooled, 1 drop of a 1 per cent phenolphthalein indicator solution was added, and the solution was titrated slowly until the color was the same as that in a similar flask containing 0.5 g of pure $NaHCO_3$ and the same volume of water and indicator; 25.75 ml of 0.2201 n. HCl were used for the titration. Exactly 50 ml of the standard HCl were pipeted into the solution, which was then heated to boiling for 10 min. and titrated with 0.2142 n. NaOH to the first appearance of the pink color, 2.74 ml being required. Calculate the percentage of Na_2CO_3 and $NaHCO_3$ in the mixture. (*Note*: A reference solution is necessary in obtaining the first end-point, or an error of several per cent may result. Simpson, *J. Ind. Eng. Chem.*, **16**, 709 (1924), recommends a mixed indicator of thymol blue and cresol red in the ratio of 6 to 1 for the titration. This titration is not advised for the analysis of mixtures containing a high ratio of hydrocarbonate to carbonate.)

10. A solid commercial preparation was found by a qualitative analysis to give an aqueous solution which could contain as possible constituents only the following ions in significant amounts: (a) The common alkali metal cations; (b) carbonate; (c) hydrocarbonate; and (d) hydroxide.

In carrying out a quantitative analysis, 50.00 ml of the original solution of the preparation, made by dissolving 145.0 g of the solid in exactly 1 l of water, were titrated with 0.500 n. HCl in a cold dilute solution, thymol blue being used as indicator; 100.0 ml of acid were required.

Next, to 25.00 ml of the original solution were added 20.00 ml of 0.5000 n. NaOH and a large excess of barium chloride. The resulting precipitate was filtered out, washed, and reserved. The filtrate was titrated with 0.1000 n. HCl in a cold dilute solution, thymol blue being used as indicator; 37.50 ml of the acid were required.

Finally, the precipitate was added to a solution containing 75.00 ml of 1 n. HCl, and the mixture was boiled for 5 min., cooled, and titrated in a cold

dilute solution with exactly N/3 NaOH, thymol blue being used as indicator; 37.50 ml of the base were required.

State (a) two methods by which an original solid material giving a solution of the above properties could be made; (b) the *p*H of the original solution above; (c) the *p*H of a solution made by diluting the original solution with 3 volumes of water; and (d) your critical opinion of the method of analysis and the accuracy of the various data.

11. *The analysis of phosphate mixtures.* An analysis of a phosphate buffer solution was desired. A 25.00-ml portion was pipeted into a flask and titrated with 0.2014 n. HCl, with methyl orange being used as indicator, until the color matched that in a comparison solution containing 0.75 g of KH_2PO_4 in the same volume of water, 23.25 ml being used. Another 25.00-ml portion was taken, thymolphthalein indicator was added, and the solution was titrated with 0.1892 n. NaOH until the color matched that in a solution of the same volume containing 0.75 g of Na_2HPO_4, 26.61 ml of the base being used. Calculate the formal concentration of the solution in monohydrogen and in dihydrogen phosphate. Calculate the *p*H of the buffer solution. (*Note*: The *p*H change at the equivalence-point in titrations involving the partial neutralization of polybasic acids is usually not sufficiently great to give a sharp end-point, and, therefore, it is difficult to titrate merely to a color change. The end-point should be obtained by matching the color with a comparison solution prepared to contain in the same volume the same amount of indicator and approximately the same amount of the salt as will be formed by the titration.)

12. *The analysis of soda ash.* In the analysis of a commercial soda ash, a 4.541-g sample was dissolved and diluted to exactly 250 ml in a volumetric flask. A portion of exactly 25 ml was then pipeted out and titrated with 0.1996 n. HCl, the titration being carried out as directed in P. XVII; 40.46 ml of the acid were required. Calculate the percentage of Na_2O in the soda ash. (*Note*: As soda ash may not be a homogeneous material, it is advantageous to dissolve a large sample and take aliquot portions of the solution.) How could the titration be performed if phenolphthalein were the only indicator available?

13. *The analysis of concentrated acids.* In the analysis of a glacial acetic acid, an approximately 5-g sample was transferred by means of a dry dropper to a previously weighed weighing bottle and the closed bottle was again weighed. The acid was then washed into a 500-ml volumetric flask, with a large funnel in the mouth of the flask to prevent loss, and the solution was diluted to the calibration mark and thoroughly mixed. A portion was transferred into a flask with a 25-ml pipet and titrated with sodium hydroxide, with phenolphthalein being used as indicator. The data obtained were as follows:

Weight of weighing bottle	20.367 g
Weight of weighing bottle and acid	25.199 g
Volume of 25-ml pipet	25.02 ml
Volume of 500-ml flask	500.6 ml
Volume of NaOH used	19.92 ml
Normality of the NaOH	0.2012 n.

Calculate the percentage concentration and the formal concentration of the acid, assuming the density of the acid to be 1.045. Which of the indi-

cators shown in Fig. 16 could be used in the titration to give results correct to within 0.2 per cent?

Applications of the Mass-Action Law

14. (a) Calculate the value of the constant K_n for the neutralization of ammonia with hydrochloric acid.

(b) Calculate the hydrogen and hydroxyl ion concentrations and the *p*H and *p*OH when to 100.0 ml of 0.2 n. NH_4OH there are added 99.8, 100.0, and 100.2 ml of 0.2 n. HCl.

(c) Which of the indicators shown in Fig. 16 could be used to give results correct to within approximately 0.2 per cent in the titration of ammonia with a strong acid?

15. *The transition range of acid-base indicators.* The general statement is made that the human eye cannot detect less than about 10 per cent of one color of a two-color indicator in the presence of the other color. Assuming this to be true, show that the transition range of a two-color indicator usually extends over about 2 *p*H units.

16. In the titration of an organic acid ($K_A = 2 \times 10^{-5}$) with a strong base, an indicator with a constant, K_{In}, having the value 5×10^{-6} was used. Assuming that the color change was noted when the indicator was 20 per cent transformed to the basic form, calculate (a) the hydrogen ion concentration at the end-point; (b) the ratio of organic acid to anion (salt) at that point; and (c) the percentage error in the titration of the acid.

17. *Displacement titrations.* Calculate the hydrogen ion concentration at the equivalence-point in the titration of an 0.2 f. KCN solution with an 0.2 n. solution of a strong acid.

18. *Displacement titrations.* Assuming that, in the titration of the KCN in Problem 17, the hydrogen ion concentration changes as it would in the titration of a 0.2 n. base having an ionization constant numerically equal to the hydrolysis constant of KCN, which of the indicators listed in Fig. 16 could be used to give results correct to within approximately 0.2 per cent?

19. *Buffer solutions.* (a) To 1 l of water 10 ml of 10 f. HCl are gradually added. Calculate approximately the H^+ concentration when 0, 0.10, 1.0, 4, 5, 6, and 10 ml have been added. Plot the *p*H as ordinate against the corresponding number of milliliters of reagent added. (In this and the following parts of this problem neglect the change in volume with addition of reagents.)

(b) Repeat these calculations and plot the *p*H for the case where 10 ml of 10 f. NaOH are similarly added to 1 l of water. On the right side of the plot, write in a scale of the values of $-\log(OH^-)$ corresponding to the *p*H scale on the left side.

(c) Repeat these calculations and plot the *p*H for the case where 10 ml of 10 f. HCl are added to 1 l of 0.05 f. NaOH.

(d) Repeat these calculations and plot the *p*H for the two cases where to 1 l of a solution 2 f. in Na_2HPO_4 and 1 f. in NaH_2PO_4 are similarly added (1) 10 ml of 10 f. HCl, and (2) 10 ml of 10 f. NaOH.

Compare the change in the hydrogen ion concentration in (a), (b), and (c) with that in (d).

(*Note*: See P. XII for a discussion of buffer solutions.)

20. *Buffer solutions.* Calculate the hydrogen ion concentration of a solution prepared by mixing 200 ml of 1 f. $HC_2H_3O_2$ and 200 ml of 1 f.

$NaC_2H_3O_2$. Calculate approximately the hydrogen ion concentration if (a) 100 ml of the solution were diluted to 200 ml; (b) 100 ml of 0.1 f. HCl were added to 100 ml of the solution; (c) 100 ml of 1 f. HCl were added to 100 ml of the solution.

21. *Buffer solutions.* It is desired to prepare 100 ml of a solution having an initial hydrogen ion concentration of 3.6×10^{-5} m. and of such composition that, upon the formation of 10 millimoles of hydrogen ion during the course of a reaction, the hydrogen ion concentration will not exceed 7.2×10^{-5}. Calculate the minimum initial concentrations of acetic acid and of acetate which will provide the desired conditions.

GRAVIMETRIC METHODS

1. A 0.5-g precipitate of silver chloride was heated in a 30-ml crucible and the crucible was closed and allowed to cool in a desiccator until it and the air in the desiccator were at 25°C. Crucible and contents were then weighed in a balance case in which the air was at 20°C., dry, and at a barometric pressure of 740 mm. Calculate in milligrams and as a percentage the error in the weight of the precipitate caused by the warm air in the crucible, neglecting the effects of convection currents and of possible unequal expansion of the balance arms caused by the warm crucible. Data: The density of dry air at 20°C. and 740 mm is 0.00117 g/cc. *Ans.* 0.6 mg; 0.12 per cent.

2. A hydrochloric acid solution was standardized by P. XVIII *C*. A pipet delivering 25.01 ml at 20°C. was used at that temperature, and the silver chloride precipitate was found to weigh 0.3584 g. The precipitate was collected on a paper with a stated ash content of 0.04 mg. Calculate the normality of the acid. Should a correction for the ash of the paper be made?

3. In a determination of the HCl content of a constant-boiling solution, a 0.5726-g sample was weighed out and diluted to 150 ml, a small excess of silver nitrate was added, the mixture was allowed to stand in the dark for 24 hr., and the precipitate was collected on a Munroe crucible, washed free of silver with a 1 per cent HNO_3 solution, washed free of acid with water, and dried at 130°C. The weight of the precipitate was 0.4561 g. The filtrate and washings were evaporated and the dissolved silver chloride was determined nephelometrically, the equivalent of 0.2 mg of HCl being found. Calculate the grams of HCl per gram of the constant-boiling solution.

4. The bismuth in an alloy was determined by precipitating and weighing it as BiOCl. Calculate the factor (called the *gravimetric factor*) by which the weight of the precipitate must be multiplied in order to obtain the weight of bismuth.

5. Calculate the gravimetric factor for each of the cases given in the accompanying table.

Substance Being Determined	Form in Which Weighed
Al_2O_3	$AlPO_4$
$(NH_4)_2SO_4$	$BaSO_4$
As_2O_3	$MgNH_4AsO_4 \cdot 6H_2O$
P	$Mg_2P_2O_7$
P_2O_5	$(NH_4)_3PO_4 \cdot 12MoO_3$

6. A 0.2500-g sample of NaCl is dissolved in water, 50.0 ml of a 0.100 n. $AgNO_3$ solution is added, and the mixture is diluted to 500 ml. Calculate the formal concentration of the excess $AgNO_3$.

7. A 0.800-g sample of pyrite (containing 87.50 per cent FeS_2) was decomposed with aqua regia and bromine, the silica was filtered out, the iron was precipitated with ammonia, and the filtrate was neutralized. Calculate the volume of 0.50 n. $BaCl_2$ required to precipitate the sulfate present as $BaSO_4$.

8. The sulfur in a pyrite (FeS_2) is being determined by converting it to sulfate and then precipitating and weighing the $BaSO_4$. If it is desired that each milligram of $BaSO_4$ obtained represent 0.1 per cent sulfur in the sample, what weight of the sample must be taken?

9. A 0.1936-g sample consisting of a mixture of pure KCl and KBr is dissolved and the halides are precipitated with $AgNO_3$. The weight of the precipitate was 0.3311 g. Calculate the percentage by weight of chloride and of bromide in the mixture. How many significant figures are justified? Explain. What would be the relative percentage error caused in each of these values by an error of 0.3 mg in weighing the silver precipitate?

10. In the analysis of an 0.5000-g sample of a mixture of soluble salts, the chloride and iodide present gave a silver precipitate weighing 0.3781 g. After heating the precipitate in a stream of chlorine, the weight was 0.2867 g. Calculate the percentage of chloride and iodide in the original sample.

11. During the course of a chloride determination, a silver chloride precipitate was allowed to stand in bright light until, when it was weighed, 10 per cent of it could be represented by the formula Ag_2Cl. What would be the relative percentage error introduced into the analysis?

12. Calculate the normality of a hydrochloric acid solution which was standardized as follows: A small beaker was carefully cleaned, dried at 120°C., and weighed. Very pure silver nitrate crystals were then added, and the beaker and crystals were again weighed. Just sufficient water to dissolve the crystals and then 50.00 ml of the hydrochloric acid solution were slowly added by means of a pipet. The beaker was put into a larger beaker and placed on a hot plate, and the mixture was evaporated to dryness without being allowed to boil. The residue and beaker were then dried at 120°C. and weighed. Data: Weight of beaker, 32.4265 g; weight of beaker and $AgNO_3$, 34.9427 g; weight of beaker and residue, 34.6755 g.

Applications of Mass-Action Principles

13. One liter of water at 100°C. dissolves 0.0211 g of silver chloride. A 0.2923-g sample of sodium chloride was dissolved in 100 ml of water, and to this was added 100 ml of 0.1000 n. $AgNO_3$. The mixture was heated to boiling and filtered. Calculate the weight of silver chloride dissolved by the filtrate.

14. In carrying out a chloride determination, the solution has a volume of 250 ml, the filtration is made at 100°C., and the weighing of the silver chloride precipitate is made accurate to 0.05 mg. Calculate the required molal concentration of the excess silver ion in the solution in order that the loss of silver chloride in the filtrate may be not greater than the weighing error. How many milliliters of 0.2 n. $AgNO_3$ would this represent?

15. In a gravimetric determination a 0.2500-g barium sulfate precipitate was obtained. Calculate the percentage error caused by the solubility of the precipitate if only an exactly equivalent amount of the precipitant had been added, the volume was 500 ml, and the temperature during the filtration was 100°C. Data: The solubility of barium sulfate at 100°C. is 0.0039 g/l.

Calculate the molal concentration of the excess precipitant necessary to reduce the error to 0.1 per cent. What volume of 0.1 n. precipitant does this represent? What would be the effect of the acidity of the solution on the solubility of the precipitate?

16. A precipitate of strontium sulfate weighing 0.5 g is washed with 250 ml of water at room temperature. If it is assumed that the wash water becomes saturated in the process, calculate the loss in weight of the precipitate and the percentage error caused. Data: A saturated solution of $SrSO_4$ at 20°C. is 8.2×10^{-4} f. Calculate what would have to be the molal concentration of sulfate ion in the wash water in order to prevent a loss of over 0.1 per cent.

17. In the preceding problems no *p*H data have been given, and it has been assumed that the solutions have been neutral. This is usually not the case in gravimetric precipitations, and the effect of the acidity of the solution is illustrated in this problem.

In making a sulfate determination, a 0.7103-g sample of pure Na_2SO_4 was dissolved in water, 25 ml of 0.50 n. $BaCl_2$ and 10.0 ml of 5.0 n. HCl were added, and the mixture was diluted to 500 ml, allowed to stand until equilibrium was attained, and filtered. Calculate the weight of the precipitate dissolving in the filtrate. *Ans.* 0.044 mg of $BaSO_4$.

The Preparation of the Sample

1. A 1000-g sample which is composed of particles of pyrite (80 per cent) and quartz (20 per cent) is to be crushed and quartered. Calculate the maximum permissible weight of the largest particle in order that the addition or removal of this particle from the quarter will not cause an error of more than 0.1 per cent in the determination of the sulfur in the sample.

The material is to be passed through a sieve in order to insure that no larger particles are present. Calculate approximately what should be the size of the sieve openings.

2. Predict the result of heating the following substances as directed in Part III of P. 3: (1) $NaHSO_4$, (2) $NiCO_3$, (3) $HgCl_2$, (4) $MgNH_4AsO_4 \cdot 6H_2O$, (5) $KClO_3$, (6) K_2SiF_6, (7) AgCN, (8) Na_2SO_3, (9) $CaC_2O_4 \cdot H_2O$, (10) $NaNH_4HPO_4 \cdot 4H_2O$, (11) $Na_2S_2O_3 \cdot 5H_2O$, and (12) KNO_3.

3. Explain the possible effects of organic matter upon the system of analysis.

4. Predict the effect of heating the following substances to fuming with an excess of concentrated (a) H_2SO_4 and (b) $HClO_4$: (1) AgI, (2) $CrCl_2(H_2O)_4 \cdot Cl \cdot 2H_2O$, (3) $KMnO_4$, (4) $CaC_2O_4 \cdot H_2O$, (5) $HgCl_2$, (6) $C_{12}H_{22}O_{11}$ (sugar), (7) $MnSO_4 \cdot 4H_2O$, (8) $CaSiF_6$, (9) $Fe_4[Fe(CN)_6]_3$ and (10) $BaSO_4$.

5. A sample composed of MnO_2 and $CaSiO_3$ is carried through the procedures for the preparation of the solution. Explain the types of solvent action occurring in each step.

6. In preparing solutions for qualitative analyses, (a) CuS, (b) pure sand, (c) PbO_2, (d) HgS, (e) CaF_2, and (f) ignited Cr_2O_3 were successively treated with the following reagents: (1) HNO_3 (6 n.), (2) HNO_3 (16 n.), (3) HCl (12 n.), (4) HCl (12 n.) and HNO_3 (16 n.), (5) $HClO_4$ (fuming), (6) HF and $HClO_4$, and (7) Na_2CO_3 and $NaNO_3$ (fusion). Predict with what reagent each substance will be dissolved and explain briefly by mass-action and solubility principles the solvent action taking place.

7. *The gravimetric determination of tin as the dioxide.* A 0.4872-g sample of a bronze was treated by P. 5, II, the nitric acid solution being evaporated *almost to dryness*, and then 5 ml of HNO_3 and 50 ml of water were added and the mixture was filtered (paper pulp being added to help retain the precipitate). The residue was collected on a quantitative paper filter and washed with hot 0.6 n. HNO_3, the paper was burned off in a porcelain crucible, and the residue was ignited at the full heat of a Meker-type burner (an oxidizing flame being used to prevent possible reduction of the oxide to the metal) for 30 min., cooled, and weighed. The weight of the ignited precipitate was 0.1247 g; calculate the percentage of tin in the alloy.

What other elements are quantitatively precipitated as insoluble acids or hydrous acidic oxides by being heated with (1) HNO_3, (2) $HClO_4$, (3) H_2SO_4, (4) HCl? (*Note*: Arsenic and phosphoric acids are so completely coprecipitated by an excess of stannic oxide that this separation cannot be used in their presence.)

The solution is evaporated *almost* to dryness to precipitate the tin more completely and to prevent the precipitate from separating in a colloidal form; if the solution were evaporated to dryness, other elements would be coprecipitated in large amounts. Devise a method for testing the ignited precipitate for coprecipitated copper and lead.

8. *The volatilization of silica* (see P. 7). A concentrated hydrofluoric acid of commerce was stated to be 47 per cent HF by weight and to have a specific gravity of 1.16. Calculate the formality of this solution and the volume theoretically required to volatilize a 0.5-g residue of pure ignited silica. Write the equation for the reaction taking place when an excess of hydrofluoric acid is added.

9. In the analysis of a specimen of a hydrated magnesium silicate, a sample was ignited at 1200°C. in a platinum crucible to constant weight. The residue was then treated with hydrofluoric and perchloric acid (as directed in P. 7) and again ignited and weighed. The following data were obtained:

Weight of empty crucible	21.2436 g
Weight of crucible and sample	22.3520
Weight of crucible and residue from ignition	22.2079
Weight of crucible and residue from HF	21.7274

Calculate the formula of the silicate.

SULFIDE PRECIPITATIONS AND SEPARATIONS

(See P. 11 and P. 61 for discussions of various sulfide separations and for values for the solubility products of certain sulfides.)

1. Show that the solubility of a sulfide of the type $M^{++}S^{=}$ in a solution saturated with H_2S is directly proportional to the solubility product of the sulfide and to the square of the hydrogen ion concentration.

2. Calculate how many milligrams of lead would remain in 100 ml of a solution in which the final hydrogen ion concentration was 0.3 m. and which was saturated with H_2S at room temperature and 1 atmosphere pressure. Discuss the uncertainty in this calculation arising from (a) the solubility-

product value, (b) activity effects, (c) supersaturation phenomena, and (d) possible complex ion formation.

3. Assuming that equilibrium was attained, calculate the solubility product of zinc sulfide from the data given for Experiments 14 and 15 of Table XXII, p. 324.

4. Calculate how many milligrams of zinc would remain in 100 ml of a solution in which the final hydrogen ion concentration was 0.3 m. and which was saturated with H_2S at room temperature and 1 atmosphere pressure. How can this result be reconciled with the conditions used in P. 11 for the precipitation of the Hydrogen Sulfide Group?

5. A solution containing zinc perchlorate is to be saturated with hydrogen sulfide at 25°C. and 1 atmosphere pressure. If it is desired that not over 0.065 mg of zinc remain in 100 ml of the solution, calculate the maximum permissible hydrogen ion concentration at the conclusion of the precipitation.

6. Calculate the solubility product of cobalt sulfide from the data of the last experiment shown in Table XXVI, p. 328, assuming that the error of −13.5 mg of cobalt represents the cobalt remaining in the solution. Are there any explanations for the divergence between this calculated value and the one shown in Table X, p. 199? Would a similar divergence result if the solubility product of nickel sulfide were calculated from the data of Table XXVI and compared with the value shown in Table X? Which of these sets of values would be the more useful in attempting to calculate the *p*H required to prevent the precipitation of cobalt and nickel as sulfides?

7. A solution having a volume of 100 ml and containing 590 mg of cobalt as the perchlorate is to be saturated with hydrogen sulfide at room temperature and atmospheric pressure. Using the solubility product of cobalt sulfide obtained in Problem 6, calculate the hydrogen ion concentration necessary to prevent the precipitation of any cobalt sulfide.

8. A solution having a volume of 100 ml and containing 590 mg of cobalt and 650 mg of zinc (as perchlorates) is to be saturated with hydrogen sulfide with the object of so completely precipitating the zinc as sulfide that not more than 0.065 mg of zinc remains in the solution and none of the cobalt is precipitated. What are the upper and lower limits between which the hydrogen ion concentration must be held in order to accomplish this separation? Discuss the various buffering materials suitable for this purpose. If sodium sulfate (Na_2SO_4) and sodium hydrosulfate ($NaHSO_4$) are used, calculate what weight of each of the substances must be used in order that the initial $[H^+]$, before precipitation of the zinc sulfide, may be that of the lower limit and that the final $[H^+]$, after the precipitation, may be that of the upper limit.

9. Hydrogen sulfide gas is passed into a liter of a solution 0.1 f. in ammonia until 0.025 formula weight of the gas has been absorbed. What is the *formal* concentration of the ammonium sulfide in the resulting solution? On the basis of an approximate calculation of the ratio of the molal concentrations of sulfide ion, S^-, to hydrosulfide ion, HS^-, state which of the following equations more nearly represents the reaction occurring:

$$NH_4OH + H_2S = NH_4HS + HOH.$$
$$2NH_4OH + H_2S = (NH_4)_2S + 2H_2O.$$

10. Calculate the ratio of the molal concentrations of sulfide ion to hydrosulfide ion in a solution 1 m. in hydroxyl ion.

11. A volume of 100 ml of a mercuric salt solution, which is also 1 f. in potassium iodide, is saturated with hydrogen sulfide at room temperature and 1 atmosphere pressure in order to precipitate the mercury as sulfide. Calculate the maximum permissible hydrogen ion concentration if it is desired that not more than 0.2 mg of the mercury remain in the solution.

12. As a result of his investigations, Knox, *Trans. Far. Soc.*, **4**, 29 (1908), gives for the solubility product of mercury sulfide the value 3×10^{-54} and for the constant $K = [Hg^{++}]\,[S^{=}]^2/[Hg\,S_2^{=}]$ the value 1.96×10^{-55}. If it is desired to dissolve 200 mg of mercury in 100 ml of a solution which is 1 f. in Na_2S, calculate what would have to be the hydroxyl ion concentration of the solution.

HYDROXIDE PRECIPITATIONS AND SEPARATIONS

(See P. 51 and P. 63 for discussions of various hydrolytic separations. See Table III, p. 544, for solubility-product data.)

1. Calculate the maximum hydrogen ion concentration at which ferric hydroxide could be so completely precipitated that not more than 0.55 mg of iron would remain in 100 ml of solution.

2. Calculate the minimum hydrogen ion concentration which will maintain 500 mg of manganese (as an ionized salt) in 100 ml of solution.

3. *Separations by the use of ammonium hydroxide and ammonium salts.* Kolthoff and Kameda, *J. Am. Chem. Soc.*, **53**, 832 (1931), have found that soluble zinc salts can be maintained in solution (up to 0.1 f.) if the *p*H is not greater than approximately 6. In attempting the separation of ferric iron from zinc by an ammonia precipitation, an excess of 1 drop (0.04 ml) of 1 n. NH_4OH over that required to precipitate the iron is added; the volume of the solution is 100 ml. Calculate what must be the ammonium ion concentration in order to avoid the precipitation of any zinc. Is ammonia and ammonium salt an efficient buffering system for this separation? What additional effect contributes toward maintaining the zinc in solution?

4. *The "basic acetate" separation* (P. 63). Given a solution 0.1 f. in both ferric and zinc salts in which it is desired to precipitate the iron as hydroxide so completely that not more than 0.01 per cent remains in the solution without at the same time causing the precipitation of any zinc, calculate the maximum and minimum hydrogen ion concentrations which will give the desired result. Calculate the geometrical mean of the maximum and minimum values, and the necessary concentrations of acetic acid and acetate ion to buffer the solution initially at this value and not have the $[H^+]$ increase to over 10^{-4} after precipitation of the iron.

5. Kolthoff, Stenger, and Moskovitz, *J. Am. Chem. Soc.*, **56**, 812 (1934), have recommended that benzoic acid and ammonium benzoate be used as a buffer system for the separation of iron, aluminum, and chromium from the bipositive metals of the Ammonium Sulfide and Alkaline Earth Groups. If it is desired to retain in 100 ml of solution as much as 500 mg of zinc, calculate the maximum ratio of the molal concentrations of benzoate to benzoic acid which can be used.

MISCELLANEOUS PROBLEMS

1. *The solubility of lead sulfate in sulfuric acid solutions* (P. 24). Calculate the molal sulfate ion concentration in sulfuric acid solutions which are 0.3 f. and 3 f., respectively. Explain why a tenfold change in the sulfuric acid concentration in this concentration range produces so little change in the solubility of lead sulfate.

2. *The stability of the ferric thiocyanate end-point in the presence of a silver chloride precipitate* (P. 27). Taking the upper value given for the thiocyanate concentration necessary to produce a detectable red color (p. 37), calculate what volume of 0.1 n. KSCN would have to be added to 100 ml of a solution saturated with a precipitate of silver chloride before a stable red color would be obtained. Repeat the calculation for a solution saturated with silver bromide.

3. *The solubility product of bismuth phosphate* (P. 54). It has been found experimentally that the solubility of $BiPO_4$ is approximately 1 mg/l (at 25°C.) in a solution 0.10 f. in NaH_2PO_4 and 0.50 f. in HNO_3. Calculate the solubility product of bismuth phosphate. Point out any approximations and assumptions involved in the calculation. *Ans.* 3×10^{-27}.

4. *The metathesis of $BaSO_4$ by a carbonate solution* (P. 81). It is desired that a 0.233-g precipitate of barium sulfate be completely metathesized into barium carbonate. If the volume of the metathesizing solution is 100 ml, calculate the minimum molal concentration of carbonate in the final solution which will accomplish this.

5. *The precipitation of barium chromate from acid solutions* (P. 82). It is desired to precipitate the barium from a solution so completely that not more than 0.1 mg per 100 ml remains. Potassium chromate is added until the amount in solution in excess of that equivalent to the barium is 0.1 f. Calculate the maximum permissible hydrogen ion concentration in the solution. In order to simplify the calculation, the hydrochromate, $HCrO_4^-$, can be assumed to be negligible in comparison with the dichromate, $Cr_2O_7^=$. (*Note*: The acidity is lower than this value in P. 82, as the precipitation is made from a hot solution and as it is desirable to avoid supersaturation effects.)

6. *The separation of barium from strontium* (P. 82). Calculate the ratio of the molal concentrations of strontium ion to barium ion in a solution in equilibrium with both solid strontium chromate and barium chromate. What does this value indicate as to the possibility of making a satisfactory separation of barium from strontium by means of the selective precipitation of barium chromate?

7. *The separation of barium from strontium* (P. 82). In P. 82 the precipitation of barium is made in a volume of approximately 50 ml of a solution containing 1 ml of 6 n. $HC_2H_3O_2$, 3 ml of 3 n. $NH_4C_2H_3O_2$, and 3 ml of 3 n. K_2CrO_4. Calculate the maximum amount of barium and of strontium which will remain in the solution if equilibrium conditions prevailed. (*Note*: It is found experimentally that considerably larger amounts of strontium than this calculated value are not precipitated in P. 82; this may be due to uncertainty in the solubility-product value, to the use of concentrations instead of activities in the above calculation, to the precipitation being

carried out in a hot solution, or to the formation of supersaturated solutions.)

8. *The conversion of ammonium salts to ammonia by hydroxyl ion.* If it is desired, in P. 96, to convert any ammonium salts to ammonia so completely that the ratio of the molal concentration of the ammonia to that of the ammonium ion is at least 1000 to 1, calculate the concentration of the excess sodium hydroxide which would be required.

9. *The metathesis of silver chloride by carbonate* (P. 111). A sample containing 2 g of silver chloride is treated by P. 111. Calculate the amount in milligrams of chloride which would theoretically be found in the solution.

10. *The separation of sulfide and cyanide* (P. 121). In P. 121 the *p*H of the solution is buffered to 5.5. Calculate the ratios of the molal concentrations of (a) H_2S to $S^=$, (b) H_2S to HS^-, (c) HCN to CN^-, (d) H_2SO_3 to HSO_3^-, and (e) HF to F^- in this solution.

11. *The metathesis of silver iodate, silver bromate, and silver oxalate by carbonate* (P. 141). Calculate the maximum number of milligrams of each of these constituents passing into solution at room temperature when an excess of the silver salt is treated with 25 ml of 3 n. sodium carbonate until equilibrium is attained.

12. *The metathesis of silver iodide by sulfide at various pH values* (P. 142). (a) Calculate approximately the hydrogen ion and sulfide ion concentrations in a solution 6 f. in NH_4OH and 1 f. in $(NH_4)_2S$. (b) Calculate the ratio of the molal concentration of iodide to sulfide in a solution in equilibrium with both silver sulfide and silver iodide. What does this value indicate in regard to the completeness of metathesis, under equilibrium conditions, of silver iodide into silver sulfide? (c) An excess of a precipitate of silver iodide is treated with 25 ml of a solution which is kept saturated with H_2S and in which the hydrogen ion concentration is kept 1 m. Calculate how many milligrams of iodide would pass into the solution.

13. *The extraction of iodine from an aqueous solution by carbon tetrachloride* (P. 143). An aqueous solution containing 250 mg of iodine in a volume of 15 ml was shaken with two successive 10-ml portions of carbon tetrachloride until equilibrium was established between the two phases and was then separated from the carbon tetrachloride solutions. Calculate the amount of iodine remaining in the aqueous layer. Explain why it has been found experimentally that the removal of iodine in P. 143 does not proceed as efficiently as these calculations would indicate.

14. *The separation of the Halide Group constituents as their silver salts.* (a) Calculate the ratio of the molal concentrations of chloride to thiocyanate in a solution in equilibrium with solid silver chloride and silver thiocyanate. (*Note:* This ratio sets the limit to the completeness that theoretically can be expected from any method of separating chloride and thiocyanate as the silver salts. The treatment of a mixed precipitate with an ammonia solution would be an example of such a method.)

(b) On the basis of the same type of calculation as was used in (a), predict which constituents of the Halide Group could be separated in a ratio of 1 part in a 1000 from any other constituent of that group by any method depending upon the difference in the solubility of the silver salts.

15. *The separation of chloride and iodide by means of ammonia.* A mixed precipitate of silver chloride and iodide is treated with 50 ml of an ammonia solution. Calculate (a) the minimum concentration of the ammonia required to dissolve 250 mg of chloride and (b) the maximum concentration which will not dissolve over 0.1 mg of iodide.

16. *The preparation of an ammoniacal magnesium nitrate solution.* In preparing a magnesium nitrate solution, 130 g of $Mg(NO_3)_2 \cdot 6H_2O$ were dissolved in water and 35 ml of 6 n. NH_4OH were added, with the result that a precipitate formed. It is desired to dilute the final solution to 1 l. Calculate how much solid NH_4NO_3 should be added so that a clear solution will result.

17. *The precipitation of arsenate and phosphate by an alkaline magnesium nitrate reagent* (P. 162). The precipitation of arsenate and phosphate is made from a solution which contains 120 milli-equivalents of ammonium ion and 20 milli-equivalents of magnesium nitrate in a volume of approximately 70 ml. Calculate the maximum number of milli-equivalents of ammonium hydroxide which could be present without causing a precipitate of magnesium hydroxide. To how many milliliters of 6 n. NH_4OH does this number correspond?

Tables

TABLE I

The Solubility-Product Values of Certain Slightly Soluble Salts (at Room Temperature)

See Table X, p. 199, for the solubility products of certain sulfides and Table III, p. 544, for those of certain hydroxides. The values below have been taken from various sources in the literature and, except for approximate calculations, should be used with caution, as in many cases they appear to have been calculated from formal solubility values without adequate corrections for activity and hydrolysis effects. Considerable experimental difficulty attends the determination of the solubility of very slightly soluble salts, and widely divergent values are often found in the literature.

Salt	Solubility Product
Barium salts:	
$BaCO_3$	7×10^{-9}
$BaCrO_4$	3×10^{-10}
BaF_2	3×10^{-6}
$Ba(IO_3)_2$	1×10^{-9}
BaC_2O_4	3×10^{-7}
$BaSO_4$	1×10^{-10}
Calcium salts:	
$CaCO_3$	1×10^{-8}
CaF_2	3×10^{-11}
$Ca(IO_3)_2$	6×10^{-7}
CaC_2O_4	2×10^{-9}
$CaSO_4$	6×10^{-5}
Cadmium salts:	
CdC_2O_4	1×10^{-8}
Copper salts:	
Cupric:	
$Cu(IO_3)_2$	2×10^{-7}
CuC_2O_4	3×10^{-8}
Cuprous:	
CuBr	4×10^{-8}
CuCl	1×10^{-6}
CuI	4×10^{-12}
CuSCN	2×10^{-11}
Iron salts:	
Ferrous:	
FeC_2O_4	2×10^{-7}
Lead salts:	
$PbCrO_4$	2×10^{-14}
$PbCl_2$	2×10^{-4}
PbClF	3×10^{-9}
$PbBr_2$	7×10^{-5}
PbF_2	5×10^{-8}
$Pb(IO_3)_2$	2×10^{-13}
PbI_2	1×10^{-8}
PbC_2O_4	3×10^{-11}
Lead salts:—*Continued*	
$PbSO_4$	2×10^{-8}
Magnesium salts:	
$MgCO_3$	3×10^{-5}
MgF_2	7×10^{-9}
MgC_2O_4	1×10^{-5}
Mercury salts:	
Mercurous:	
Hg_2Br_2	1×10^{-21}
Hg_2Cl_2	2×10^{-18}
Hg_2I_2	7×10^{-29}
Hg_2SO_4	6×10^{-7}
Silver salts:	
$AgC_2H_3O_2$	4×10^{-3}
$AgBrO_3$	6×10^{-5}
AgBr	5×10^{-13}
Ag_2CO_3	5×10^{-12}
AgCl	1×10^{-10}
Ag_2CrO_4	2×10^{-12}
$Ag.Ag(CN)_2$	2×10^{-12}
$AgIO_3$	2×10^{-8}
AgI	1×10^{-16}
$AgNO_2$	7×10^{-4}
$Ag_2C_2O_4$	5×10^{-12}
Ag_2SO_4	8×10^{-5}
AgSCN	1×10^{-12}
Strontium salts:	
$SrCO_3$	2×10^{-9}
$SrCrO_4$	3×10^{-5}
SrF_2	3×10^{-9}
SrC_2O_4	1×10^{-7}
$SrSO_4$	5×10^{-7}
Zinc salts:	
$ZnCO_3$	3×10^{-8}
ZnC_2O_4	3×10^{-9}

TABLE II

Molal and Formal Reduction Potentials (at 25°C.)

Because of the value of the molal and formal potentials in predicting the behavior of the elements in their various oxidation states, this table has not been restricted to the so-called common elements or to the acidic constituents included in this book. The values below were collected or calculated by Dr. Clifford S. Garner from various sources; a considerable number of the formal potential values were calculated from measurements made over a number of years by selected students as part of the course in analytical chemistry at the California Institute of Technology. For a comprehensive treatment of the potentials of the elements in their various oxidation states, see Latimer, *Oxidation Potentials*, Prentice-Hall, 1938.

See the discussion of electronic reactions, pp. 47–53, for the distinction between *molal* and *formal* potentials and for illustrations of the use of these values.

Reaction	Molal Potential, E_0 (v)	Formal Potential, E_0' (v)			
		HCl (1 f.)	$HClO_4$ (1 f.)	H_2SO_4 (1 f.)	Other Solutions
$Li_{(s)} = Li^+ + E^-$	+2.957	..	..	..	..
$Rb_{(s)} = Rb^+ + E^-$	+2.924	..	..	..	..
$K_{(s)} = K^+ + E^-$	+2.922	..	..	..	..
$Sr_{(s)} = Sr^{++} + 2E^-$	+2.9	..	..	..	..
$Ba_{(s)} = Ba^{++} + 2E^-$	+2.9	..	..	..	..
$Ca_{(s)} = Ca^{++} + 2E^-$	+2.88	..	..	..	..
$Na_{(s)} = Na^+ + E^-$	+2.712	..	..	..	..
$Mg_{(s)} = Mg^{++} + 2E^-$	+1.9	..	..	..	..
$Al_{(s)} = Al^{+++} + 3E^-$	+1.7	..	..	..	..
$2N_3^- = 3N_{2(g)} + 2E^-$	+1.2	..	..	..	..
$Mn_{(s)} = Mn^{++} + 2E^-$	+1.03	..	..	..	..
$Fe_{(s)} + 2OH^- = Fe(OH)_{2(s)} + 2E^-$	+0.86	..	..	..	..
$H_{2(g)} + 2OH^- = 2H_2O_{(l)} + 2E^-$	+0.829	..	..	..	..
$Zn_{(s)} = Zn^{++} + 2E^-$	+0.758	..	..	..	..
$Fe(OH)_{2(s)} + OH^- = Fe(OH)_{3(s)} + E^-$	+0.65	..	..	..	..
$Cr_{(s)} = Cr^{++} + 2E^-$	+0.6	..	..	..	..
$Pb_{(s)} + 2OH^- = PbO_{(s)} + H_2O_{(l)} + 2E^-$	+0.58	..	..	..	..
$S^= = S_{(s)} + 2E^-$	+0.51	..	..	..	..
$H_2Se_{(g)} = Se_{(s)} + 2H^+ + 2E^-$	+0.5	..	..	..	..

$Fe_{(s)} = Fe^{++} + 2E^-$	+0.44	..	..	..	..
$H_{2(g)} = 2H^+(10^{-7}m) + 2E^-$	+0.414	..	..	..	..
$Cr^{++} = Cr^{+++} + E^-$	+0.4	..	..	..	..
$Cd_{(s)} = Cd^{++} + 2E^-$	+0.398	..	..	..	..
$2Cu_{(s)} + 2OH^- = Cu_2O_{(s)} + H_2O_{(l)} + 2E^-$	+0.34	..	..	..	..
$Tl_{(s)} = Tl^+ + E^-$	+0.336	+0.551	+0.33	+0.33	..
$Co(CN)_6^{---} = Co(CN)_6^{--} + E^-$	+0.3	..	..	..	..
$Co_{(s)} = Co^{++} + 2E^-$	+0.28	..	..	..	..
$Ni_{(s)} = Ni^{++} + 2E^-$	+0.23	..	..	..	..
$V^{++} = V^{+++} + E^-$	+0.2	..	+0.21	..	..
$Ag_{(s)} + I^- = AgI_{(s)} + E^-$	+0.151	..	..	..	..
$Sn_{(s)} = Sn^{++} + 2E^-$	+0.14	..	+0.16	..	..
$Pb_{(s)} = Pb^{++} + 2E^-$	+0.12	..	+0.14	+0.29	+0.32 (2 f. NaAc)
$2Hg_{(l)} + 2I^- = Hg_2I_{2(s)} + 2E^-$	+0.042	..	..	..	..
$2Ag_{(s)} + H_2S_{(g)} = Ag_2S_{(s)} + 2H^+ + 2E^-$	+0.04	..	..	..	..
$H_{2(g)} = 2H^+ + 2E^-$	±0.000	+0.005	+0.005	..	+0.005 (1 f. HNO_3)
$2OH^- + NO_2^- = NO_3^- + H_2O_{(l)} + 2E^-$	−0.0	..	..	..	..
$Ti^{+++} + H_2O_{(l)} = TiO^{++} + 2H^+ + E^-$	−0.04	..	..	−0.04	..
$Ag_{(s)} + Br^- = AgBr_{(s)} + E^-$	−0.073	..	..	..	..
$Ag_{(s)} + SCN^- = AgSCN_{(s)} + E^-$	−0.095	..	..	..	−0.159 (0.1 f. KSCN)
$Hg_{(l)} + 2OH^- = HgO_{(s)} + H_2O_{(l)} + 2E^-$	−0.098	..	..	..	..
$2Hg_{(l)} + 2Br^- = Hg_2Br_{2(s)} + 2E^-$	−0.139	..	..	..	..
$SO_{2(g)} + 2H_2O_{(l)} = HSO_4^- + 3H^+ + 2E^-$	−0.14	..	..	−0.07	..
$Sn^{++} = Sn^{++++} + 2E^-$		−0.14	..	..	..
$Co(NH_3)_6^{++} = Co(NH_3)_6^{+++} + E^-$		..	..	..	−0.16 (3.3 f. NH_4OH)
$H_2S_{(g)} = S_{(s)} + 2H^+ + 2E^-$	−0.17	..	..	..	..
$Cu^+ = Cu^{++} + E^-$	−0.17	−0.45	..	..	..
$Pt_{(s)} + 4Cl^- = PtCl_4^{--} + 2E^-$	−0.2	..	..	..	..
$Sb_{(s)} + H_2O_{(l)} = SbO^+ + 2H^+ + 3E^-$	−0.21	..	−0.213	−0.213	..
$Ag_{(s)} + Cl^- = AgCl_{(s)} + E^-$	−0.224	..	..	..	..
$As_{(s)} + 3H_2O_{(l)} = H_3AsO_3 + 3H^+ + 3E^-$	−0.24	..	−0.249	−0.25	..
Saturated calomel half-cell		..	..	..	−0.246
$2Hg_{(l)} + 2Cl^- = Hg_2Cl_{2(s)} + 2E^-$	−0.269	..	..	..	..
Normal calomel half-cell	..	..	..	..	−0.282
$Bi_{(s)} + H_2O_{(l)} = BiO^+ + 2H^+ + 3E^-$	−0.31	..	..	..	−0.34 (0.02 f. HCl)

TABLE II—*Concluded*

Reaction	Molal Potential, E_0 (v)	Formal Potential, E_0' (v)			
		HCl (1 f.)	$HClO_4$ (1 f.)	H_2SO_4 (1 f.)	Other Solutions
$H_2S_{(g)} + 4H_2O_{(l)} = HSO_4^- + 9H^+ + 8E^-$	−0.316	..	..	−0.294	..
$Cu_{(s)} = Cu^{++} + 2E^-$	−0.345	..	..	..	..
$Fe(CN)_6^{=} = Fe(CN)_6^{=} + E^-$	−0.356	−0.71	−0.72	−0.72	−0.56 (0.1 f. HCl) −0.48 (0.01 f. HCl) −0.46 (0.01 f. NaOH)
$4OH^- = O_{2(g)} + 2H_2O_{(l)} + 4E^-$	−0.40	..	..	..	..
$U^{++++} + 2H_2O_{(l)} = UO_2^{++} + 4H^+ + 2E^-$	−0.4	..	..	−0.4	..
$V^{+++} + H_2O_{(l)} = VO^{++} + 2H^+ + E^-$	−0.4	..	..	−0.360	..
$PtCl_4^= + 2Cl^- = PtCl_6^= + 2E^-$	−0.44	..	..	..	..
$2Ag_{(s)} + CrO_4^= = Ag_2CrO_{4(s)} + 2E^-$	−0.446	..	..	..	..
$CuCl_2^- = Cu^{++} + 2Cl^- + E^-$	−0.46	..	..	..	..
$MoO^{+++} + 2H_2O_{(l)} = MoO_{2(s)} + 4H^+ + E^-$	−0.5	..	..	..	..
$2I^- = I_{2(s)} + 2E^-$	−0.536	..	..	..	..
$3I^- = I_3^- + 2E^-$	−0.54	..	..	..	..
$H_3AsO_3 + H_2O_{(l)} = H_3AsO_4 + 2H^+ + 2E^-$	..	−0.577	−0.577	..	..
$MnO_4^= = MnO_4^- + E^-$	−0.6	..	..	..	..
$2Hg_{(l)} + SO_4^= = Hg_2SO_{4(s)} + 2E^-$	−0.621	..	..	..	..
$Hg_2Cl_{2(s)} + 2Cl^- = 2HgCl_2 + 2E^-$	−0.63	..	..	..	..
$H_2O_2 = O_{2(g)} + 2H^+ + 2E^-$	−0.69	..	..	..	..
$C_6H_4(OH)_2 = C_6H_4O_2$ (quinone) $+ 2H^+ + 2E^-$	−0.699	−0.696	−0.696	−0.696	..
$Mo(CN)_8^{=} = Mo(CN)_8^{=} + E^-$	−0.73	..	..	..	..
$Sb_2O_{3(s)} + 2H_2O_{(l)} = Sb_2O_{5(s)} + 4H^+ + 4E^-$	−0.73	..	..	..	..
$Se_{(s)} + 3H_2O_{(l)} = H_2SeO_3 + 4H^+ + 4E^-$	..	..	..	..	−0.75 (0.1 f. $HClO_4$)
$Fe^{++} = Fe^{+++} + E^-$	−0.782	−0.700	−0.732	−0.68	−0.61 (H_2SO_4 1 f.; H_3PO_4 0.5 f.)
$2Hg_{(l)} = Hg_2^{++} + 2E^-$	−0.798	−0.274	−0.776	−0.674	−0.282 (1 f. KCl)
$Ag_{(s)} = Ag^+ + E^-$	−0.799	−0.228	−0.792	−0.77	..
$CuI_{(s)} = Cu^{++} + I^- + E^-$	−0.85	..	..	..	..

$Hg_2^{++} = 2Hg^{++} + 2E^-$	..	..	−0.907	..	..
$HNO_2 + H_2O_{(l)} = 3H^+ + NO_3^- + 2E^-$	..	..	..	..	−0.92 (1 f. HNO_3)
$Hg_{(l)} + H_2O_{(l)} = HgO_{(s)} + 2H^+ + 2E^-$	−0.93	..	..	..	..
$Cl^- + 2OH^- = ClO^- + H_2O_{(l)} + 2E^-$	−0.94	..	..	..	..
$NO_{(g)} + 2H_2O_{(l)} = NO_3^- + 4H^+ + 3E^-$	−0.94	..	..	..	..
$NO_{(g)} + H_2O_{(l)} = HNO_2 + H^+ + E^-$	−0.98	..	..	..	..
$VO^{++} + H_2O_{(l)} = VO_2^+ + 2H^+ + E^-$	−1.000	−1.02	−1.02	−1.0	..
$IrCl_6^{=} = IrCl_6^- + E^-$	..	−1.02	..	..	..
$I_{2(s)} + 4Cl^- = 2ICl_2^- + 2E^-$	.	−1.06	..	..	−1.05 (4 f. HCl)
$2Br^- = Br_{2(l)} + 2E^-$	−1.066	..	..	..	..
$\frac{1}{2}I_{2(s)} + 3H_2O_{(l)} = IO_3^- + 6H^+ + 5E^-$	−1.19	..	..	..	..
$H_2SeO_3 + H_2O_{(l)} = H_2SeO_4 + 2H^+ + 2E^-$	−1.2	..	..	..	..
$2H_2O_{(l)} = O_{2(g)} + 4H^+ + 4E^-$	−1.23	.	..	..	..
$Mn^{++} + 2H_2O_{(l)} = MnO_{2(s)} + 4H^+ + 2E^-$	−1.24	..	−1.24	..	..
$Tl^+ = Tl^{+++} + 2E^-$	−1.25	−0.77	−1.26	−1.22	−1.23 (1 f. HNO_3)
$2Cr^{+++} + 7H_2O_{(l)} = Cr_2O_7^= + 14H^+ + 6E^-$	−1.3	..	..	..	..
$ICl_2^- + 2Cl^- = ICl_4^- + 2E^-$	..	..	..	..	−1.31 (4 f. HCl)
$2Cl^- = Cl_{2(g)} + 2E^-$	−1.359	..	..	..	..
$Au_{(s)} + H^+ + 4Cl^- = HAuCl_4 + 3E^-$	..	−1.4	..	..	..
$Cl^- + 3H_2O_{(l)} = ClO_3^- + 6H^+ + 6E^-$	1.45	.	..	..	..
$Mn^{++} + 4H_2O_{(l)} = MnO_4^- + 8H^+ + 5E^-$	−1.45	..	..	..	..
$Pb^{++} + 2H_2O_{(l)} = PbO_{2(s)} + 4H^+ + 2E^-$	−1.47	..	−1.47	−1.628	..
$Ce^{+++} = Ce^{++++} + E^-$	..	..	−1.7	−1.44	−1.61 (1 f. HNO_3)
$Cl^- + H_2O_{(l)} = HClO + H^+ + 2E^-$	−1.50	..	..	..	..
$MnO_{2(s)} + 2H_2O_{(l)} = MnO_4^- + 4H^+ + 3E^-$	−1.59	..	..	..	..
$2Bi^{+++} + 5H_2O_{(l)} = Bi_2O_5 + 10H^+ + 4E^-$	−1.7	..	..	..	..
$2H_2O_{(l)} = H_2O_2 + 2H^+ + 2E^-$	−1.77	..	..	..	..
$Co^{++} = Co^{+++} + E^-$	..	..	..	−1.82	−1.83 (1 f. HNO_3) −1.85 (4 f. HNO_3)
$Ag^+ = Ag^{++} + E^-$	..	..	..	..	−1.91 (1 f. HNO_3) −2.00 (4 f. $HClO_4$)
$2SO_4^= + 2H^+ = H_2S_2O_8 + 2E^-$	(?)	..	..	..	..
$O_{2(g)} + H_2O_{(l)} = O_{3(g)} + 2H^+ + 2E^-$	−2.07	..	.	..	..
$2F^- = F_{2(g)} + 2E^-$	−2.88	..		..	..

TABLE III

THE APPROXIMATE PRECIPITATION *p*H AND SOLUBILITY PRODUCTS OF THE OXIDES AND HYDROXIDES OF CERTAIN ELEMENTS
(Arranged in the Order of Their Precipitation as the Hydrogen Ion Concentration Is Decreased)

Element and Oxidation State	Precipitation *p*H	Approx. $K_{S.P.}$	Element and Oxidation State	Precipitation *p*H	Approx. $K_{S.P.}$
Si^{IV}, Sn^{IV}, Sb^{V}	<1[a]	..	Pb^{II}	7	
Bi^{III}, Sb^{III}	2	..	Fe^{II}		
Fe^{III}	3	10^{-36}	Cd^{II}, Ni^{II}, Co^{II}	8	
Sn^{II}			Mn^{II}	9	10^{-14}
Al^{III}	5	..	Ag^{I}	..	10^{-8}
Cr^{III}, Cu^{II}	6		Mg^{II}	11	10^{-11}
Zn^{II}		10^{-17}			

The *p*H values, which are taken largely from the data of Britton, *J. Chem. Soc.*, **127**, 2110-2159 (1925), are given only to show the approximate *p*H at which precipitation occurs in solutions 0.005 to 0.025 f. in the various salts used; they do not indicate the *p*H at which quantitative precipitation can be obtained. This precipitation *p*H will be shifted by temperature changes, by the concentration of the precipitating cation, by the presence of complex-forming anions or of cations which may cause the formation of stable colloidal systems, and, in certain cases, by a slow rate of hydrolysis and precipitation. The solubility-product values have been taken from various sources and should be used only for approximate predictions, as their application is subject to certain of the effects mentioned above as well as to the effect of partial hydrolysis and basic-salt formation.

[a] These acidic oxides are dissolved in acid solutions only when complex-forming anions are present.

TABLE IV

IONIZATION CONSTANTS OF ACIDS AND BASES (AT 25°C.)

Acid or Base	Formula	Ionization Constant
Acids:		
Acetic	$HC_2H_3O_2$	1.8×10^{-5}
Arsenic	H_3AsO_4	$K_1 = 5.6 \times 10^{-3}$ $K_2 = 1.7 \times 10^{-7}$ $K_3 = 3 \times 10^{-12}$
Arsenious	H_3AsO_3	$K_1 = 6 \times 10^{-10}$ $K_2 = 3 \times 10^{-14}$
Benzoic	$HC_7H_5O_2$	6×10^{-5}
Boric	H_3BO_3	6.4×10^{-10}
Carbonic	H_2CO_3	$K_1 = 3 \times 10^{-7}$ $K_2 = 6 \times 10^{-11}$
Chromic	H_2CrO_4	$K_1 = 1.8 \times 10^{-1}$ $K_2 = 3.2 \times 10^{-7}$
Formic	$HCHO_2$	2×10^{-4}
Hydrocyanic	HCN	2×10^{-9}
Hydrofluoric	HF	7.4×10^{-4}
Hydrogen sulfide	H_2S	$K_1 = 9.1 \times 10^{-8}$ $K_2 = 1.2 \times 10^{-15}$
Hypochlorous	HClO	1.1×10^{-8}
Hydrazoic	HN_3	2×10^{-5}
Iodic	HIO_3	2×10^{-1}
Nitrous	HNO_2	4.5×10^{-4}
Oxalic	$H_2C_2O_4$	$K_1 = 5.9 \times 10^{-2}$ $K_2 = 6 \times 10^{-5}$
Phosphoric	H_3PO_4	$K_1 = 7.5 \times 10^{-3}$ $K_2 = 2 \times 10^{-7}$ $K_3 = 5 \times 10^{-13}$
Phosphorous	H_3PO_3	$K_1 = 5 \times 10^{-2}$
Phthalic	$H_2C_8H_4O_4$	$K_1 = 1.2 \times 10^{-3}$ $K_2 = 3.1 \times 10^{-6}$
Sulfuric	H_2SO_4	$K_2 = 1.2 \times 10^{-2}$
Sulfurous	H_2SO_3	$K_1 = 1.3 \times 10^{-2}$ $K_2 = 5 \times 10^{-6}$
Bases:		
Ammonium hydroxide	NH_4OH	1.8×10^{-5}
Hydrazine	N_2H_5OH	3×10^{-6}

TABLE V

Dissociation Constants of Certain Complex Ions

In general, these values should be used only to give the approximate magnitude of the indicated effect. Usually, as is indicated by the silver-chloride complexes, the system is complicated by the formation of more than one complex compound, and, in addition, these compounds are formed only at such high concentrations that activity values are very uncertain.

Expression	Dissociation Constant	Expression	Dissociation Constant
$\frac{[Bi^{+++}]\,[Cl^-]^4}{[BiCl_4^-]}$	3×10^{-6}	$\frac{[Hg^{++}]\,[SCN^-]^4}{[Hg(SCN)_4^-]}$	1×10^{-22}
$\frac{[Cd^{++}]\,[NH_3]^2}{[Cd(NH_3)_4^{++}]}$	1×10^{-7}	$\frac{[HgCl_2]\,[Cl^-]^2}{[HgCl_4^-]}$	1×10^{-2}
$\frac{[Cd^{++}]\,[CN^-]^4}{[Cd(CN)_4^-]}$	1×10^{-17}	$\frac{[Hg^{++}]\,[S^-]^2}{[HgS_2^-]}$	2×10^{-55}
$\frac{[Cu^{++}]\,[NH_3]^4}{[Cu(NH_3)_4^{++}]}$	5×10^{-10}	$\frac{[Ag^+]\,[NH_3]^2}{[Ag(NH_3)_2^+]}$	6.8×10^{-8}
$\frac{[Cu^+]\,[CN^-]^3}{[Cu(CN)_3^-]}$	5×10^{-28}	$\frac{[Ag^+]\,[Cl^-]^2}{[AgCl_2^-]}$	1×10^{-5}
$\frac{[Cu^+]\,[Cl^-]^2}{[CuCl_2^-]}$	2×10^{-5}	$\frac{[Ag^+]\,[Cl^-]^3}{[AgCl_3^-]}$	5×10^{-6}
$\frac{[Cu^+]\,[Cl^-]^3}{[CuCl_3^-]}$	6×10^{-5}	$\frac{[Ag^+]\,[Cl^-]^4}{[AgCl_4^-]}$	2×10^{-5}(?)
$\frac{[Hg^{++}]\,[Cl^-]^4}{[HgCl_4^-]}$	6×10^{-17}	$\frac{[Ag^+]\,[CN^-]^2}{[Ag(CN)_2^-]}$	1×10^{-21}
$\frac{[Hg^{++}]\,[Br^-]^4}{[HgBr_4^-]}$	2×10^{-22}	$\frac{[Ag^+]\,[NO_2^-]}{[Ag(NO_2)_2^-]}$	1.5×10^{-3}
$\frac{[Hg^{++}]\,[I^-]^4}{[HgI_4^-]}$	5×10^{-32}	$\frac{[Ag^+]\,[S_2O_3^-]^2}{[Ag(S_2O_3)_2^-]}$	1×10^{-13}
$\frac{[Hg^{++}]\,[CN^-]^4}{[Hg(CN)_4^-]}$	4×10^{-42}	$\frac{[Zn^{++}]\,[NH_3]^4}{[Zn(NH_3)_4^{++}]}$	3×10^{-10}

TABLE VI

International Atomic Weights

(1938)

Element	Symbol	Atomic Number	Atomic Weight	Element	Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	163.5	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0081	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.84	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	175.0	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

J. Am. Chem. Soc., **60**, 737 (1938).

Reagents and Chemicals

The concentrations and method of preparation of the various solutions and reagents required in this system of analysis are given below.

The following conventions in regard to stating the concentration of the reagent to be used have been adopted in the procedures:

1. Where the concentration of an acid or base is not stated, a 6 n. solution is to be used.
2. Where the concentration of a salt solution is not stated, a 1 n. (metathetical) solution is to be used.
3. All other concentrations are specifically stated.

Only reagents of the specified concentration should be used.

In preparing the reagents indicated below, only the best available c.p. chemicals should be used. The percentage composition and specific gravity of the concentrated acids of various manufacturers may vary slightly from those stated, but not sufficiently to necessitate an adjustment of the amounts given below.

Solutions

Solutions of Acids and Bases

Acids:

Acetic, 6 n. Dilute 345 ml of 99.5 per cent (glacial) acid to 1 l.
Formic, 90 per cent. Use 87 to 90 per cent acid of sp.gr. 1.20.
Hydrobromic, 9 n. Use 48 per cent acid of sp.gr. 1.49.
Hydrochloric, 12 n. Use 36 per cent acid of sp.gr. 1.19.
Hydrochloric, 6 n. Dilute 500 ml of the 36 per cent acid to 1 l.
Hydrofluoric, 27 n. Use 48 per cent acid.
Hydriodic, 7 n. Use 57 per cent acid of sp.gr. 1.70.
Nitric, 16 n. Use 69 per cent acid of sp.gr. 1.42.
Nitric, 6 n. Dilute 375 ml of the 69 per cent acid to 1 l.
Perchloric, 9 n. Use 60 per cent acid of sp.gr. 1.54.
Phosphoric, 15 f. Use 85 per cent acid of sp.gr. 1.7.
Phosphorous, 6 f. Dissolve 50 g of H_3PO_3 crystals in water and dilute to 1 l.
Sulfuric, 36 n. Use 95 per cent acid of sp.gr. 1.84.
Sulfuric, 6 n. Dilute 165 ml of the 95 per cent acid to 1 l.

Bases:

Ammonium hydroxide, 15 n. Use the 29 per cent solution of sp.gr. 0.90.
Ammonium hydroxide, 6 n. Dilute 400 ml of 15 n. to 1 l.

Barium hydroxide, saturated solution, approximately 0.4 n. Shake 65 g of $Ba(OH)_2 \cdot 8H_2O$ with 1 l of water in a closed vessel, let it settle, and decant the solution through a filter. Keep in bottle with siphon outlet and inlet provided with soda-lime tube.

Potassium hydroxide, 6 n. Dissolve 400 g of 85 per cent KOH in water, cool, and dilute to 1 l.

Sodium hydroxide, 6 n. Dissolve 255 g of 95 per cent NaOH in water, cool, and dilute to 1 l.

SOLUTIONS OF SALTS

Salt	Concentration	Formula	Formula Weight	Grams per Liter[a]
Ammonium acetate	3 n.	$NH_4C_2H_3O_2$	77.06	230
Ammonium chloride	3 n.	NH_4Cl	53.50	160
Barium nitrate	0.5 n.	$Ba(NO_3)_2$	261.39	65
Cadmium nitrate	1 n.	$Cd(NO_3)_2 \cdot 4H_2O$	308.49	154
Calcium nitrate	1 n.	$Ca(NO_3)_2 \cdot 4H_2O$	236.16	118
Ferric nitrate	1 n.	$Fe(NO_3)_3 \cdot 9H_2O$	404.00	135
Ferric sulfate	3 n.; 1 f.	$Fe_2(SO_4)_3$	399.86	400
Lead acetate	1 n.	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	379.30	190
Lead nitrate	1 n.	$Pb(NO_3)_2$	331.24	166
Mercuric chloride	sat. soln.	$HgCl_2$	271.52	100
Potassium chromate	3 n.; 1.5 f.	K_2CrO_4	194.21	292
Potassium cyanide	1 n.	KCN	65.10	68
Potassium ferricyanide	1 n.	$K_3Fe(CN)_6$	329.19	110
Potassium ferrocyanide	1 n.	$K_4Fe(CN)_6 \cdot 3H_2O$	422.33	106
Potassium iodate	0.3 n.; 0.3 f.	KIO_3	214.03	65
Potassium iodide	1 n.	KI	166.03	166
Potassium nitrite	6 n.	KNO_2	85.11	600
Potassium oxalate	3 n.	$K_2C_2O_4 \cdot H_2O$	184.22	276
Potassium permanganate	0.2 n.; 0.2 f.	$KMnO_4$	158.03	32
Potassium thiocyanate	1 n.	KSCN	97.17	98
Silver nitrate	1 n.	$AgNO_3$	169.89	170
Sodium acetate	1 n.	$NaC_2H_3O_2 \cdot 3H_2O$	136.07	136
Sodium carbonate	3 n.	Na_2CO_3	105.99	159
Sodium chlorate	1 f.	$NaClO_3$	106.45	106
Sodium hydroarsenate	1 f.	$Na_2HAsO_4 \cdot 7H_2O$	312.04	312
Sodium hydrocarbonate	1 f.	$NaHCO_3$	84.00	84
Sodium hydrosulfate	6 f.	$NaHSO_4 \cdot H_2O$	138.08	800
Sodium nitrite	1 n.	$NaNO_2$	69.01	71

[a] These are the weights to be taken of the best available chemicals.

COMPOSITE SOLUTIONS

Ammonium aurin tricarboxylate, 0.0024 f.; 0.1 per cent. Dissolve 1 g of ammonium aurin tricarboxylate (aluminon), $(NH_4)_3C_{22}H_{12}O_9$, in 1 l of water, or, optionally, dissolve 1 g of aurin tricarboxylic acid, $C_{22}H_{14}O_9$, in 100 ml of 1.5 n. NH_4OH and dilute with water to 1 l.

Ammonium carbonate, 6 n. in $(NH_4)_2CO_3$ and 6 n. in NH_4OH. Add 470 ml of 15 n. NH_4OH to 240 g of solid "ammonium carbonate" (an approximately equimolal mixture of ammonium hydrocarbonate, NH_4HCO_3, and ammonium carbamate, $NH_4NH_2CO_2$) and dilute with water to 1 l.

Ammonium molybdate, 1 n. in $(NH_4)_2MoO_4$. Add 100 ml of 6 n. NH_4OH to 90 g of solid phosphate-free "ammonium molybdate," $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, and dilute with water to 1 l.

Ammonium (mono) sulfide, 6 n. Immerse a liter bottle containing 200 ml of 15 n. NH_4OH in ice water and pass a slow stream of H_2S into the solution until the gas is no longer absorbed. Add 200 ml of 15 n. NH_4OH and dilute with water to 1 l.

Antimony trichloride, 0.1 f. Dissolve 22.8 g of $SbCl_3$ in enough 3 n. HCl to make 1 l. (The antimony "test solution" may be substituted for this reagent.)

Bismuth nitrate, 0.1 f. in $Bi(NO_3)_3$ and 0.5 f. in HNO_3. Add 31 ml of 16 n. HNO_3 to 49 g of $Bi(NO_3)_3\cdot 5H_2O$ and *slowly* dilute with water to 1 l.

Bromine solution, saturated (approximately 0.2 f. in Br_2). Add small excess of liquid Br_2 to water.

Dimethylglyoxime (diacetyldioxime), 0.1 n. Dissolve 12 g of the solid in enough 95 per cent alcohol to make 1 l of solution.

Hydrogen peroxide, 1 f. Use the 3 per cent solution.

Magnesium nitrate, 0.5 f. in $Mg(NO_3)_2$, 3 f. in NH_4NO_3, and 0.2 f. in NH_4OH. Dissolve 128 g of $Mg(NO_3)_2\cdot 6H_2O$ and 240 g of NH_4NO_3 in water, add 33 ml of 6 n. NH_4OH, and dilute with water to 1 l.

Magnesium uranyl acetate, 3 n. in $MgC_2H_3O_2$, 0.5 n. in $UO_2(C_2H_3O_2)_2$, and 2 n. in $HC_2H_3O_2$. Dissolve 100 g of $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ and 120 ml of 99.5 per cent $HC_2H_3O_2$ in water, add 330 g of $Mg(C_2H_3O_2)_2\cdot 4H_2O$, and dilute to 1 l. Filter if the solution is not clear after 1 or more days.

Para-nitrobenzene-azo-resorcinol, 0.02 f.; 0.5 per cent. Dissolve 5 g of the compound in enough 0.3 n. NaOH to make 1 l of solution.

Potassium mercuric iodide, 0.5 n. in K_2HgI_4 and 3 n. in NaOH. Dissolve 166 g of KI in water, add 68 g of $HgCl_2$ and 500 ml of 6 n. NaOH, and dilute with water to 1 l. Allow any precipitate to settle, decant the clear solution, and keep it in a dark bottle.

Sodium cobaltinitrite, 1 f. in $Na_3Co(NO_2)_6$. Add 500 g of $NaNO_2$ and 291 g of $Co(NO_3)_2\cdot 6H_2O$ to 450 ml of water, then add 100 ml of 6 n. $HC_2H_3O_2$, stir for 2 to 3 min., let stand for 24 hr., filter, and dilute to 1 l. (This reagent is not stable and should be prepared within a month of the time it is to be used.)

Sodium sulfide, 1.5 f. in Na_2S, 0.5 f. in Na_2S_2, and 1 f. in NaOH. Dissolve 480 g of $Na_2S\cdot 9H_2O$ and 40 g of NaOH in the minimum amount of water, dissolve 16 g of powdered sulfur in this solution, and dilute to 1 l.

Stannous chloride, 0.5 f. in $SnCl_2$ and 3 f. in HCl. Dissolve 113 g of $SnCl_2\cdot 2H_2O$ (iron-free) in 250 ml of 12 n. HCl and dilute to 1 l. Add 10 to 20 g of "mossy" tin to the storage bottle.

Thiourea, 1 f. Dissolve 76 g of thiourea in water and dilute to 1 l.

Turmeric, half saturated. Shake an excess of turmeric with 95 per cent ethyl alcohol, filter, and dilute with an equal volume of alcohol.

Suspensions

Starch indicator. See p. 71.

Asbestos, for quantitative filters. Purchase a washed and ignited long-fiber asbestos (of the amphibole, non-hydrated type). Cut the required amount into lengths of about 0.5 cm and triturate with a little water in a mortar until all large particles are disintegrated. Heat with 6 n. HCl for several hours, filter on a Büchner funnel, and wash free of chloride. Shake with water and decant and discard the very fine powdery material. Again shake with water and decant so that about one-fifth of

the asbestos is poured off. Use this suspension to complete the filtering mat when filtering finely divided precipitates. Add sufficient water to the remainder to make a thin suspension for general use.

Standard Solutions

See the pages indicated below for detailed directions for the preparation and standardization of these solutions.

Constituents	Concentration		Page
	Normal	Formal	
Ferrous sulfate	0.1	0.1	67
Hydrochloric acid	0.2	0.2	107
Iodine (potassium tri-iodide)	0.1	0.05	69, 75
Potassium dichromate	0.1	$\frac{1}{6}$	82
Potassium cyanide	0.1	0.2	229
Potassium permanganate	0.1	0.02	59, 65
Potassium thiocyanate	0.1	0.1	42
Silver nitrate	0.1	0.1	27
Sodium hydroxide	0.2	0.2	99, 102
Sodium thiosulfate	0.1	0.1	79, 82

Hydrogen Ion Indicators

Common Name	Molecular Weight	Concentration		Solvent
		Formal ($\times 10^3$)	Grams per Liter	
Bromphenol blue	856	3.5	3	Ethanol
Bromthymol blue	624	1.6	1	Ethanol
Methyl orange	327	3.1	1	Water
Methyl red	269	7.4	2	Ethanol
Phenolphthalein	318	6.3	2	Ethanol
Phenol red	354	2.7	1	Ethanol
Thymol blue	466	2.1	1	Ethanol
Thymolphthalein	430	2.3	1	Ethanol

The alcoholic solutions of the above indicators should not be used for determining the *p*H of unbuffered solutions.

Mixed Indicators

Methyl orange and indigo carmine. Dissolve 1 g of methyl orange and 2.5 g of indigo carmine in 1 l of water.

Methyl orange and xylene cyanole FF. Dissolve 2 g of methyl orange in 500 ml of water and 2.8 g of xylene cyanole FF in 500 ml of ethanol and mix the two solutions.

Thymol blue and cresol red. Dissolve 3 g of thymol blue and 0.5 g of cresol red in 1 l of ethanol.

Indicator Papers

Litmus

Nitrazine (sodium dinitrophenylazo-naphthol disulphonate)

Wide-range indicator test papers (see P. 3, Note 6)

Pure Liquids

Alcohol, ethyl (ethanol) 99.5 per cent
Alcohol, ethyl (ethanol) 95 per cent
Alcohol, methyl (methanol)
Alcohol, tertiary butyl
Bromine
Carbon tetrachloride
Ether, ethyl
Ether, isopropyl
Nitrobenzene

Solids

Primary Standards

The compounds listed below are useful as primary standards. Those marked with an asterisk may be purchased from the United States Bureau of Standards; the others should be of a special grade intended for standardization purposes or should be prepared by the analyst.

*Arsenious oxide
*Benzoic acid
Potassium dichromate
*Potassium hydrophthalate (acid phthalate)
Potassium iodate
Silver nitrate
Sodium carbonate
*Sodium oxalate
Sodium tetraborate decahydrate (borax)

Reagents

Acid tartaric
Aluminum (turnings)
Ammonium chloride
Ammonium hydrofluoride (bifluoride)
Ammonium nitrate
Ammonium sulfate
Devardo's alloy (Cu, 50; Al, 45; Zn, 5)
Ferric sulfate (anhydrous)
Ferrous sulfate ($FeSO_4 \cdot 7H_2O$)
Lead (granular)
Manganese chloride ($MnCl_2 \cdot 4H_2O$)
Marble (chips)
Nickel (foil)
Potassium bromate
Potassium chlorate
Potassium iodide
Quartz (powdered)
Silver carbonate
Silver sulfate
Sodium bismuthate
Sodium carbonate
Sodium chloride
Sodium hydrocarbonate (bicarbonate)
Sodium hydrosulfate ($NaHSO_4 \cdot H_2O$)
Sodium hydrosulfite (bisulfite)
Sodium peroxide
Sodium peroxyborate ($NaBO_3 \cdot 4H_2O$)
Sodium peroxysulfate ($Na_2S_2O_8$)
Sodium sulfate
Zinc (granular)

Test Solutions

It is desirable that standard test solutions be available for the use of the instructor in preparing "unknowns" and for the student in preparing solutions for practice analysis and in making comparisons in order to obtain estimates of the amounts of constituents which have been separated. The practice used by A. A. Noyes[1] of preparing a *stock test solution* of 100 mg/ml and diluting this to give a *test solution* of 10 mg/ml for the reagent shelf has been adopted. There

[1] Noyes, *Qualitative Analysis*, 8th Ed., Macmillan, 1922, p. 175.

are shown below the weights of the solid compounds of the formulas given in the second column which must be taken to prepare 1 l of a *stock test solution* of the constituent shown in the first column. The accompanying notes explain where special methods or solvents are necessary in preparing these solutions. Where the composition of the solids is so uncertain that the concentrations of the resulting solutions are not sufficiently accurately known (to within 0.5 per cent for the basic constituents and 1 to 5 per cent for the acidic constituents), methods of standardization are suggested.

BASIC CONSTITUENTS

Constituent	Formula of Substance Weighed	Grams per Liter
Ag^{I}	$AgNO_3$ Dry at 105° to 110°C.	157.5
Pb^{II}	Pb (metal) Dissolve the metal, preferably freshly cleaned foil or sticks, in hot 8 n. HNO_3, evaporate off most of the excess HNO_3 on a water bath, cool, and dilute to 1 l.	100.0
Bi^{III}	Bi_2O_3 Ignite between 600° to 700°C. before weighing. Dissolve in 160 ml of 9 n. $HClO_4$, heating if necessary, and dilute to 1 l.	111.5
Cu^{II}	Cu (metal) Prepare as directed for Pb^{II}.	100.0
Cd^{II}	Cd (metal) Prepare as directed for Pb^{II}.	100.0
As^{III}	As_2O_3 Add 230.5 g of anhydrous Na_2CO_3 and 750 ml of water to the As_2O_3 in a large beaker and warm until a clear solution is obtained, cool, and dilute to 1 l. Note on label of bottle that solution contains 100.0 mg of sodium per milliliter. To prepare a *test* solution with no sodium, warm 13.20 g of As_2O_3 in a covered flask with 500 ml of 12 n. HCl, cool, and dilute to 1 l.	132.0
As^{V}	As_2O_5 Use for qualitative experiments only.	154
Hg^{I}	$Hg_2(NO_3)_2 \cdot 2H_2O$ Use for qualitative experiments only. Dissolve in 0.6 n. HNO_3.	140

BASIC CONSTITUENTS—*Continued*

Constituent	Formula of Substance Weighed	Grams per Liter
Hg^{II}	Hg (metal) Prepare as directed for Pb^{II}.	100.0
Sb^{III}	$SbCl_3$ Dissolve in 6 n. HCl; dilute with 3 n. HCl to prepare a test solution. Solutions should be standardized. Standardization; Pipet 25 ml of the test solution into a 200-ml flask, add 2 g of powdered tartaric acid, and treat by the last paragraph of P. 43. See also the discussion of P. 47.	190
Sn^{II}	$SnCl_2 \cdot 2H_2O$ Dissolve in 6 n. HCl. Keep test solution in contact with mossy tin. Stannous chloride solutions are not stable unless protected from oxygen; therefore use for qualitative experiments only.	190
Sn^{IV}	Sn (metal) Dissolve the metal, freshly cleaned sticks, in 500 ml of warm 12 n. HCl, and add liquid Br_2 if the metal dissolves slowly. Heat in a covered vessel until excess Br_2 is expelled, cool, and dilute to 1 l.	100.0
Fe^{II}	$FeCl_2 \cdot 4H_2O$ Dissolve in 0.6 n. HCl. Keep in contact with iron wire. Use for qualitative experiments only.	356
Fe^{III}	$Fe(NO_3)_3 \cdot 9H_2O$ Standardization: Pipet 25 ml of test solution into a 200-ml flask, add 10 ml of 12 n. HCl, evaporate to 10 to 15 ml, and treat by the last two paragraphs of P. 53*A*.	725
Zn	Zn (metal) Prepare as directed for Pb^{II}. Use zinc sticks, freshly scraped clean of oxide.	100.0
Ni^{II}	$Ni(NO_3)_2 \cdot 6H_2O$ Standardization: Pipet 50 ml of the test solution into a 100-ml volumetric flask, dilute to the calibration, and pipet out a 25-ml portion into a 200-ml flask. Add 5 ml of 3 n. NH_4Cl, then add NH_4OH until a clear blue alkaline solution is obtained, and treat as directed in the last paragraph of P. 65.	498
Co^{II}	$Co(NO_3)_2 \cdot 6H_2O$ Standardization: Pipet 25 ml of the test solution into a 100-ml volumetric flask, dilute to the calibration, pipet 25 ml of this solution into a 400-ml flask, and treat by the last paragraph of	495

BASIC CONSTITUENTS—*Continued*

Constituent	Formula of Substance Weighed	Grams per Liter
Mn^{II}	$Mn(NO_3)_2$(50 per cent solution) Standardization: Pipet 25 ml of the test solution into a 250-ml volumetric flask, dilute to the calibration, pipet 25 ml of this solution into a 200-ml flask, add 25 ml of 6 n. HNO_3, cool the solution in ice water, add 10 to 15 g of sodium bismuthate, swirl the solution for 1 to 2 min., add 50 ml of cold water, filter the mixture through a sintered-glass (or asbestos) filter, wash the residue with cold 0.6 n. HNO_3 (free of oxides of nitrogen) until it is colorless, and rapidly titrate the filtrate and washings with standard ferrous sulfate solution, adding 2 to 5 ml after the solution is colorless. Titrate the excess ferrous sulfate with standard permanganate solution. See Hillebrand and Lundell, *Inorganic Analysis*, Wiley, 1929, pp. 343–346, for a discussion, a procedure, and references regarding this material.	650
Al^{III} (50 mg/ml)	$Al(NO_3)_3 \cdot 9H_2O$ Standardization: Pipet a 25-ml portion of the test solution and treat as directed in P. 73 and P. 74. See Hillebrand and Lundell, pp. 393–398, for a detailed discussion and procedure.	700
Cr^{III}	$Cr(NO_3)_3 \cdot 9H_2O$ Standardization: Pipet 25 ml of the test solution into a 100-ml volumetric flask, dilute to the calibration, and pipet 25 ml of this solution into a 600-ml flask. Add 25 ml of water and slowly sprinkle in an excess of solid Na_2O_2, boil until excess peroxide is decomposed, cool, dilute to 80 ml and treat by last paragraph of P. 75.	770
Ba^{II} (Test solution)	$Ba(NO_3)_2$ Dry at 105° to 110°C.	19.02
Sr^{II}	$Sr(NO_3)_2$ Dry at 105° to 110°C.	241
Ca^{II}	$Ca(NO_3)_2 \cdot 4H_2O$ Standardization: Pipet 25 ml of the test solution into a 100-ml volumetric flask, dilute to the calibration, pipet 25 ml of this solution into a 400-ml beaker, dilute to 200 ml, add 5 ml of 6 n. HCl, and heat to 80° to 90°C. Add 3 g of $H_2C_2O_4 \cdot 2H_2O$ dissolved in 50 ml of water and 2 drops of methyl red indicator solution, then add NH_4OH until the solution just changes to yellow, and allow the solution to stand for at least an hour. Filter and wash the precipitate as directed in the second paragraph of P. 86, and then treat the precipitate by the first paragraph of P. 87.	590

BASIC CONSTITUENTS—*Continued*

Constituent	Formula of Substance Weighed	Grams per Liter
Mg^{II} (50 mg/ml)	$Mg(NO_3)_2 \cdot 6H_2O$ Standardization: Pipet 25 ml of the test solution into a 500-ml volumetric flask, dilute to the calibration, and pipet 50 ml of this into a large beaker. Add 5 ml of HCl, dilute to 100 ml, add 10 ml of 1 f. Na_2HAsO_4, and cool the solution. Add 2 drops of methyl red indicator solution and then NH_4OH, slowly, until the solution turns red. Constantly stir the solution without scratching the sides of the vessel. Add 5 ml of 15 n. NH_4OH and let the mixture stand for 12 hr. Filter and wash the precipitate as directed in P. 88 and then treat as directed in the first two paragraphs of P. 89.	535
Na^I	Na_2CO_3 Dry at 250°C. before weighing. Add 200 ml of water and then 6 n. HNO_3 until the solution is just acid to litmus. Cool and dilute to 1 l.	230.5
K^I	KNO_3 Dry at 105° to 110°C. for 2 hr.	258.6
NH_4^+	NH_4NO_3 Dry over H_2SO_4 before weighing.	445
	ACIDIC CONSTITUENTS	
$S^=$ (50 mg/ml)	$Na_2S \cdot 9H_2O$ Standardization: Pipet 25 ml of the test solution into a 100-ml volumetric flask, dilute to the calibration, pipet 25 ml of this solution into a flask, and treat as directed in P. 122.	380
CN^-	NaCN Standardization: Pipet 25 ml of the test solution into a 100-ml volumetric flask, dilute to the calibration, pipet 25 ml of this solution into a 200-ml flask, add 5 ml of 6 n. NH_4OH, and treat as directed in P. 123, Note 4.	190
$SO_3^=$	$Na_2SO_3 \cdot 7H_2O$ Standardization: Pipet 75 ml of standard iodine solution into a 500-ml flask, and then pipet 25 ml of the test solution into the iodine solution, add 100 ml of water, and titrate the excess iodine with standard thiosulfate solution.	315
$Fe(CN)_6^{\equiv}$	$K_4Fe(CN)_6 \cdot 3H_2O$	199.3
$Fe(CN)_6^{\equiv}$	$K_3Fe(CN)_6$ Dry at 105° to 110°C.	155.3
I^-	KI Dry at 105° to 110°C.	130.8

ACIDIC CONSTITUENTS—*Continued*

Constituent	Formula of Substance Weighed	Grams per Liter
SCN^-	KSCN Standardization: Fill a buret with the test solution, withdraw 25 ml into a 200-ml flask, add an excess of standard silver nitrate from a second buret, and then proceed as directed in the second paragraph of P. VI.	170
Br^-	KBr Dry at 105° to 110°C.	149.0
Cl^-	NaCl Dry at 105° to 110°C.	164.9
IO_3^- (10 mg/ml)	KIO_3 Dry at 105° to 110°C.	12. 5
BrO_3^- (10 mg/ml)	$KBrO_3$ Dry at 105° to 110°C.	13.07
ClO_3^- (10 mg/ml)	$KClO_3$ Dry at 105° to 110°C.	14.69
ClO^-	NaOCl (5 per cent solution) Dilute 750 ml to 1 l to prepare a solution of approximately 50 mg of ClO^- per milliliter. Solution is unstable. Standardization: Pipet 25 ml of test solution into a 100-ml volumetric flask, dilute to the mark, and pipet 25 ml of this solution into a 200-ml flask containing 3 g of KI, 10 ml of 6 n. $HC_2H_3O_2$, and 20 ml of 3 n. $NaC_2H_3O_2$ in 100 ml of solution. Titrate the iodine set free with standard thiosulfate solution.	
ClO_4^- (10 mg/ml)	$KClO_4$ Dry at 105° to 110°C.	13.96
IO_4^- (5 mg/ml)	KIO_4 Dry at 105° to 110°C.	6.02
$AsO_4^{\equiv}$	$Na_2HAsO_4 \cdot 7H_2O$	224.2
$PO_4^{\equiv}$	KH_2PO_4 Dry at 105° to 110°C.	142.3
$AsO_3^{\equiv}$	As_2O_3 Dissolve in 150 ml of 6 n. NaOH, cool, and dilute to 1 l.	80.7
$PO_3^{\equiv}$	H_3PO_3 Dissolve the crystals in water; use for qualitative experiments only.	105

ACIDIC CONSTITUENTS—*Concluded*

Constituent	Formula of Substance Weighed	Grams per Liter
SO_4^- (50 mg/ml)	K_2SO_4 Dry at 105° to 110°C.	90.75
$S_2O_8^-$ (10 mg/ml)	$K_2S_2O_8$ Use for qualitative experiments only.	14.0
F^-	$KF \cdot 2H_2O$ Dissolve in water, add 10 ml of 6 n. NaOH and keep in paraffined bottles. Use for qualitative experiments only.	500
NO_3^-	KNO_3 Dry at 105° to 110°C.	163
NO_2^-	$NaNO_2$ Use for qualitative experiments only.	155
BO_2^- (10 mg/ml)	$Na_2B_4O_7 \cdot 10H_2O$	22.3
$C_2H_3O_2^-$	$KC_2H_3O_2$ Use for qualitative experiments only.	166

Equipment

Desk Equipment

It is recommended that the following equipment be available in the desk locker; less frequently used articles should be obtained from the storeroom as needed.

Returnable Articles

2 beakers, 150 ml
1 beaker, 250 ml
4 beakers, 400 ml
2 beakers, 600 ml
1 bottle, n.m.g.s., 500 ml
2 bottles, n.m.g.s., 1250 ml
1 buret, glass stopcock
1 buret, for rubber pinchcock
2 burners, Tirrill, with 1 fishtail
1 casserole, 75 ml
1 casserole, 210 ml
1 clamp, buret, double
1 clamp, buret, single
1 clamp, pinch
2 crucibles, porcelain, no. 0 with lids
2 crucibles, porcelain, perforated bottom, with disks
1 crucible funnel, with rubber tubing
1 cylinder, graduated, 10 ml
1 cylinder, graduated, 100 ml
1 desiccator, 150 mm
2 filter disks, beveled
1 flask, conical, 50 ml
2 flasks, conical, 125 ml
4 flasks, conical, 200 ml
3 flasks, conical, 500 ml
1 flask, 300 ml
1 flask, ring neck, 1000 ml
1 flask, round bottom, 100 ml
1 flask, filter, 500 ml
1 flask, ground-glass stoppered, 200 ml
1 flask, volumetric, 100 ml
1 flask, volumetric, 500 ml
1 two-hole rubber stopper to fit each of the above sizes of flasks
3 funnels, 6.5 mm
2 funnels, separatory, 60 ml
1 funnel support
1 horn spoon
1 mortar and pestle, 80 mm
1 pipet, transfer, 10 ml
1 pipet, measuring, 10 ml
1 pipet, transfer, 25 ml
1 spatula, porcelain, 120 mm
1 support, iron, with 3 iron rings
12 test tubes, pyrex, with lip, 120 x 18 mm
1 test tube, pyrex, 175 x 22 mm
1 test tube, pyrex, 200 x 38 mm
1 test-tube rack
1 thermometer (360°C.)
1 thistle tube
2 triangles, nichrome
1 tongs, nichrome
2 tripods
4 watch glasses, 40 mm
2 watch glasses, 75 mm
2 watch glasses, 100 mm
2 weighing bottles, 40 x 25 mm

Non-Returnable Articles

1 brush, camel's-hair
1 box labels
1 box of matches
1 file, triangular
6 ft. gas tubing
2½ ft. glass rod, 4 mm
5 ft. glass tubing, 6 mm
2 policemen, rubber
2 rubber nipples
100 sheets filter paper, qualitative, 11 cm
100 sheets filter paper, qualitative, 9 cm
1 sheet glazed paper, 6 x 6 in.
1 sponge
1 test-tube brush
2 towels
1 tube litmus paper, blue
1 tube litmus paper, red
2 pieces wire gauze, 125 x 125 mm
18 in. rubber tubing, suction

Miscellaneous Equipment

Balance, analytical, and weights
Balance, laboratory or solution, 2 kg capacity, 10 mg sensitivity
Balance, trip
Baths, sand
Baths, steam
Burners, Meker type and blast
Condenser, small size, and adapter
Crucibles, iron
Crucibles, nickel
Crucibles, platinum
Desiccator, vacuum
Drying oven, electric
Flasks, distilling, 250 ml
Flasks, Kjeldahl, 200 ml
Filter pumps, water aspirators
Filters, paper, quantitative, assorted sizes and grades
Filters, sintered glass
Glass wool
Glass beads
Hot plate, electric
Hydrogen sulfide equipment, generator or pressure cylinder
Magnifying lens
Mortar and pestle, agate
Mortar and pestle, steel
Platinum wire, sealed into glass rods

Index

A

Absolute error, 512
Accidental errors, 513
Accuracy:
  definition, 512
  problems, 512
Acetate:
  behavior on heating with acid, 162
  detection, 490
  reaction with ethanol, 490
Acetate–acetic acid buffer solution, 282, 332, 422
Acetate (basic) separation, 282, 332
Acetic acid:
  adsorption on charcoal, 112
  odor, as test, 490
  reaction with ethanol, 490
Acetic acid–acetate buffer solution, 282, 332, 422
Acidic constituents:
  analysis of, 407–502
  estimation of, 412
  Ferrocyanide Group, 433
  Halide Group, 443
  identification in preparation of solution, 162
  instability of, 409
  interference in basic analysis, 167
  occurrence in native materials, 412
  oxidizing constituents, detection of, 415
  Oxy-Halogen Group, 459
  Phosphate Group, 469
  preliminary observations, 158
  preliminary tests, 415
  preparation of solution, 413
  reducing constituents, detection of, 417
  separation into groups, 411
  Sulfide-Cyanide Group, 421
  systems of analysis for, 409
  treatment of sodium carbonate residue, 493
Acidimetry:
  applications of, 109
  displacement methods, 104
  neutralization methods, 89
Acids (*see also* Standard solutions):
  concentration of, 548
Acids (*cont.*):
  conventions as to concentrations, 548
  dilution for wash solutions, 211
  ionization constants, 90
    table, 545
  neutralization equilibria, 90
  preparation of reagents, 548
  specific gravity of concentrated, 516
  standardization against iodate, problem, 526
  standard solutions of, 97
Acrolein, use with zinc sulfide, 327
Activity:
  and molal potentials, 50
  definition, 40
Activity coefficient, 41
Activity effects:
  hydrochloric acid in sulfide separations, 202
  in sulfate-hydrosulfate buffer, 325
  on solubility of precipitates, 111
Adsorption:
  and coprecipitation, 119
  in ammonia precipitation, 123, 286
  in chloride titration with silver, 399
  in precipitation methods, 38
  of acetic acid on charcoal, 120
  of iodine on cuprous iodide, 244
  of silver nitrate on silver iodide, 122
Adsorption indicators, 39
  dichlorofluorescein, 400
  eosin, 400
  fluorescein, 400
  in chloride titration with silver, 400
  tetrabromfluorescein, 400
Adsorption isotherm, 120
Agate mortar and pestle, use of, 156
Air oxidation:
  of iodide, 298
  of iron, 300
  of sulfide, 291
Alcohols (*see also* Methanol, Ethanol):
  behavior with hypochlorite, 461
  evaporation with perchloric acid, 395
  in precipitation of Alkaline Earth Group, 361

Alcohols, tertiary, resistance to oxidation of, 461
Alkali Group:
analysis, 385–406
detection, 387
separation, 195
Alkalimetry:
applications of, 109
displacement methods, 104
neutralization methods, 89
Alkaline Earth Group:
analysis, 360–384
coprecipitation with Ammonium Sulfide Group, 167
detection, 364
precipitation, 364
separation, 195
test analyses, 368
Alkaline Earth Group elements:
behavior in hydroxide solutions, 282
behavior with oxalate, 167
coprecipitation, 367
properties, 366
separation, 366
Aluminon:
behavior with various substances, 355
preparation of reagent solution, 549
Aluminum:
behavior:
in basic acetate precipitation, 333
with ammonium hydroxide, 284
with hydroxide and peroxide, 312
complex compounds:
with oxalate, 167
with tartrate, 311
confirmatory test, 356
detection, 317, 355
determination, colorimetric, 355
estimation, 356
precipitation, 355
separation, 290
separation from manganese, cobalt, nickel, and zinc with ammonia, 284
standardization of test solution, 555
Aluminum Group:
analysis, 346–359
separation, 195, 309
separation from Zinc Group, 200
separation, optional, 314
Aluminum hydroxide:
ignition of, 357
precipitate, drying of, 131
precipitation, 114
Aluminum hydroxide (*cont.*):
reduction on heating, 357
solubility in ammonia, 291
Aluminum metal,
reduction of acidic constituents by, 483
Aluminum oxide, behavior on heating, 164
Aluminum solder, 521
Amides, 402
Ammonia (*see also* Ammonium salts):
behavior in preparation of solution for acidic analysis, 413
complex compounds, 282, 401
detection, 401, 403, 404
estimation, 401, 404
group precipitation with, 281
coprecipitation in, 123
oxidation by ferricyanide, 436
Ammonia-nitrate molal potential, 173
Ammoniated compounds, 401
Ammonium acetate, acetic acid impurity in, 370
Ammonium aurintricarboxylate, 355
preparation of reagent solution, 549
Ammonium arseno-molybdate, 307
Ammonium carbonate, preparation of reagent solution, 549
Ammonium chloride:
behavior with nitric acid and chloride, 362
effect on Alkaline Earth Group precipitation, 361
effect on hydrogen sulfide precipitations, 204
in separation of calcium and magnesium, 376
removal of, 362
Ammonia compounds, behavior in hydroxide solutions, 401
Ammonium hydroxide:
as group precipitant, 281
equilibria in solutions, 403
Ammonium monosulfide, preparation of reagent solution, 550
Ammonium molybdate, 307
preparation of reagent solution, 550
Ammonium phosphate hexahydrate, drying of precipitate, 129
Ammonium phospho-molybdate, 307
Ammonium salts:
behavior on heating, 162
behavior with nitric acid, 362, 385
removal in Alkali Group analysis, 385

Ammonium sulfide:
behavior with Tin Group sulfides, 254
in separation of Copper and Tin Groups, 213
mercury separation with, 221
preparation of monosulfide reagent, 550
Ammonium Sulfide Group:
analysis, 280-359
behavior with oxalate, 167
coprecipitation with Hydrogen Sulfide Group, 204
detection, 289
precipitation, 281, 288
precipitation of alkaline earth oxalates with, 167
separation, 193, 281
separation into groups, 309, 314
separation of cobalt and nickel, 202
Ammonium Sulfide Group elements:
behavior in basic acetate separation, 333
in hydroxide solutions, 282
behavior with ammonium hydroxide, 284
complex compounds with oxalate, 313
coprecipitation with manganese dioxide, 348
Ammonium sulfide reagent, 447
Ammonium sulfide solutions, ion concentrations, 198
Ammonium thiocyanate, 32
Ampco metal, 522
Amylose, 70
Analysis:
for acidic constituents, 407
for basic constituents, 151
gravimetric methods of, 110
order of, 168
volumetric methods of, 22
sequence of, 168
summation of results, 520
Analytical balance (*see also* Weighing):
care of, 10, 21
chainomatic, 14
construction of, 3
damping, 9
determination of sensitivity, 13
principles of, 3
problems, 509
rider, precautions in use of, 13
Analytical balance (*cont.*):
rest point, 8
rules for use, 21
sensitivity, 5, 13
unequal arm length, 14
use, 8
Analytical results, summation, 520
Antimony:
complex compounds with tartrate, 271
detection, 255, 270, 272
determination in ores, 273
estimation, 272
in reduction of tin with nickel, 276
oxidation by iodine, 271
reduction by hydrogen sulfide, 270
reduction of tin, 276
separation from tin, 200
separation in alloys, 178
standardization of test solution, 554
titration with iodate, 273
Antimony chloride:
behavior on heating, 162
volatilization of, 271
Antimony sulfide:
behavior with ammonium sulfide, 254
behavior with nitric acid, 221
Antimony trichloride, preparation of reagent solution, 550
Approximate methods of calculation, 514
"Aqua regia," solvent action of, 179
Arsenate:
behavior with silver, 418
confirmatory test, 474
detection, 417, 474
effect on basic analysis, 167
estimation, 473
oxidation of iodide, 473
reaction with molybdate, 307
removal in basic constituent analysis, 167
separation from arsenite and oxalate, 471
Arsenic:
behavior in phosphate removal, 307
detection, 255, 260, 262
elimination of, 307
estimation, 263
oxidation by bromate, 256
separation:
from bismuth and tin, 200
from Tin Group elements, 258

Arsenic acid:
behavior with iodide, 382
reduction:
by bromide, 259
by iodide, 382
by phosphorous acid, 259
Arsenic chloride:
distillation, 259
volatility, 157, 162, 256
Arsenic sulfide:
behavior with ammonium sulfide, 254
precipitation, 115, 205
Arsenious acid:
oxidation by iodine, 71, 263
Arsenious acid-tri-iodide, equilibrium constant, 72
Arsenious oxide:
as primary standard, 71
drying of, 75
impurities in, 75
purification of, 75
solutions:
stability of, 76
standardization with iodate, problem, 524
Arsenite:
behavior with silver, 418
detection, 417, 476
estimation, 476
oxidation:
by peroxide, 475
by nitrite, 475
separation from arsenate and phosphate, 471
Arsenopyrite, 522
Asbestos, 142
for filters, 134
preparation, 550
Asbestos filters, 134, 140
Gooch, preparation, 140
preparation, 209
Ash of filter papers, 134
Aspirator:
use for drying precipitates, 129
use of, 142
Atomic weights, table, 547
Auto-catalytic reactions, 62
Average deviation:
of single measurement, 512
of the mean, 513

B

Balance (*see* Analytical balance)
Barium:
confirmatory test, 372
Barium (*cont.*):
detection, 367
estimation, 371
flame test, 372
precipitation as chromate, 367
separation, 367
Barium carbonate:
solubility product, 363
use for separations, 282
Barium chromate:
behavior with sulfuric acid, 371
solubility, 519
Barium hydroxide:
reagent, preparation of, 549
standard solution, 98
Barium sulfate:
coprecipitation with, 126, 127
coprecipitation of nitrate with, 478
metathesis with carbonate, 363
precipitate:
isomorphism in, 125
drying of, 128
precipitation, 115, 118, 478
effect of particle size, 117
solubility, 117, 519
in hydriodic acid, 190
problem, 531
solubility product, 363
Bases (*see also* Standard solutions):
concentration of, 548
conventions as to concentration of, 548
dilution for wash solutions, 211
ionization constants, table, 545
neutralization equilibria, 90
preparation of reagent, 548
standard solutions, 97
standardization, 100, 525
Basic acetate separation, 282, 332
Basic constituents:
analysis, 152–406
elimination of organic material, 166
effect of phosphate, 305
preliminary observations, 158
preparation of sample, 153
preparation of solution, 169
separation into groups, 193
Benzoic acid:
as standard, 100
in hydroxide separations, 282
ionization constant, 334, 525
standardization of bases, problem, 525
Bicarbonate (*see* Hydrocarbonate)

Bismuth:
behavior with sulfuric acid, 230
confirmatory test for, 241
hydrolysis in sulfuric acid, 230
complex compounds with chloride, 238
detection, 237, 238
estimation:
gravimetric, 239
volumetric, 238
precipitation, 236
separation, 236
Bismuthate, oxidation of manganese, 352, 555
Bismuth chloride, hydrolysis of, 223
Bismuth nitrate reagent, preparation, 550
Bismuth oxychloride (*see* Bismuthyl chloride)
Bismuth phosphate
solubility:
in acids, 305
problem, 536
Bismuthyl chloride:
drying of precipitate, 128, 130
precipitation, 238
Bismuthyl hydroxide:
behavior with stannite, 241
coprecipitation with, 124
solubility, 236
in acids, 238
stability, 236
Bismuthyl pyrosulphate, hydrated, 230
Bismuthyl sulfate, 230
Blast burner, temperature of, 148
Boat, 500
Boiling of solutions:
directions, 207
prevention of bumping, 261
Borax:
as primary standard, 103, 108
preparation of standard, 108
titration with hydrochloric acid, 108
Borda's method of weighing, 15
Boric acid, behavior:
with curcumin, 488
with methyl alcohol, 497
with tumeric, 488
Borate (*see also* Boric acid):
behavior with silver, 418
detection, 488, 498
Bromate:
behavior with silver, 443
detection, 416, 417, 418, 444, 460
Bromate (*cont.*):
indication of, 460
reduction by nitrite, 418, 459
by peroxide, 459
Bromide:
behavior with permanganate and cyanide, 453
detection, 418, 456
estimation, 457
oxidation by permanganate, 455
reduction in acid solution, 425
separation from other halides, 448
Bromine:
as oxidizing agent, 256
behavior with iodide, 457
extraction:
with carbon tetrachloride, 455
with various solvents, 450
oxidation:
of cobalt, 296
of iron, 296
of nickel, 296
of sulfur, 296
of thiocyanate, 296
Bromine solution reagent, preparation, 550
Bromine cyanide, 449, 453
Bromoform:
extraction:
of bromine, 450
of iodine, 450
Bromphenol blue indicator, 101
Buffer solutions, 73
acetic acid—acetate, 282, 332, 422
benzoic acid—benzoate, 282, 334
fluoride—hydrofluoric acid, 245
formic acid—formate, 282, 322, 334
in hydroxide separations, 282
problems, 529
succinic acid—succinate, 282, 334
sulfate-hydrosulfate, 217, 323, 324, 454
Bulbs, calibration, 30
Bumping, 261
Bunsen burner, temperature of, 148
Buoyancy, correction in weighing, 16
Bureau of standards:
primary standards, 552
tolerance of glassware, 44
Buret:
calibration, 46
care of, 44
cleaning, 45
filling, 60, 228
reading, 45
Burners, use of, 148

C

Cadmium:
complex compounds, 236, 433
detection, 247
determination, 249
estimation, 249
precipitation, 247
precipitation of complex iron cyanides, 433
Cadmium ferrocyanide, oxidation by nitric acid, 433
Cadmium tetrammino ion, 236
Cadmium sulfide:
adsorption by, 124
behavior with ferric salts, 249
coprecipitation of cadmium salts, 249
precipitate, 247
Calcium:
confirmatory test, 380
coprecipitation with strontium chromate, 372
detection, 375
estimation, 378
precipitation as oxalate, 375
separation from magnesium, 367, 375
standardization of test solution of, 555
Calcium fluoride, precipitation, 480
Calcium oxalate:
drying of precipitate, 131
precipitation, 376
Calcium sulfate monohydrate, particle size and solubility, 117
Calculation:
approximate methods, 514
of titration-curve data, 35
of solubility products, 35
of weight calibration, 19
significant figures, 12
Calibrating bulbs, 30
Calibration:
of buret, 46
of pipet, 44
of volumetric apparatus, 30, 45
relative, 75
problems, 516
of weights, 16
Carbon dioxide:
absorption by hydroxides, 99
adsorption of, 501
equilibrium solubility in water, 100
error in neutralization titrations, 103
Carbon dioxide (*cont.*):
saturated solution, 105
supersaturation in distilled water, 100
test for, 163
Carbon disulfide extraction:
of iodine, 450
of bromine, 450
Carbon tetrachloride extraction:
of iodine, 450
of bromine, 450
Carbonate:
behavior:
on heating with acid, 162
with alkaline earth elements, 288
with silver, 418
decomposition, 499
detection, 499
estimation, 499
in preparation of solution for acidic analysis, 413
metathesis of barium sulfate, 363
preliminary identification of, 163, 164
test for, 500
Carbonate-hydrocarbonate:
buffer solution, 73, 75, 263
mixtures, analysis of, 527
Catalysis:
homogeneous, 78
heterogeneous, 78
Cerium, behavior in basic acetate precipitation, 333
Ceric ammonium sulfate, 84
Ceric sulfate, as oxidizing agent, 85
Ceric sulfate solutions, 84, 89
oxidation reduction indicators for, 88
Chainomatic balance, 14
Chalcopyrite, 522
Chlorate:
detection, 417, 419, 460
reduction:
by nitrite, 418, 459, 486
by peroxide, 459
of iodine, 461
Chloride:
complex compounds:
with bismuth, 238, 308
with iron, 298
with lead, 233
with mercury, 259
with tin, 259
detection, 418
effect on solubility of zinc sulfide, 325

Chloride (*cont.*):
estimation, 457
oxidation by ferrate, 302
reduction:
of iron, 301
of permanganate, 301
separation from other halides, 448
titration with silver, 396
calculation of error, 396
end-point correction, 401
Chlorine, detection of, 165
Chlorine dioxide, explosion with, 350
Chloroform extraction:
of iodine, 450
of bromine, 450
Chromate:
behavior with silver, 418
detection, 416, 420
indicator:
in chloride titration, 396
in silver titration, 38
reduction by iodide, 358
Chromate-dichromate equilibrium constant, 369
Chromium:
behavior:
in basic acetate precipitation, 333
with ammonium hydroxide, 284
with hydroxide and peroxide, 312
complex compounds:
with oxalate, 167
with tartrate, 311
coprecipitation with bismuth phosphate, 305, 308
detection, 317
determination, 308
estimation, 358
oxidation by peroxide, 282, 311
separation, 290
standardization of test solution, 555
Chromium dihydroheptasulfate, solubility in hydriodic acid, 190
Chromium hydroxide:
precipitation, 469
coprecipitation of zinc, 123
Chromium sulfate, solubility, 177
Cleaning of volumetric apparatus, 29, 45
Cleaning solution, 30
Clear-point titration, 122
"Closed-tube" test, 162
Cobalt:
behavior:
in basic acetate precipitation, 333
with ammonium hydroxide, 289
with hydroxide and peroxide, 312
Cobalt (*cont.*):
behavior (*cont.*):
with nitrite, 340
with peroxide, 349
complex compounds, 337
coprecipitation:
with Hydrogen Sulfide Group, 204
with iron hydroxide, 283
with stannic sulfide, 204
with zinc sulfide, 326
detection, 340, 341
estimation, 344
oxidation:
by peroxyborate, 344
by sodium peroxide, 282
separation from nickel, 336, 340
standardization of test solution, 554
Cobalt hydroxide, color changes, 335
Cobalt sulfide:
allotropic forms, 321
precipitation, 328
solubility, 202
Coefficient of expansion of glass, 30
Colloidal particles, charge on, 121
Colloidal solutions, 118
Common ion effects in solubility of precipitates, 111
Complex compounds:
aluminum:
with oxalate, 167
with tartrate, 311
Ammonium Sulfide Group elements with oxalate, 313
and coprecipitation, 126
antimony with tartrate, 271
bismuth with chloride, 238, 308
cadmium:
with acetate, 433
with ammonia, 236
chromium:
with oxalate, 167
with tartrate, 311
cobalt with various compounds, 337
copper:
with ammonia, 236
with cyanide, 247
with iodide, 243
effect on molal potentials, 50
in ammonia precipitation, 286
in hydroxide separations, 282
in sulfide separations, 202
iron (ferric):
with chloride, 298
with fluoride, 245
with phosphoric acid, 302
with sulfuric acid, 302

Complex compounds (*cont.*):
lead with chloride, 233
magnesium with oxalate, 376, 472
manganese with oxalate, 347
mercury with chloride, 259
molybdophosphoric acid, 307
nickel:
with ammonia, 342
with cyanide, 342
of ammonia, 401
silver:
with ammonia, 226
with cyanide, 342, 427, 443
tin with chloride, 259
Complex compound formation and solubility of precipitates, 112
Complex ions, dissociation constants, table, 545
Composite reagents, preparation of solutions, 549
Concentrated acids, analysis, 528
Concentration:
conventions in regard to, 548
effect on potentials, 50
of acids, 548
of bases, 548
of reagents, 548
units, 24
problems, 515
Condenser, test-tube, 187
Coning and quartering, 155
Conventions as to concentration of reagents, 548
Coördination compounds (*see also* Complex compounds):
cobalt, 337
Copper:
behavior:
with hydrogen sulfide, 247
with iodide, 242
complex compounds:
with ammonia, 236
with cyanide, 247
with iodide, 243
detection, 236, 237
determination, 243
determination in alloys and ores, 245
precipitation with thiocyanate, 243
separation from cadmium, 200, 242
titration with cyanide, 244
Copper Group:
analysis, 220–250
separation, 193
Copper Group (*cont.*):
separation from Tin Group, 200, 211, 215
solution of sulfides, 221
Copper Group sulfides:
solution of, 221
behavior with nitric acid, 221
Copper sulfide, coprecipitation of zinc with, 123, 204, 327
Copper tetrammino ion, 236
Copper (cuprous) thiocyanate precipitation, 243, 453
Coprecipitation:
adsorption effects, 119
Ammonium Sulfide Group elements with manganese dioxide, 348
and complex compounds, 126
and compound formation, 123
calcium with strontium chromate, 372
causes of, 119
chromate by barium chromate, 371
chromium with bismuth phosphate, 305, 308
cobalt:
by zinc sulfide, 327
with iron hydroxide, 283
concentration effects, 126
double-salt formation, 124
effect of conditions of precipitation, 127
effect of methods of precipitation, 127
effect of solubility on, 126
effect on composition and purity of precipitates, 119
effects, general observations, 125
in ammonia precipitations, 123, 286
in Hydrogen Sulfide Group precipitations, 203
methods for minimizing, 127
mixed crystals, 124
nickel with iron hydroxide, 283
occlusion, 125
of Alkaline Earth Group elements, 367
solid solutions, 124
strontium with barium chromates 368
temperature effects, 126
with calcium oxalate, 377
zinc:
by copper sulfide, 327
with iron hydroxide, 283
with tripositive hydroxides, 311

Course of instruction, 505
Crocoite, 522
Crucibles:
  Gooch, 135
  Monroe-type, 137
  platinum filtering, 137
  porous porcelain, 137
  sintered-glass, 129, 136
  sintered-quartz, 137
Cubic centimeter, 30
Curcumin, behavior with boric acid, 488
Cyanamides, 402
Cyanide:
  behavior:
    on heating with acids, 162
    with alkali, 402
    with zinc and sulfuric acid, 493
  complex compounds with silver, 427
  confirmatory test, 428, 429
  detection, 418, 422, 428, 494
  determination, 226
  estimation, 426, 428
  preliminary identification, 164
  reduction by aluminum, 484
  separation from sulfide, 426
  standardization of test solution, 556
  titration:
    of copper, 244
    of nickel, 342
    of silver, 429
    with silver, 423, 429, 455
Cyanide solutions:
  preparation of, 229
  standardization of, 229, 343

D

Damping of analytical balance, 9
Decantation, 210
  aid to, 373
Decrement:
  definition, 8
  effect of, 9
Density:
  absolute, 30
  relative, 30
Desiccants, 28
Desiccator, use of, 28
Determinate errors, 512
Devarda's alloy, 484
Deviation (*see* Average deviation)
Dichlorofluorescein:
  as adsorption indicator, 39
  indicator in chloride titration, 400
Dichromate, oxidation by iodide, 81
Dichromate solutions, titration of iron, 84
Dichromate-hydrochromate equilibrium constant, 369
Digestion of precipitates, 118
Dimethylglyoxime, 340
  preparation of reagent solution, 550
Diphenylamine, 89
Diphenylamine sulfonic acid, 89
Displacement as hydrogen ion effect, 172
Displacement methods, 104
  applications, 109
  problems, 529
Dissociation constants:
  of complex ions, table, 546
  tri-iodide ion, 69
Distribution law, 120
Distribution ratio:
  bromine in various solvents-water, 450
  definition, 450
  iodine in various solvents-water, 450
Double weighing, 15
Drainage:
  of burets, 45
  of pipets, 45
Droppers, 31
Drying in desiccator, 28
Drying of precipitates, 128
Drying oven, use of, 29

E

Ebullition tube, 261
Electrical cell, 48
Electrode potential (*see* Molal potentials)
  Electrometric titrations, 57
Electromotive force, 49
Electron transfer reactions, 47
Electronic reactions:
  balancing equations, 61
  general principles, 47
End-point:
  calculation from potentials, 51
  correction, 46
    in chloride titration with silver, 399, 401
    in hydrochloric acid titration with sodium hydroxide, 406
    in permanganate-ion titration, 305
  chromate in chloride titration, 396

End-point (*cont.*):
determination, 23
use of reference solutions, 102
in carbonate titration, 105
in iodometric methods, 68
in iron-permanganate titration, 86, 302
in neutralization reactions, 91, 95, 102
in oxidation-reduction reactions, 55
in precipitation reactions, 32
in silver-cyanide titration, 227
in titration of polybasic acids, 528
in volumetric methods, 23
overrunning, 76
Eosin, as adsorption indicator, 39, 400
Equations:
balancing electronic, 61
symbols, 25
writing, 25
Equilibrium constant (*see also* Solubility product):
ammonium hydroxide, 401
arsenious acid-tri-iodide, 72
calculation from potentials, 52
chromate-dichromate, 369
definition, 33
hydrochromic acid-dichromate, 369
hydrogen ion—hydroxyl ion, 91
iodine-iodide, 69
nitrous oxide—nitrate, 173
tri-iodide-hydroxyl ion, 72
Equipment, lists of, 559, 560
Equivalence-point:
definition, 23
in volumetric methods, 33
Equivalent weight, 25
Error:
absolute, 512
accidental, 513
determinate, 512
indeterminate, 512
relative, 512
residual, 513
Ethanol:
for drying precipitates, 128
reaction with acetic acid, 490
Ether (*see also* Ethyl ether, Isopropyl ether):
precautions in use of, 300
Ethyl alcohol (*see* Ethanol)
Ethyl ether:
for drying precipitates, 128
care in use, 297
separation of iron by, 292
Evaporating:
in conical flasks, 237
to dryness, 176
Exchange adsorption, 39
Explosions with perchloric acid, 166, 394
Extraction with organic solvents, 449

F

Ferrate, 302
Ferric (*see* Iron, ferric)
Ferricyanide:
behavior with iodide, 441
color of solutions, 435
detection, 416, 418, 435, 437, 441
effect on basic-constituent analysis, 167
estimation, 441
oxidation of ammonia, 436
precipitation, 433
reduction by aluminum, 484
Ferrocyanide:
color of solutions, 435
confirmatory test, 438
detection, 417, 418, 435, 437, 446
effect on basic-constituent analysis, 167
estimation, 440
reduction by aluminum, 483
titration with permanganate, 439
titration of zinc, 331
Ferrocyanide Group:
analysis, 432–441
detection, 434
precipitation, 434
separation, 436
Ferrous (*see* Iron, ferrous)
Filtering:
by decantation, 210
facilitation of, 118, 219
media, 133
precipitates, 132
Filtering crucibles, 135
Filtering flask, 142
Filter paper:
reduction of permanganate, 380
removing from funnel, 148
removing precipitates from, 180
use of, 147
Filters:
asbestos, 134, 140
Gooch, 135
preparation, 140
paper, 133
preparation, 147

Flask:
ground-glass-stoppered, use of, 142
suction, 142
use of, 209
Fluorescein as adsorption indicator, 39, 400
Fluoride:
behavior with alkaline earth elements, 167
confirmatory test, 481
detection, 420, 480
effect of basic-constituent analysis, 167
estimation, 480
precipitation as calcium fluoride, 480
Formal concentration, 24
Formal potentials, 50
table of values, 540
Formic acid:
reduction:
of mercury, 177
of oxidizing constituents, 160, 177
of silver, 177
Formic acid–formate buffer solution, 322, 382
Fusion:
of precipitates, 128
with sodium carbonate, 189

G

Gases, identification of, 162
Gauss' method of weighing, 15
Gay-Lussac titration for silver, 223
Geissler buret, 44
Glass, action of hydroxides on, 100
Gold, solution of by "aqua regia," 179
Gooch crucible, preparation, 142
Gooch filters, 135
preparation, 140
Gram equivalent, 25
Gravimetric factor, definition, 530
Gravimetric methods:
general principles, 110
operations of, 132
problems, 530
standardization of hydrochloric acid, 139
Grinding of samples, 156
Group separations:
acidic constituents, 411
basic constituents, 193

H

Half cell, 48
Halides:
behavior on heating with sulfuric acid, 162, 495
detection, 496
oxidation by various substances, 448
Halide Group, 411
analysis, 442–458
detection, 418, 444
metathesis by sulfide, 446
precipitation, 443
Heterogeneous catalysis, 78
Homogeneous catalysis, 78
Hydrazine, determination of, problem, 523
Hydriodic acid:
as solvent for tin dioxide, 190
behavior with hot sulfuric acid, 495
in sulfide precipitations, 206
reduction of sulfates, 190
solvent action, 190
Hydrocarbonate-carbonate:
buffer solution, 73, 75, 263
mixtures, analysis of, 527
Hydrocarbonate titration, indicator for, 101
Hydrochloric acid:
anhydrous, preparation of, 394
effect on hydrolysis of ferric iron, 298
reaction with Tin Group sulfides, 251
solution:
constant-boiling, 103
as standard, 100
composition of, 525
preparation, 103
standard, 98
standardization, 107
gravimetric, 110, 139
volumetric, 103
with sodium oxalate, 526
solvent action of, 173, 178
titration:
of carbonate, 107
of borax, 108
Hydrochromate-chromate equilibrium constant, 368
Hydrochromate-dichromate equilibrium constant, 369
Hydrogen cyanide volatilization, 422

Hydrofluoric acid:
behavior:
with hot sulfuric acid, 495
with silica, 185, 481
danger of, 187
formation with calcium fluoride, 481
ionization of, 422
ionization constants, 495
use of, 187
Hydrofluoric acid, concentrated, density of, 533
Hydrogen electrode, 49, 94
Hydrogen ion, 89, 171
buffer solutions, 73
effects:
in solution of sample, 172
solubility of precipitates, 114
indicators, table, 550
test papers, 164, 470
Hydrogen peroxide:
behavior in hydroxide separations, 311
in permanganate titration, 63
oxidation of arsenite, 475
oxidation of sulfite, 501
preparation of reagent solution of, 550
Hydrogen sulfide (*see also* Sulfide):
detection, 290
ionization constant, 198
oxidation:
by nitric acid, 221
to sulfur, 208
reduction of antimony, 270
saturating solutions with, 208
test for, 290
volatilization, 422
Hydrogen Sulfide Group:
analysis, 196–279
elements:
amphoteric nature, 212
behavior in various hydrogen ion concentrations, 212
precipitation from perchloric acid, 203
precipitation, 197, 200
separation, 193
separation of Copper and Tin Group, 211
Hydrogen sulfide solutions, ion concentrations in various saturated solutions, 198
Hydrolysis:
effect on potentials, 50
in ammonia precipitation, 286
Hydrolysis (*cont.*):
of ferric iron in hydrochloric acid, 298
of salts, 91
Hydrolysis constant, 106
Hydrosulfate-sulfate buffer solution, 217, 323, 454
dilution of, 325
Hydrorubianic acid, 247
Hydrous hydrated oxides, 212
Hydrous oxides, 212
Hydroxide precipitates, color of, 335
Hydroxide separations, 281
problems, 535
Hydroxide solutions:
standardization:
with benzoic acid, 525
with potassium hydrophthalate, 100
Hydroxides:
of Hydrogen Sulfide Group Elements, 212
precipitation *p*H, 544
Hydroxide-peroxide separation, 309
Hydroxyl ion, 89
solubility effects, 114
Hydroxyl ion–tri-iodide equilibrium constant, 72
Hygroscopic water, 163
Hypochlorite:
behavior:
with alcohols, 461
with alkali, 459
detection, 461
estimation, 461
test analyses, 462
reduction by iodine, 461
standardization of test solution of, 557

I

Ignition:
loss on, 159
determination, 163
Imides, 402
Indigo carmine, 108
Indeterminate errors, 512
Indicators:
adsorption, 39, 400
chromate for chloride titration, 38, 396
ferric ion, 32
for carbonate titrations, 101
for phosphoric acid titrations, 101
for precipitation methods, 37
for hydroxide titrations, 101

Indicators (*cont.*):
in displacement reactions, 105
in neutralization reactions, 102
in system of analysis, 218
in volumetric methods, 23
iodine monochloride, 85
mixed, 106
neutralization, 95
oxidation-reduction, 85
preparation of, 551
reference solution, 102
salt effect, 97
solvent effects, 97
table, 551
temperature effects, 97
test papers, 164, 470
transition range, 92, 96
problems, 529
Indicator constant, 95
Induced precipitation, 327
Induced reactions, 81
Inter-ionic attraction theory, 40
Iodate:
behavior with silver, 443
detection, 416, 418, 420, 444
indication of, 460
oxidation of antimony, 271
reduction:
by nitrite, 418
to iodine, 417
standardization:
against arsenious oxide, problem, 524
of acids, problem, 526
test for, 70
titration of antimony, 271
Iodate-iodide, use in hydroxide separations, 282
Iodide:
as reducing agent, 68
behavior:
with arsenic acid, 382
with copper, 242
with ferricyanide, 441
detection, 417, 418, 448
estimation, 452
oxidation:
by air, 298
by arsenate, 473
by ferric iron, 298
by iron, 449
by various substances, 448
to iodate, 416
to iodine, 416
to iodine monochloride, 416
reaction with dichromate, 81
Iodide (*cont.*):
reduction:
of chromate, 358
in acid solution, 425
separation from other halides, 448
Iodimetric methods, 68
Iodine:
adsorption by cuprous iodide, 244
as oxidizing agent, 68
as potential indicator, 88
extraction:
with organic solvents, 449
with various solvents, 450
hydrolysis of, 68, 72
oxidation of antimony, 271
oxidation to monochloride, 417
reaction with arsenious acid, 72
reaction with thiosulfate, 68, 78
solubility, 69, 523
standard solution, 69
Iodine solutions:
stability of, 69
standardization of, 71
titration:
of arsenious acid, 72
of sulfite, 430
of tin, 276
with thiosulfate, 68, 83, 263, 371, 382
Iodine cyanide, 449, 453
Iodine monochloride:
as indicator, 85, 271
problems, 524
Iodometric methods, 68
applications of, 84
end-point, 68
problems, 521
Ion attraction theory, 40
Ionization constant:
in buffering solutions, 33
succinic acid, 334
table of values, 545
Ionization methods, 89
problems, 525
Irreversible reactions, 62
Iron (*see also* Iron, ferric):
basic acetate precipitation, 332
behavior:
with ammonium hydroxide, 284
with hydroxide and peroxide, 312
with peroxide, 349
with silver, 51
confirmatory test, 336
detection, 294, 317
determination in ores, 304
estimation, 299, 303

Iron (*cont.*):
iodometric determination, problem, 522
oxidation state, determination, 297
reduction of tin, 277
removal from samples, 156
separation, 284, 290
Iron wire as primary standard, 61
Iron, ferric:
as indicator, 32
behavior with thiocyanate, 449
complex compounds:
with chloride, 298
with fluoride, 245
with phosphoric acid, 302
with sulfuric acid, 302
detection, 297
oxidation of iodide, 298, 449
reduction of, 301
reduction:
by mercury, 304
by stannous chloride, 301
standardization of test solution, 554
ferric chloride:
behavior on heating, 162
separation with ether, 292
ferric ferricyanide, 439
ferric ferrocyanide, 439
ferric hydroxide:
coprecipitation with, 124
drying of precipitate, 131
ferric oxides, behavior on heating, 164
ferric thiocyanate, as indicator, 32
Iron, ferrous:
detection, 297
oxidation:
by air, 300
by bromine, 296
by sodium peroxide, 282
reaction:
with dichromate, 55, 84
with nitrates and nitrites, 486
with permanganate, 52, 53
reduction:
of acidic constituents, 464
of periodate, 467
titration:
in hydrochloric acid solution, 301
with dichromate, 55, 84, 89
with permanganate, 67, 86, 249, 299
Iron (*cont.*):
ferrous ammonium sulfate as primary standard, 61
ferrous ferricyanide, 439
ferrous ferrocyanide, 439
ferrous hydroxide, oxidation, 290
ferrous sulfate:
standard solution, 66
titration by permanganate, 353
ferrous sulfate solution, stability of, 66
Isomorphism, 124
Isopropyl ether, separation of iron by, 292

J

Jones reductor, 301

K

Kjeldahl flask, 405

L

Labeling apparatus, 143
Labels, charring of, 29
Lakes, 355, 383
Lead:
complex compounds with chloride, 233
detection, 231
estimation:
gravimetric, 231
volumetric, 232
precipitation as sulfate, 229
reduction of silver sulfide, 427
reduction of stannic tin, 277
separation, 229
Lead chloride, solubility in water, 223, 519
Lead chromate:
solubility in acetic acid–acetate solution, 233
behavior with hydrochloric acid, 233
Lead dioxide, oxidation of manganese by, 352
Lead sulfate:
drying of precipitate, 128, 130
solubility:
in acetate solutions, 233
in hydriodic acid, 190
in sulfuric acid, 229

Liebig titration:
estimation:
of cyanide, 226
of silver, 226
Light-sensitive solutions, storage of, 32
Limiting quantities of reagents, explanation of, 211
Liter, 24, 30
Litmus, use of, 218
Long swings, point of rest by, 8, 10
Loss on ignition, 159
determination of, 163

M

Magnesium:
complex compounds with oxalate, 376
confirmatory test, 383, 384
detection, 380
estimation, 381
precipitation:
as magnesium ammonium arsenate, 381
as magnesium ammonium phosphate, 307, 380
in presence of ammonium chloride, 361
standardization of test solution of, 556
Magnesium ammonium arsenate:
hydrolysis, 471
metathesis by silver, 474
precipitation, 381, 471
Magnesium ammonium phosphate:
hydrolysis, 471
drying of precipitate, 131
precipitation, 307, 380, 471
Magnesium hydroxide:
precipitation, 114
reaction with nitro-benzene-azo-resorcinol, 383
Magnesium nitrate, preparation of reagent solution, 550
Magnesium oxalate:
complex compounds, 472
solubility, 376
supersaturation, 376
Magnesium pyrophosphate, ignition of precipitate, 131
Magnesium uranyl acetate, preparation of reagent solution of, 550
Magnet steel, 522
Manganese:
behavior:
in basic acetate precipitation, 333
in oxalate-sulfide solutions, 314
with ammonium hydroxide, 284
with hydroxide and peroxide, 312
complex compounds with oxalate, 347
coprecipitation:
with chromium hydroxide, 283
with Zinc Group, 305
detection, 318, 351
estimation, 352, 353, 555
colorimetric, 351
oxidation:
by air, 290
by bromine, 318
by bismuthate, 351, 555
by chlorate, 347
by sodium peroxide, 282
by various reagents, 352
separation from zinc, cobalt, and nickel, 200
standardization of test solution, 555
test for, 350, 353
Manganese dioxide:
behavior:
with ferrous iron, 351
with iodide, 351
determination in ores, 354
precipitation, 347
reduction by nitrite, 457
Mass, definition, 3
Mass-action constants:
indicator constant, 95
solubility product, 34
equilibrium constant, 33
ionization constant, 90
hydrolysis constant, 106
Mass-action law:
deviations from, 40
statement of, 33
Mass concentration, 24
Mechanical inclusion (*see* Occlusion)
Meker burner, temperature of, 148
Mercury:
behavior with iron, 301
complex compounds with chloride, 259
detection, 265, 268
determination in cinnibar, 518
determination of oxidation state, 266
estimation, 267

Mercury (*cont.*):
reduction:
by formic acid, 177
of iron, 304
of permanganate, 304
with phosphite, 267
separation from antimony and tin, 264
test for, 207
titration with thiocyanate, 267
Mercury chlorides, behavior on heating, 162
Mercury, mercuric:
detection, 266
oxidation of stannous chloride, 301
reduction by phosphorous acid, 264
titration with thiocyanate, 267
mercuric sulfide:
behavior:
with ammonium sulfide, 221, 254
with hydrochloric acid, 251
with nitric acid, 221
coprecipitation of zinc, 204
dissociation constant of sulfosalt, 213
solubility product, 535
solubility in acid, 177
solubility in sodium disulfide, 213
mercuric thiocyanate, 267
Mercury, mercurous:
detection, 266
oxidation, 267
Metallic solids:
cleaning, 156
sampling, 155
Metathesis:
in preparation of solution for acidic analysis, 413
of slightly soluble compounds, 363
Metathetical reactions, 25
Methanol, behavior with boric acid, 497
Methyl alcohol (*see* Methanol)
Methyl orange indicator, 101, 105
Methyl red indicator, 101
Milli-equivalents, use of, 518
Milliliter, 30
Mixed crystals, 124
Mixed indicators, 106
preparation of, 551
for carbonate-hydrocarbonate titration, 527
Mohr buret, 44
Mohr titration, 396
Molal concentration, 24
Molal potentials, 49
and formal potentials, 50
in electronic reactions, 55
in volumetric analysis, 24
iodine-iodine monochloride, 86
nitric oxide-nitrate, 173
nitrous oxide-nitrate, 173
silver-silver ion, 50
table of values, 540
Molar concentration, 24
Molybdic acid, 307
Morse-Blalock bulb, 30
Munroe-type crucibles, 137

N

Nernst equation, 50
Nessler reagent, 403
Neutralization:
as hydrogen ion effect in solvent action, 172
indicators, 95
methods, 89
applications, 109
reactions, 89
end-point determination, 95
Nickel:
behavior:
in basic acetate precipitation, 333
with ammonium hydroxide, 284
with peroxide, 349
with hydroxide and peroxide, 312
complex compounds:
with ammonia, 342
with cyanide, 342
coprecipitation:
with Hydrogen Sulfide Group, 204
with iron hydroxide, 283
detection, 340, 341
estimation, 343
reduction of tin, 275
separation from cobalt, 336, 340
standardization of test solution, 554
titration with cyanide, 342
Nickel chloride, precipitation of, 114
Nickel coin, 522
Nickel dimethylglyoxime, drying of precipitate of, 128
Nickel silver, 522
Nickel sulfide:
allotropic forms, 321
coagulation of, 291
colloidal, 291
formation of, 319

Nickel sulfide (*cont.*):
solubility, 202
Nitrates:
behavior on heating with sulfuric acid, 162
detection and estimation, 483
reduction:
by aluminum, 483
by Devarda's alloy, 483
by ferrous iron, 486
by zinc, 483
test for, 485
Nitrate-ammonia molal potential, 173
Nitric acid:
as oxidizing agent, 172
as solvent, 177
oxidation of ammonia, 362
oxidation of sulfides, 221
solvent action, 171
standard solution, 98
substances insoluble in, 177
treatment of sample with, 171
Nitrides, 402
Nitrite:
behavior:
with thiourea, 487
with various anions, 418
detection, 415, 417, 483, 487, 488
estimation, 483
oxidation:
of arsenite, 475
of sulfite, 479
preliminary identification, 164
reduction:
by aluminum, 483
by Devarda's alloy, 483
by zinc, 483
of bromate, 459
of chlorate, 459, 486
of manganese dioxide, 457
of permanganate, 457
test for, 485
Nitrobenzene:
use:
in silver-cyanide titration, 429
in silver-thiocyanate titration, 239
p-Nitrobenzene-azo-resorcinol:
confirmatory test for magnesium, 383
preparation of reagent solution, 550
Nitrous oxide–nitrate equilibrium constant, 173
Non-metallic solids, sampling, 154
Normal concentration, 25
Notebooks, 11

O

Occlusion as cause of coprecipitation, 125
Operations of gravimetric methods, 132
Observations on original sample, 158
Organic material:
behavior on heating, 162
effect on analysis, 159
elimination, 166
estimation, 161
test for, 159, 161, 162, 163
Ostwald bulb, 30
Oxalate:
behavior:
on heating with sulfuric acid, 162
with chlorate, 347
with nitric acid, 341
with silver, 418, 443
complex compounds:
with Ammonium Sulfide Group elements, 313
with chromium, 167
with magnesium, 376, 472
with manganese, 347
detection, 420, 444, 476
effect on analysis, 159, 167
estimation, 476
separation from arsenate and phosphate, 471
solutions, stability of, 62, 167
Oxalic acid:
as primary standard, 61, 100
as standard, 100
behavior with perchlorates, 189
titration with permanganate, 60, 374, 379
Oxidation, general principles, 47
Oxidation-reduction indicators, 85
Oxides:
precipitation of, 544
reporting analysis as, 520
Oxidizing agents, definition, 47
Oxidizing constituents:
detection, 415
effects in acidic analysis, 412
estimation, 417
in original sample, 160
reduction by formic acid, 160
test for, 180, 485
Oxygen:
behavior in permanganate titration, 64
test for, 163

"Oxygen error," 81
  hydrocarbonate for, 384
Oxy-Halogen Group. 411
  analysis, 459–467
  detection, 418
  precipitation, 459

P

Paper filters, 133
  preparation of, 147
Paraffin, protection of hydroxide containers, 100
Particle size:
  effect on solubility, 116
  samples, 156
Penny method for iron, 55
Peptization, 122
Perborate (*see* Peroxyborate)
Perchlorate:
  behavior:
    in systematic analysis, 459
      with ammonium salts, 362
      with ferrous salts, 464
      with manganese salts, 465
      with nitrite, 418
      with oxalate, 189
  detection, 464
  estimation, 464
  reduction by ammonium salts, 362
  removal in Alkaline Earth Group precipitation, 362
Perchloric acid:
  evaporation with alcohol, 395
  explosions, 166, 167, 394
  fuming:
    care in use of, 169
    for removal of acidic constituents, 168
    properties of, 166
    solvent action of, 182
  precipitation of silicic acid, 183
  reduction:
    by ferrous salts, 464
    by manganese salts, 465
  standard solution, 98
  sulfide precipitations from, 203
Periodate:
  behavior in systematic analysis, 459
  detection, 416, 467
  oxidation of manganese, 352
  reduction:
    by iron, 467
    by nitrite, 418
Permanganate:
  detection, 416
  oxidation:
    of ferrous iron, 302
    of ferrous sulfate, 353
    of oxalate, 353
  reaction with iron, 52
  reduction:
    by chloride, 299, 301
    by filter paper, 380
    by mercury, 304
    by nitrite, 457
Permanganate methods, 53
  applications of, 67
  problems, 520
Permanganate solutions:
  behavior in titrations, 55–59
  for thiosulfate standardization, 83
  oxidation-reduction indicators for, 88
  preparation of standard, 59
  rate effects in titrations, 57
  reaction with oxalate, 62
  stability of, 59, 63
  standardization, 60
  titration:
    of ferrocyanide, 439
    of iron, 54, 86, 249, 299, 353
    of thiocyanate, 453
Peroxide (*see also* Hydrogen peroxide):
  in hydroxide separations, 310
  oxidation of arsenite, 475
  reduction:
    of bromate, 459
    of chlorate, 459
Peroxyborate, oxidation of cobalt, 344
Peroxysulfate:
  as oxidizing agent, 321
  behavior in systematic analysis, 479
  oxidation and reduction of, 436
  oxidation of manganese, 352
Persulfate (*see* Peroxysulfate)
*p*H, definition, 93
o-phenanthroline ferrous complex, 89
Phenolphthalein indicator, 95
  transition range, 101
Phosphate:
  as reagent in preparation of solution for acidic analysis, 413
  behavior:
    with alkaline earth elements, 288, 305
    with silver, 418

Phosphate (*cont.*):
confirmatory test, 475
detection of, 307, 420, 475
effect on precipitation of manganese with Zinc Group, 305
estimation of, 305, 308
in precipitation of Ammonium Sulfide Group, 288
reaction with ammonium molybdate, 307
removal, 306
in basic constituent analysis, 305
separation from arsenite and oxalate, 471
test for, 307
Phosphate Group, 411
analysis, 468–477
confirmatory test, 470
detection, 469
precipitation, 469
separation of phosphate and arsenate from arsenite and oxalate, 471
Phosphate mixtures, analysis of, 528
Phosphite:
detection, 417, 470
oxidation by silver, 469
Phosphorus acid:
effect on precipitation of tin, 269, 274
impurities in, 274
reduction:
of bromine, 259
of mercury, 264
Phosphoric acid:
complex compounds with iron, 302
effect:
in iron-iodide reaction, 303
on precipitation of tin, 269, 274
in permanganate titration of iron, 302
Physical equilibrium, law of, 449
Pipets:
calibration, 44
cleaning, 44
use, 44
Platinum filtering crucibles, 137
Platinum metals, solution by "aqua regia," 179
Platinum ware:
care of, 145, 191
cleaning, 145
Point of rest:
determination by:
method of long swings, 8, 10
method of short swings, 9, 12
Policeman, use of, 144
Post-precipitation, 327
Potassium:
confirmatory test, 393
detection, 385
estimation, 392
precipitation as perchlorate, 389
separation from sodium, 385, 389, 391
separation from sodium, test analyses, 391
test for, 387
Potassium bromate, as oxidizing agent, 256
Potassium chloroplatinate, 392
Potassium cobaltinitrite, 340, 387
precipitation, 115
Potassium chlorate, behavior in concentrated nitric acid, 350
Potassium cyanide (*see also* Cyanide solutions):
care in use of, 248
Potassium dichromate (*see also* Dichromate):
purification, 82
standard solution, 84
Potassium ferrocyanide, as primary standard, 439
Potassium ferrous ferrocyanide, 439
Potassium hydrophthalate:
as standard, 100, 103
reaction with sodium hydroxide, 101
titration with sodium hydroxide, 102
Potassium iodate for standardization of thiosulfate, 521
Potassium iodate solutions, 85
oxidation-reduction indicators for, 88
Potassium manganous ferrocyanide, 439
Potassium mercuric iodide:
preparation of reagent solution, 550
reaction with ammonia, 403
Potassium perchlorate:
occlusion with, 125
precipitation of, 114
solubility:
in various solvents, 390
in ethyl alcohol-ether mixtures, 390

Potassium permanganate (*see also* Permanganate solutions):
as oxidizing agent, 53
purity of, 59
Potassium thiocyanate (*see also* Thiocyanate solutions):
as primary standard, 32
Porcelain boat, 500
Potential (*see* Molal potentials)
Potential indicators, 85
iodine monochloride, 271
Potentiometric titrations, 56
Preparation of the sample, 152-169
Preparation of the solution, 169-192
fusion with sodium carbonate, 189
treatment:
with nitric acid, 171
with hydrochloric acid, 178
with hydrochloric and nitric acid, 179
with perchloric acid, 182
Precipitates (*see also* Coprecipitation):
composition, 119, 128
drying, 128
factors affecting solubility, 110
filtering, 132
fusion of, 128
ignition of, 146
mechanism of formation, 116
physical characteristics, 116
purity, factors affecting, 119
reduction on ignition of filter paper, 134
removal:
from filter paper, 180
from vessels, 144
solubility, factors affecting, 111-116
stability, 128
transferring, 180, 216, 257
treatment with solutions, 216
used in gravimetric analysis, table, 132
washing, 137, 144, 210, 211
Precipitation (*see also* Coprecipitation):
arsenic sulfide, 205
barium sulfate, 115, 118, 478
cadmium sulfide, 247
copper thiocyanate, 243
Hydrogen Sulfide Group, 200
mechanism, 116
of sulfides, conditions for, 200
Tin Group, 216
Precipitation methods (volumetric), 26
applications, 46
principles, 32
problems, 517
Precision:
definition, 512
of weighing samples, 29, 176
Preliminary observations on original sample, 158, 160
Preliminary tests:
for acidic constituents, 415
for basic constituents, 158
Preparation of the sample, 152-169
problems, 532
Preparation of solution:
for acidic constituent analysis, 413-420
for basic constituent analysis, 169-192
problems, 532
Preventative solution, 303
Primary standards, 26, 60
arsenious oxide, 71
borax, 103
potassium bromate, 80
potassium dichromate, 80
potassium ferrocyanide, 439
potassium iodate, 80, 521
potassium thiocyanate, 32
sodium carbonate, 104
table, 552
Problems and questions, 509
Prussian blue, 439
Pulverizing samples, 156
Pyrite, 522
determination of sulfur in, 127
Pyrolusite, 552
manganese dioxide determination in, 354

Q

Quantitative paper filters, 134
Quartering, 155
Questions and problems, 509

R

Rate (*see* Reaction rate)
Reaction rate effects:
in arsenate-iodide reaction, 382
in oxidation of iodide by iron, 298
in precipitations, 115
in reduction of permanganate by chloride, 301

Reaction rate effects (*cont.*):
in sulfide precipitations, 202, 205
in titrations, 57
in volumetric methods, 22
Reagents:
concentration of, 548
conventions as to concentrations of, 548
limiting quantities of, 211
preparation of, 548
Reagents and chemicals, preparation of, 548, 549
Red brass, 522
Reducing agents:
definition, 47
for reduction of iron, 301
Reducing constituents:
behavior in heating with sulfuric acid, 162
detection, 417
effects in acidic analysis, 412
estimation, 418
preliminary identification, 164
Reduction, general principles, 47
Reference half-cell, 49
Relative calibration, 75
Reprecipitation to reduce coprecipitation, 128
Residual errors, 513
Rest point (*see* Point of rest)
Rider, precautions with use of, 13
Rolling of sample, 157
Rosocyanine, 488

S

Salt bridge, 48
Salt effect with indicators, 97
Samples:
grinding, 156
iron removal, 156
particle size, 156
preparation, 153
pulverizing, 156
size of, 156
weighing, 28, 176
Sampling:
accuracy of, 154
metallic solids, 155
methods of, 154
non-metallic solids, 154
principles, 153
solutions, 155
suspensions, 155
water, 157
Secondary standards, 82
Sensitivity of analytical balance:
definition, 5
determination of, 13
weighing by, 14
Separating funnel, 296
Ship-nail brass, 522
Short swings, determination of point of rest by, 9, 12
Significant figures, 11
Silica:
detection, 185
determination, 188
elimination, 185
estimation, 183, 185
introduced into analysis, 354
Silicates (*see also* Silica):
behavior on heating, 164
Silicic acid (*see also* Silica):
drying of precipitate, 131
precipitation of, 183
Silicon dioxide, 184
Silicon tetrafluoride, hydrolysis of, 481
Silver:
behavior with various anions, 418
complex compounds:
with ammonia, 226
with cyanide, 226, 342, 427, 443
detection, 197, 223, 225
determination in alloys, 517
estimation, 208, 223, 225, 226
Gay-Lussac titration, 223
in original sample, 159
insoluble salts of, 443
oxidation of ferrous iron, 51
precipitation, 223
precipitates, color of, 445
reaction with thiocyanate, 42
reduction of ferric iron, 51
reduction by formic acid, 177
removal, 197
separation from Copper Group elements, 223
solubility in cyanide solutions, 226
test for, 160, 206
titration:
of cyanide, 423, 455
with cyanide, 226, 423
with thiocyanate, 42, 239, 426, 428
Silver-ammonia complex dissociation constant, 113
Silver arsenate precipitation, 469
Silver arsenite precipitation, 469
Silver bromate, metathesis of, 443

Silver bromide, drying of precipitate, 128
Silver chloride:
  behavior with nitric acid, 222
  decomposition of, 187
  precipitate, drying of, 128, 130
  precipitation, 114, 118
  solubility:
    in ammonia solutions, 113
    in potassium chloride solutions, 111, 112
    in potassium cyanide solutions, 228
    in silver nitrate solutions, 112
    problem, 531
Silver chromate:
  solubility, 519
  solubility product, 398
Silver cyanide:
  coagulation with nitrobenzene, 429
  complex ion, 443
Silver ferricyanide, solubility, 436
Silver ferrocyanide precipitation, 436
Silver Group, 197
Silver halides:
  effect of light on, 225
  metathesis with sulfide, 446
  solubility in ammonia, 226, 447
Silver iodate, metathesis of, 443
Silver iodide:
  drying of precipitate, 128
  precipitation, 122
Silver nitrate:
  stability of, 26, 27
  standard solution, 26
  titration of chloride, 396
Silver oxalate:
  metathesis of, 443
  precipitation, 469
Silver phosphate:
  precipitation, 469
  solubility, 519
Silver salts, colors of, 419, 470
Silver sulfate, solubility, 43
Silver sulfide:
  behavior with nitric acid, 221
  reduction by lead, 427
Silver thiocyanate:
  adsorption of nitrobenzene, 239
  drying of precipitate, 128
  solubility in ammonia, 447
Single deflection weighing, 14
Sintered-glass crucibles, 129, 136
  cleaning, 145
Sintered-quartz crucibles, 137
Soda ash, analysis of, 528
Sodium:
  detection, 389, 394
  estimation, 395, 400
  precipitation as chloride, 394
  separation from potassium, test analyses, 391
  test for, 387
Sodium bicarbonate (*see* Sodium hydrocarbonate)
Sodium carbonate:
  as primary standard, 104
  fusion of sample, 189
  solubility in sodium hydroxide, 99
  titration with hydrochloric acid, 107
Sodium chromate as indicator, 38
Sodium cobaltinitrite, preparation of reagent solution, 550
Sodium dinitrophenyl-azo-naphthol disulfonate, 470
Sodium hydrocarbonate:
  as standard, 104
  to eliminate oxygen error, 384
Sodium hydroxide:
  impurities in, 99
  standard solution, 99
    standardization of, 100
Sodium magnesium uranyl acetate, 387
Sodium oxalate (*see also* Oxalate solutions, Oxalic acid):
  as primary standard, 61
  reaction with permanganate, 61
  stability of, 66
Sodium perchlorate, solubility in ethyl alcohol–ether mixtures, 390
Sodium peroxide:
  behavior in hydrogen separations, 311
  oxidation:
    of chromium, 282
    of cobalt, 282
    of iron, 282
    of manganese, 282
Sodium sulfide:
  preparation of reagent solution, 550
  solution of Tin Group, 213
  solutions, ion concentrations in, 198
Sodium tetraborate:
  as primary standard, 103, 108
  preparation of standard, 108
  titration with hydrochloric acid, 108

Sodium thiosulfate (*see* Thiosulfate solutions)
Solder, 522
Solid solutions,
as cause of coprecipitation, 124
Solubility (*see also* Precipitates, Solubility product):
of original sample, 159
of precipitates, 110
of various sulfides, 200
table of values, 539, 544
tests, 160
Solubility product:
calculation of, 35
definition, 34
deviations from, 40
effects in precipitation, 111
in volumetric analysis, 24
of mercury sulfide, 535
of silver chloride, 111
of sulfides, 199
predictions from, 199
Solutions:
determination of solid content, 157
preparation for analysis, 157
sampling, 155
standard (*see* Standard solutions)
transferring, 143, 209
Solvent action:
"aqua regia," 179
fuming perchloric acid, 182
fuming sulfuric acid, 182
hydrochloric acid, 179
hydrogen ion, 172
nitric acid, 172
various reagents, 170
Solvent effects, table, 170
Solvents:
effect on indicators, 97
in preparation of solutions, 170
Solvents, organic, identification of, 158
Spotting, 157
Spray trap, 406
Standard solutions:
acids and bases, 97
care of, 43
ceric sulfate, 84
conservation of, 228
containers for, 43
light-sensitive, 32
list of, 551
methods of preparing, 26
potassium iodate, 85
siphon for, 80
Standard solutions (*cont.*)
storage of, 43, 80
table of, 551
volume change in mixing, 32
Standard weights, 20
Stannic (*see* Tin, stannic)
Stannous (*see* Tin, stannous)
Starch, 70
color with iodine solutions, 264
color with tri-iodide ion, 69
Starch indicator:
in strong acid solution, 264
preparation of solution, 70
Stibnite, analysis of, 271, 273
Stirring rods, 31, 141
Stock test solutions, 552
Stoichiometry in volumetric methods, 23
Storage bottle for standard solutions, 80
Strontium:
confirmatory test, 375
coprecipitation with barium chromate, 368
detection, 372
estimation, 374
precipitation as chromate, 372
separation from calcium and magnesium, 367, 372
Strontium chromate, precipitation of, 114
Strontium oxalate, 374
Strontium sulfate:
metathesis with carbonate, 363
solubility in hydriodic acid, 190
solubility, problem, 531
Substitution weighing, 15
Succinic acid:
ionization constant, 334
use in hydroxide separations, 282
Suction flask, 142
Sulfate:
detection, 420, 478, 479
effect in iron-iodide reaction, 299
estimation, 478
in precipitation of Alkaline Earth Group, 362
precipitation as barium sulfate, 478
removal in Alkaline Earth Group analysis, 385
test for, 190
Sulfate-hydrosulfate buffer solutions, 217, 323, 454
dilution of, 325

Sulfide:
confirmatory test, 427
detection, 418, 422, 426, 494, 501
ion concentrations in sulfide solutions, 198
oxidation by air, 291
separation from cyanide, 426
standardization of test solution, 556
test for, 330
Sulfide separations, 197
of Ammonium Sulfide Group, 311
of Ammonium Sulfide Group elements, 287
of Copper and Tin Groups, 213
of Hydrogen Sulfide Group, 203
problems, 533
Sulfides, Copper Group, behavior with nitric acid, 221
Sulfides, Tin Group:
behavior:
with ammonium sulfide, 254
with hydrochloric acids, 251, 256
color, 219
Sulfides, various:
behavior:
in separations, 200
on heating with acid, 162
with zinc and sulfuric acid, 493
color of, 208
in original sample, 159
preliminary identification of, 164
solubility products, 199
Sulfide-Cyanide Group, 411
analysis, 421-431
detection, 422
Sulfite:
behavior on heating with acid, 162
confirmatory test, 431
detection, 417, 420
estimation, 430
oxidation, 430
by nitrite, 479
by peroxide, 501
preliminary identification of, 164
separation, 430
standardization of test solution, 556
titration with iodine, 430
volatilization as sulfur dioxide, 429
Sulfur:
behavior with bromate, 256
determination in pyrite, 127
oxidation of, 362
by nitric acid, 385
precipitation from disulfide reagent, 218
Sulfur monobromide, 256
Sulfuric acid:
behavior with barium chromate, 371
complex compound with iron, 302
fuming, solvent action of, 182
solution:
of metallic sulfides, 493
of metallic cyanides, 493
standard solution, 98
volatilization of halogen acids, 495
Sulfurous acid, ionization of, 422
Summation of analyses, 520
Supersaturation:
of distilled water with carbon dioxide, 100
in precipitation, 115, 118
magnesium ammonium phosphate, 472
magnesium ammonium arsenate, 472
magnesium oxalate, 376
Suspensions:
determination of solid content, 157
preparation for analysis, 157
sampling, 155
Symbols in equations, 25

T

Tartrate:
complex compounds:
with aluminum and chromium, 311
with antimony, 271
Temperature effects:
in precipitation, 114
on coprecipitation of cobalt by zinc, 327
with indicators, 97
Test papers, 164, 470
Test solutions, preparation of, 552
Test-tube condenser, 187
Tetra brom fluorescein, indicator in chloride titration, 400
Thallous chloride, solubility, 42
Thiocyanate:
behavior:
with silver, 443
with zinc, 446
with zinc and sulfuric acid, 493
detection, 417, 418, 450
oxidation:
by bromine, 296
by nitrate, 453
by various substances, 448
reduction by aluminum, 484
standardization of test solution, 557

Thiocyanate solutions:
preparation of standard, 32
reaction with silver, 32
stability, 32
standardization, 32
titration:
of mercury, 267
of silver, 32, 42, 426, 428
with permanganate, 453
Thiosulfate:
behavior:
in systematic analysis, 479
on heating with acids, 162
with acids, 430
with silver, 419
detection, 417
reaction with iodine, 78
reduction to sulfide, 419
use in hydroxide separations, 282
Thiosulfate solutions:
preparation, 77
stability, 77
standardization, 80, 82, 83, 521
Thiourea:
behavior with nitrite, 487
preparation of reagent solution, 550
Thymol blue indicator, 102
Thymolphthalein indicator, 102
Tin:
complex compounds with chloride, 259
detection, 255, 274
determination as dioxide, problem, 532
determination of oxidation state, 275
estimation, 275
reduction by nickel, 275
separation and determination in alloys, 178
Tin chlorides, behavior on heating, 162
Tin dioxide:
drying of precipitate, 131
solubility in hydriodic acid, 190, 192
Tin, stannic:
reduction by antimony, 276
reduction:
by iron, 277
by lead, 277
by zinc, 277
stannic chloride:
complex compounds, 259
volatility, 259
Tin, stannic (*cont.*):
stannic sulfide:
behavior:
with ammonium sulfide, 254
on heating, 164
coprecipitation:
of cobalt, 204
with antimony, 269
Tin, stannous:
detection, 275
titration with iodine, 276
stannous chloride:
oxidation:
by air, 275, 276
by mercury, 301
preparation of reagent solution, 550
reduction of iron, 301
Tin Group:
analysis, 251
rapid qualitative, 254
quantitative, 256
detection, 255
precipitation, 216
separation, 193
separation from Copper Group, 200, 211, 213, 215
test analyses, 253
Tin Group Sulfides:
color, 219
detection, 218
Tirrill burner, temperature of, 148
Titanium, in iron separation, 297
Titer, 64
Titration:
adsorption indicators, 39, 400
end-point correction, 401
curves, 35
electrometric, 57
filling of burets, 228
potentiometric, 56
rapid, 76
reference solutions, use of, 102
Titration error in chloride titration, 396
Titration curves:
neutralization reactions, 92
precipitation titrations, 35, 36
permanganate titrations, 54
Transferring:
precipitates, 144, 180, 216, 257
solutions, 143, 209
weighed material, 31
Transition range of indicators, 92, 96, 529

Transposition weighing, 15
Triangles, 148
Tri-iodide ion:
  color with starch, 69
  dissociation constant, 69
Tri-iodide-arsenious acid equilibrium constant, 72
Tri-iodide hydroxyl ion, equilibrium constant, 72
Trimethyl borate, 498
Turmeric, 488
  preparation of reagent solution of, 550
Turnbull's blue, 439

U

Units:
  concentration, 24
  volume, 30

V

Vacuum, in drying precipitates, 128
Viscosity of water, 115
Volatile materials:
  loss in evaporation, 157
  recovery on evaporation, 181
Volhard titration:
  of manganese, 520
  of silver, 32
Volume changes in standard solutions, 32
Volume concentration, 24, 26
Volumetric analysis (*see* Volumetric methods)
Volumetric flask, use of, 235
Volumetric glassware:
  calibration, 30
    problems, 516
  cleaning of, 29, 45
  filling burets, 60, 228
  tolerances for, 44
Volumetric methods, 22 (*see also* Titrations)
  classification of, 23
  criteria for, 22
  determination of end-point, 23
  displacement reactions, 104
  iodometric methods, 68
  neutralization methods, 89
  oxidation and reduction methods, 47
  permanganate methods, 53
  precipitation methods, 26, 32
  problems, 515
  types of reactions, 23

W

Wash bottles, 31
Washing precipitates, 137, 144, 210, 211
  facilitating, 219
Water:
  in crystals, 163
  in original sample, 159
  tests for, 159, 161
  viscosity of, 115
Water aspirator, 142
Water-soluble constituents, determination of, 176
Weighed precipitates:
  composition, 128
  stability, 128
Weighing, 3
  difference method, 28
  direct method, 28
  double weighing method, 15
  effect of decrement, 9
  effect of unequal arm lengths, 14
  methods, 14, 28
  precision, 27, 29
  samples, 28, 176
  sensitivity method, 14
  single-deflection method, 14
  substitution method, 15
  transposition method, 15
Weight, definition, 3
Weight concentration, 24, 26
Weight-formal, 26
Weight-molal, 26
Weights:
  standard, 20
  calibration, 19
  care of, 19
  correction for buoyancy, 16
  standard, 17
Witte plate, 142

Z

Zero point of balance, 8
Zimmerman-Reinhardt solution, 303
Zinc:
  behavior:
    in basic acetate precipitation, 333
    with ammonium hydroxide, 284
    with cyanides in sulfuric acid, 493
    with hydroxide and peroxide, 309
    with sulfides in sulfuric acid, 493
    with thiocyanate, 446
  coprecipitation:
    with chromium hydroxide, 283
    with copper sulfide, 204, 327

Zinc (*cont.*):
coprecipitation (*cont.*):
with Hydrogen Sulfide Group, 204
iron hydroxide, 283
mercuric sulfide, 204
nickel and cobalt sulfide, 321
tripositive hydroxides, 311
precipitation of complex iron cyanides, 433
precipitation as sulfide, 322
reduction:
of nitrate, 484
of nitrite, 484
of tin, 277
Zinc (*cont.*):
separation, 321, 326
from cobalt and nickel, 200
titration with ferrocyanide, 331
Zinc Group:
analysis, 320-345
separation, 195, 309
separation from Aluminum Group, 200
Zinc sulfide:
coprecipitation of cobalt, 327
precipitation, 328
solubility, 199, 324, 326
solution in hydrochloric acid, 321