A MANUAL OF QUALITATIVE CHEMICAL ANALYSIS

McGREGORY

GINN AND COMPANY

A MANUAL OF QUALITATIVE CHEMICAL ANALYSIS

By J. E. McGregory, *Professor of Chemistry and Mineralogy in Colgate University.*

Cloth. Octavo. XIV + 133 pages. List price, $1.00; mailing price, $1.10.

This book is intended for beginners in Qualitative Analysis. It assumes that the student has learned the properties and relations of the common elements and compounds. It is comprehensive enough for those who expect to be chemists; but is so arranged that those who study the subject for a limited time only may get the greatest amount of disciplinary good, and at the same time gain some knowledge of the analysis of simple substances. Methods of procedure are not multiplied; but those given are practical and well established, and all the preliminary steps to be taken and precautions to be observed are fully and clearly explained. It is well adapted, therefore, to the requirements both of colleges and of the best secondary schools.

The book is divided into four parts. Part I contains the reactions with all important reagents for the common metals and acids in solution. This elementary part of the work is intended to form the basis of all advanced study, and should be thoroughly mastered. Part II gives the reactions employed in the analysis of simple dry substances, and is commonly called Blowpipe Analysis. A systematic presentation of these reactions is often omitted in text-books; but, since they are used for preliminary testing in advanced work, every chemist must know them. This part of the book is also of the very highest educational value to the general student in developing the powers of observation. Part III contains the approved methods for separating the metals and acids in solution; and Part IV, the methods employed in the systematic examination of complex solids. The complete book is intended to cover one year of work as commonly given in our colleges.

62—10-3

GINN & COMPANY Publishers

A

MANUAL OF QUALITATIVE CHEMICAL ANALYSIS

BY

J. F. McGREGORY
PROFESSOR OF CHEMISTRY AND MINERALOGY IN
COLGATE UNIVERSITY

GINN & COMPANY
BOSTON · NEW YORK · CHICAGO · LONDON

47.9

The Athenæum Press
GINN & COMPANY · PROPRIETORS · BOSTON · U.S.A.

PREFACE

An examination of most of the works on the subject of qualitative analysis will show that they belong in one of two general classes which may be described as follows: first, the exhaustive treatise, of which such a work as that of Fresenius will serve as an example; second, the abbreviated treatise, often very much abbreviated, in which the author attempts to cover the whole work in a few lessons.

For graduate students, or for the better class of beginners who are able to devote the most of their time to the study, books of the first class may be invaluable. But the great majority of the students in our colleges do not become chemists. They study analytical chemistry at the most but a short time, and what they acquire is, and should be, to a considerable extent, of disciplinary value to them. To the great majority of our students, therefore, the exhaustive treatise, especially at the beginning of their course, is a means of confusion rather than an intelligent guide.

The second class of text-books is also likely to fail with the average student, since it teaches him to analyze an unknown substance in such a purely mechanical way that the actual knowledge of the subject acquired is small, and the disciplinary value of the work becomes a minimum.

This little manual was first written to meet the wants of the author's own classes, in which it has been used for several years, and has now been carefully revised for this edition. In it the attempt has been made to retain the essentials of the larger works, omitting the rare metals and acids, and, at the same time, to avoid the "short cuts" so often found in smaller works. It is presupposed that the student has had a thorough course of instruction in general chemistry, at least through the non-metallic elements, before beginning this work.

All laboratory work ought to be carried on under the immediate supervision of a competent instructor. The work should also be accompanied by a sufficient number of examinations to bring out all the essential points connected with the work. The author's own plan is to give frequent oral examinations throughout the course, especially in the earlier parts.

In the introduction will be found certain definitions and general principles, which the student should know at the beginning of this course. The author has thought it best to omit all consideration of the dissociation theory, believing that, however valuable the study of this subject may be to the chemist, its introduction as a basis of study in qualitative analysis is not to be recommended, and that its consideration should, therefore, be deferred until a later time when the student shall have a larger number of facts at his command.

Special attention ought to be given to Parts I and II, which deal with simple substances only. The reactions here given are often partially or entirely omitted in a text-book; but since they form the basis of all the more advanced portions of the work, they ought to be thoroughly mastered.

In the separation of the metals in Part III only one practical and well-established method is given, it being the author's experience where several methods are given, either that only one is used or that the student is likely to get them confused. Later in the course the student may learn other methods as it seems desirable.

Part IV has been inserted in order to make the work more complete. It is not essential for all students, and, if it is found necessary to shorten the course, may be omitted.

The appendix contains tables and some useful information for both students and instructor.

The author desires to express his thanks to his assistant, Mr. R. B. Smith, and to all others who, either by suggestion or criticism, have so kindly assisted him in this work; also to Professor R. W. Thomas for his careful reading and criticism of the manuscript.

J. F. M.

HAMILTON, N.Y., September, 1, 1903.

CONTENTS

PART I

PART II

REACTIONS FOR DRY SUBSTANCES

PART III

SYSTEMATIC EXAMINATION FOR METALS IN SOLUTION

SYSTEMATIC EXAMINATION FOR METALS IN SOLUTION

SYSTEMATIC EXAMINATION FOR ACID RADICALS IN SOLUTION

PART IV

APPENDIX

INTRODUCTION

Analytical Chemistry treats of the composition of substances and of the methods by which we determine the same. There are two general divisions of analytical chemistry, viz.: *qualitative* and *quantitative* analysis.

Qualitative Analysis has for its object the determination of the constituent elements of a body. It consists in the separation of each of the elements, either in the free state, or, as more commonly happens, in the form of some compound which is characteristic and easily recognized.

Quantitative Analysis belongs to a more advanced course, and has for its object the determination of the percentage amounts of the constituents of a body, and thus of the actual constitution of the body.

Every simple inorganic substance consists of two parts. The first, which is a metal or positive radical, is chemically combined with the second, which is a non-metal or negative radical. The more complex substances may contain several metals, or positive radicals, and often contain more than one acid, or negative radical. These may be chemical combinations or merely mechanical mixtures.

By subjecting a substance to various conditions we obtain a series of phenomena which we call its reactions; and any known substance which is employed in effecting a reaction is called a *reagent*. The subjecting of a substance to the action of reagents, by means of which its constituent elements are recognized, is the process employed in qualitative analysis.

We may subject the substance to the action of reagents either in its original solid condition — if it be a solid — or in solution. These two methods of examination are known as the *dry way* and the *wet way*.

The dry way may be employed for the complete analysis of simple substances, and is a valuable aid in making preliminary tests of complex substances. This comprises what is known as Blowpipe Analysis, which is fully explained in Part II of this work.

The wet way is more generally used in qualitative analysis, because its reactions are, for the most part, simpler and more rapid. It can be employed with all kinds of substances. Solids and gases can generally be obtained in solution in water, or some other convenient liquid, in which they will dissolve without losing their characteristic properties.

When a substance in solution is acted upon by a reagent the results are always in accordance with a law which may be stated as follows: *When two substances which are in contact in solution can, under the conditions of the reaction, form a substance which is insoluble or volatile, the insoluble or volatile substance will always be formed and continue to be formed until one of the factors is exhausted.* An insoluble compound thus formed is called a *precipitate*, and precipitation is the most common form of reaction in analytical chemistry.

A precipitate may be of almost any color and the color may be characteristic, or if, as is more often the case, it is not especially so, other precipitates are formed with other reagents until the combination of results is such as to determine the substance with certainty. Sometimes a precipitate which is not characteristic becomes so by its solubility or insolubility in some other reagent or in an excess of the reagent first used. Solubility in excess is confined to a few reagents. These are the alkaline hydroxids and a few alkaline salts.

The treatment of a substance with a reagent sometimes results in the formation of a gas, which is recognized by its color or odor or by some other characteristic property. This almost always results from the decomposition of some acid radical by means of some acid used as a reagent.

In order to avoid constant mistakes, the student should thoroughly understand every reaction which he uses. In acquiring this knowledge he should, especially in the earlier and simpler portion of the course, accustom himself to the use of all the common reagents. In the more advanced portion of his course a more systematic and selective use of reagents will be necessary.

The student should first be required to perform all the reactions in Part I. He should write out the chemical equation in every case in a suitable *notebook*, and *at the time the reaction is made.* He may then be given some simple solutions and, by the use of the reactions he has just been performing, find what the unknown solution contains. Having found the substance contained in a solution, he should try all the reactions given for that substance. He should also compare each reaction with all similar reactions given by other substances, noting points of difference, and in this way make each reaction as comprehensive as possible.

Many students seem to feel that all that is required of them is to find out what is in the unknown solution. This is undoubtedly the goal toward which their course of study is tending ; but if, at the beginning of his course, that is *all* that the student desires, a much shorter method would be to ask the instructor. The value of an elementary course of study in analytical chemistry is not simply *to find out* what a solution or solid substance contains, but *to learn how to find out* what it contains.

It will be observed that in Part III all tables such as are often included in a text-book and intended for aid in the separation of the metals have been omitted. This is because, in the author's judgment, the use of them in the hands of the majority of students is pernicious. When such tables are used the student almost always depends upon them rather than upon the full text, and so is frequently led into error because of something which has been omitted. The information given in a table is necessarily brief, and the average student can acquire such information by a few hours of study. With such information in his head he will work much faster and with more satisfaction to himself and his instructors, and when in doubt he will consult the text and not a table.

Every student should be required to keep a notebook in which to record the results of all his work in the laboratory. He should also be encouraged, if not required, to make use of some large and fairly complete text-book on general chemistry for collateral reading, especially in connection with those compounds which he meets with in the course of his work. Such a course of action, if persisted in, will give to the student a much more comprehensive view of the subject, and will, in addition, provide him with a fund of information which will always be of value to him.

The instructor should require the student to do clean and careful work. Work done in a careless way, with dirty apparatus and on a dirty desk, is of little or no value. Clean, intelligent work, accompanied by a reasonable amount of reading and study, will give to the student, even if his course is only a short one, a glimpse at least of the immense and interesting field of study and research which is always open to the chemist.

QUALITATIVE ANALYSIS

PART I

REACTIONS FOR THE METALS IN SOLUTION

LEAD, Pb''

Lead dissolves easily in HNO_3 with formation of $Pb(NO_3)_2$.

$$3\ Pb + 8\ HNO_3 = 3\ Pb(NO_3)_2 + 4\ H_2O + 2\ NO.$$

It dissolves in hot concentrated H_2SO_4.

$$Pb + 2\ H_2SO_4 = PbSO_4 + 2\ H_2O + SO_2.$$

It is not attacked by dilute H_2SO_4 or HCl.

For the reactions use lead nitrate, $Pb(NO_3)_2$.

1. **Sodium Hydroxid** precipitates white $Pb(OH)_2$ or a white basic hydroxid, $Pb_2O(OH)_2$, according to the conditions which exist.

$$Pb(NO_3)_2 + 2\ NaOH = Pb(OH)_2 + 2\ NaNO_3.$$
$$2\ Pb(NO_3)_2 + 4\ NaOH = Pb_2O(OH)_2 + 4\ NaNO_3 + H_2O.$$

Soluble in excess of the reagent (4 vols.), easily soluble in concentrated NaOH, forming sodium plumbite, Na_2PbO_2.

$$Pb(OH)_2 + 2\ NaOH = Na_2PbO_2 + 2\ H_2O.$$

2. **Ammonium Hydroxid** precipitates a white basic salt, $(PbO)_2Pb(NO_3)_2$.

$$3\ Pb(NO_3)_2 + 4\ NH_4OH = (PbO)_2Pb(NO_3)_2 + 4\ NH_4NO_3 + 2\ H_2O.$$

Insoluble in excess of the reagent.

3. **Sodium or Ammonium Carbonate** precipitates white $PbCO_3$.

$$Pb(NO_3)_2 + Na_2CO_3 = PbCO_3 + 2\ NaNO_3.$$

If the solution is hot a white basic carbonate, $Pb_3(OH)_2(CO_3)_2$, is precipitated. This is known commercially as white lead.

$$3Pb(NO_3)_2 + 3Na_2CO_3 + H_2O = Pb_3(OH)_2(CO_3)_2 + 6NaNO_3 + CO_2.$$

4. **Hydrogen or Ammonium Sulfid** precipitates black PbS.

$$Pb(NO_3)_2 + (NH_4)_2S = PbS + 2\ NH_4NO_3.$$

Insoluble in cold dilute acids. Soluble in warm dilute HNO_3, forming $Pb(NO_3)_2$ and free sulfur.

$$3\ PbS + 8\ HNO_3 = 3\ Pb(NO_3)_2 + 4\ H_2O + 2\ NO + 3\ S.$$

Concentrated HNO_3 oxidizes PbS to $PbSO_4$.

$$3\ PbS + 8\ HNO_3 = 3\ PbSO_4 + 4H_2O + 8\ NO.$$

If the HNO_3 is of medium strength both reactions will go on at the same time.

5. **Acid Sodium Phosphate** precipitates white $Pb_3(PO_4)_2$.

$$3\ Pb(NO_3)_2 + 2\ Na_2HPO_4 = Pb_3(PO_4)_2 + 4\ NaNO_3 + 2\ HNO_3.$$

Easily soluble in HNO_3.

6. **Potassium Cyanid** precipitates white $Pb(CN)_2$.

$$Pb(NO_3)_2 + 2\ KCN = Pb(CN)_2 + 2\ KNO_3.$$

Insoluble in excess of the reagent.

7. **Potassium Iodid** precipitates yellow PbI_2.

$$Pb(NO_3)_2 + 2\ KI = PbI_2 + 2\ KNO_3.$$

The precipitate is soluble in boiling water (4 vols.), from which solution it crystallizes, on cooling, in golden yellow scales.

8. **Potassium Chromate** precipitates yellow $PbCrO_4$.

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2\ KNO_3.$$

Soluble in NaOH (5 vols. of dilute or 1 vol. of concentrated) and in HNO_3. Insoluble in acetic acid.

9. **Potassium Ferrocyanid** precipitates white $Pb_2Fe(CN)_6$.

$$2\ Pb(NO_3)_2 + K_4Fe(CN)_6 = Pb_2Fe(CN)_6 + 4\ KNO_3.$$

10. **Hydrochlorid Acid, or any soluble chlorid,** precipitates white $PbCl_2$.

$$Pb(NO_3)_2 + 2\ HCl = PbCl_2 + 2\ HNO_3.$$

Easily soluble in boiling water, from which, unless the solution is too dilute, it will crystallize, on cooling, in long white needles.

11. **Sulfuric Acid, or any soluble sulfate,** precipitates white $PbSO_4$.

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2\ HNO_3.$$

Easily soluble in ammonium tartrate or ammonium acetate. [Add tartaric or acetic acid, and then excess of NH_4OH.]

12. **Metallic Zinc** will entirely precipitate the lead in crystalline form.

$$Pb(NO_3)_2 + Zn = Pb + Zn(NO_3)_2.$$

NOTE. The chemical equations have been given under Lead as a guide for the student. Such equations will generally be omitted, but the student should be required to write them for himself.

SILVER, Ag′

Silver dissolves easily in HNO_3 with formation of $AgNO_3$. Insoluble in HCl and in H_2SO_4.

For the reactions use silver nitrate, $AgNO_3$.

1. **Sodium Hydroxid** precipitates brown Ag_2O. Insoluble in excess. Soluble in NH_4OH, forming NH_4AgO.

2. **Ammonium Hydroxid** precipitates the same. Very easily soluble in excess, forming NH_4AgO. [For the formation of this precipitate dilute the NH_4OH with 10 vols. of H_2O, and use only one or two drops of the reagent.] If the silver solution is very acid no precipitate will be formed.

3. **Sodium Carbonate** precipitates light yellow Ag_2CO_3. Insoluble in excess. Soluble in NH_4OH and in $(NH_4)_2CO_3$.

4. **Hydrogen or Ammonium Sulfid** precipitates black Ag_2S. Soluble in HNO_3. Insoluble in NH_4OH.

5. **Acid Sodium Phosphate** precipitates yellow Ag_3PO_4. Soluble in NH_4OH and in HNO_3.

6. **Potassium Cyanid** precipitates white AgCN. Soluble in excess, forming AgCN(KCN). From this solution HNO_3 precipitates AgCN.

7. **Potassium Iodid** precipitates light yellow AgI. Only very slightly soluble in NH_4OH, but easily soluble in KCN. Insoluble in HNO_3.

8. **Potassium Chromate** precipitates red-brown Ag_2CrO_4. Soluble in HNO_3 and in NH_4OH.

9. **Potassium Sulfocyanate** precipitates white AgSCN. Soluble in NH_4OH.

10. **Potassium Ferrocyanid** precipitates white $Ag_4Fe(CN)_6$. Difficultly soluble in NH_4OH.

11. **Hydrochloric Acid, or any Soluble Chlorid,** precipitates white AgCl. Soluble in NH_4OH, forming $(NH_3)_3(AgCl)_2$, and in KCN. From these solutions HNO_3 reprecipitates the AgCl.

12. **Metallic Zinc, Copper, or Mercury** will precipitate the silver in crystalline form.

13. **Reducing Agents,** such as sulfurous acid, stannous chlorid, or ferrous sulfate, will precipitate the silver as a fine gray powder.

MERCURY (Mercurous), Hg′

Mercury dissolves easily in HNO_3. If the mercury is in excess there is formed mercurous nitrate, $HgNO_3$; but if the HNO_3 is in excess, mercuric nitrate, $Hg(NO_3)_2$, is formed.

Mercury dissolves in hot concentrated H_2SO_4, forming mercuric sulfate, $HgSO_4$, and SO_2. It is insoluble in HCl.

For the reactions use a solution of $HgNO_3$.

1. **Sodium Hydroxid** precipitates black Hg_2O. Insoluble in excess of the reagent. Decomposed by boiling into HgO and Hg.

2. **Ammonium Hydroxid, or Ammonium Carbonate,** precipitates a black mixture of amido-mercuric nitrate, $HgNH_2NO_3$, and finely divided mercury.

3. **Sodium Carbonate** precipitates a brownish-black basic carbonate.

4. **Hydrogen or Ammonium Sulfid** precipitates black HgS mixed with Hg. Soluble in aqua regia. If this precipitate is boiled with concentrated HNO_3 it is changed into a white basic compound, $Hg(NO_3)_2(HgS)_2$.

5. **Potassium Iodid** precipitates yellowish-green HgI. If an excess of the reagent is added potassium mercuric iodid, $HgI_2(KI)_2$, is formed. This dissolves in the liquid, while metallic mercury is precipitated as a gray powder.

6. **Potassium Chromate** precipitates brick-red Hg_2CrO_4. Difficultly soluble in HNO_3.

7. **Hydrochloric Acid, or a Soluble Chlorid,** precipitates white HgCl (calomel). The addition of NH_4OH changes this precipitate to a black mixture of amido-mercuric chlorid, $HgNH_2Cl$, and finely divided mercury.

8. **Sulfuric Acid,** in not too dilute solutions, precipitates white Hg_2SO_4.

9. **Stannous Chlorid,** in very small quantity, precipitates white HgCl. In excess of the reagent the precipitate is reduced to gray metallic mercury.

10. **Metallic Copper, or Zinc,** in solutions slightly acidified with HCl, precipitates metallic mercury.

11. **Sulfurous Acid** reduces a mercurous solution to metallic mercury, which can often be collected in a globule by boiling with HCl.

MERCURY (Mercuric), Hg″

Mercury and most mercurous compounds can be changed to mercuric by heating with concentrated HNO_3.

For the reactions use a solution of $HgCl_2$, or $Hg(NO_3)_2$.

1. **Sodium Hydroxid** precipitates yellow $Hg(OH)_2$.

Insoluble in excess. Soluble in warm acids. If only a few drops of the reagent are used a brown basic compound is formed.

2. **Ammonium Hydroxid, or Ammonium Carbonate,** precipitates white amido-mercuric chlorid, $HgNH_2Cl$.

3. **Sodium Carbonate** precipitates a brown basic carbonate, $HgCO_3(HgO)_3$.

4. **Hydrogen or Ammonium Sulfid** precipitates at first a white double salt, $HgCl_2(HgS)_2$. Excess of the reagent causes this precipitate to change to yellow, orange, and finally to black HgS. Insoluble in concentrated HNO_3. Long-continued boiling with HNO_3 changes it into a white basic compound. [See Mercurous 4.]

5. **Potassium Iodid** precipitates scarlet-red HgI_2. Easily soluble in excess, forming $HgI_2(KI)_2$. The precipitate is first yellow, then salmon red, and finally scarlet red.

6. **Potassium Chromate** precipitates, from not too dilute solutions, orange red $HgCrO_4$.

7. **Metallic Copper** precipitates, from solutions acidified with HCl, gray metallic mercury.

8. **Stannous Chlorid** precipitates first white mercurous chlorid, HgCl, and in excess, gray metallic mercury.

Other reducing agents produce a similar change.

BISMUTH, Bi'''

Bismuth dissolves easily in HNO_3, in hot concentrated H_2SO_4, and in aqua regia, but not in HCl.

The ordinary bismuth salts are not soluble in H_2O except in the presence of considerable free acid, usually HNO_3 or HCl.

For the reactions use a solution of $Bi(NO_3)_3$, in dilute HNO_3.

1. **Water** in large quantities precipitates, if too much free acid is not present, white basic bismuth nitrate, $Bi(OH)_2NO_3$.

If much free HNO_3 is present the addition of ammonium chlorid, or of HCl, will cause the precipitation of white BiOCl. These precipitates are insoluble in tartaric acid. [See Antimony 1.]

2. **Sodium or Ammonium Hydroxid** precipitates white $Bi(OH)_3$. Insoluble in excess. Changed by boiling to yellow Bi_2O_3.

3. **Sodium or Ammonium Carbonate** precipitates white basic bismuth carbonate $(BiO)_2CO_3$.

4. **Hydrogen or Ammonium Sulfid** precipitates dark brown Bi_2S_3. Insoluble in $(NH_4)_2S$. Soluble in HNO_3.

5. **Acid Sodium Phosphate** precipitates white $BiPO_4$. Insoluble in dilute acids.

6. **Potassium Iodid** precipitates brown BiI_3. Soluble in excess.

7. **Potassium Chromate** precipitates yellow basic bismuth chromate $2\,[(BiO)_2CrO_4]Bi_2O_3$. Insoluble in NaOH. [See Lead 8.] Soluble in HNO_3.

8. **Sodium Stannite,** which is formed by adding NaOH to a solution of $SnCl_2$ until the precipitate first formed is dissolved, reduces the bismuth solution and forms a black precipitate, which is a mixture of Bi and Bi_2O_3; or, if the reagent is added in large excess, and hot, it precipitates metallic bismuth.

COPPER, Cu''

Copper dissolves easily in HNO_3, forming $Cu(NO_3)_2$ and NO, and in hot concentrated H_2SO_4, forming $CuSO_4$ and SO_2. It is only very slightly soluble in dilute H_2SO_4 or HCl.

For the reactions use a solution of $CuSO_4$.

1. **Sodium Hydroxid** precipitates light blue $Cu(OH)_2$. Insoluble in excess of the reagent. Soluble in NH_4OH.

If the precipitate is boiled with an excess of the reagent it becomes black, owing to the formation of $Cu(OH)_2(CuO)_2$.

2. **Ammonium Hydroxid** precipitates a light blue basic salt. Easily soluble in excess of the reagent, forming $CuSO_4(NH_3)_4H_2O$, which gives a deep-blue color to the solution (a very characteristic reaction). If KCN is added to this blue solution the color disappears, owing to the formation of $Cu(CN)_2(KCN)_2$.

3. **Sodium Carbonate** precipitates a blue basic carbonate, $Cu_2(OH)_2CO_3$. On boiling, this precipitate loses CO_2 and forms black $Cu(OH)_2(CuO)_2$.

4. **Hydrogen or Ammonium Sulfid** precipitates black CuS. Soluble in KCN and in HNO_3. Insoluble in dilute H_2SO_4. [See Cadmium 4.]

5. **Acid Sodium Phosphate** precipitates greenish-blue $Cu_3(PO_4)_2$. Soluble in NH_4OH.

6. **Potassium Cyanid** precipitates greenish-yellow $Cu(CN)_2$. Easily soluble in excess of the reagent, forming $Cu(CN)_2(KCN)_2$. From this solution H_2S will not precipitate the copper. [See Cadmium 6.]

7. **Potassium Iodid** precipitates white Cu_2I_2 and free iodin. The latter colors the precipitate brown. If H_2SO_3 is added the precipitate appears white.

8. **Potassium Sulfocyanate** precipitates black $Cu(SCN)_2$. If H_2SO_3 is added in excess the copper is reduced and white $Cu_2(SCN)_2$ is formed.

9. **Potassium Ferrocyanid** precipitates red-brown $Cu_2Fe(CN)_6$. [This is an exceedingly delicate reaction, one part of copper showing a reddish coloration in 200,000 parts of water.]

10. **Metallic Iron** precipitates copper from a solution.

CADMIUM, Cd″

Cadmium dissolves easily in HNO_3, and slowly in H_2SO_4 and HCl.

For the reactions use a solution of $Cd(NO_3)_2$.

1. **Sodium Hydroxid** precipitates white $Cd(OH)_2$. Insoluble in excess of the reagent.

2. **Ammonium Hydroxid** precipitates the same compound. Easily soluble in excess of the reagent.

3. **Sodium or Ammonium Carbonate** precipitates white $CdCO_3$. Insoluble in excess of the reagent. Soluble in NH_4OH.

4. **Hydrogen or Ammonium Sulfid** precipitates yellow CdS. Insoluble in $(NH_4)_2S$ or in KCN. Soluble in warm dilute H_2SO_4 or HNO_3. [See Copper 4.]

5. **Acid Sodium Phosphate** precipitates white $Cd_3(PO_4)_2$. Soluble in NH_4OH and in dilute acids.

6. **Potassium Cyanid** precipitates white $Cd(CN)_2$. Soluble in excess of the reagent, with formation of $Cd(CN)_2(KCN)_2$. From this solution H_2S precipitates CdS. [See Copper 6.]

7. **Potassium Chromate** precipitates a yellow basic chromate $Cd_2(OH)_2CrO_4$. Since this precipitate forms slowly, use a slight excess of the reagent and allow it to stand for a few minutes. Insoluble in NaOH. [See Lead 8.]

ARSENIC, As'''

This element exists in both trivalent and pentavalent relations, and has very few metallic properties. It does not dissolve in the acids to form salts, and we have already learned that it forms acids quite analogous to those of phosphorus. The principal reactions of arsenic are therefore to be found among those of the acids.

Arsenious oxid, As_2O_3, dissolves in HCl, and this solution may be used for the reactions.

1. **Hydrogen Sulfid** precipitates yellow As_2S_3. Insoluble in HCl. Soluble in NH_4OH or $(NH_4)_2CO_3$. It dissolves in $(NH_4)_2S$, forming ammonium sulfarsenite, $(NH_4)_3AsS_3$, and in yellow ammonium sulfid, $(NH_4)_2S_x$, forming ammonium sulfarsenate, $(NH_4)_3AsS_4$. HCl precipitates from these solutions, in the first case As_2S_3, in the second As_2S_5.

The other reagents for the metals give no precipitates with arsenic solutions.

If a solution containing pentavalent arsenic is treated with H_2S it is reduced, and the arsenic precipitated as As_2S_3, together with sulfur. This action takes place very slowly in a cold solution, but is immediate if the solution is hot.

A solution of sodium arsenate, Na_3AsO_4, may be used for this reaction.

ANTIMONY (Stibium), Sb'''

Antimony forms both trivalent and pentavalent compounds. It does not dissolve in HCl. With hot concentrated H_2SO_4 it forms $Sb_2(SO_4)_3$. With dilute HNO_3 it forms Sb_2O_3, and with concentrated HNO_3 it forms metantimonic acid, $HSbO_3$. It dissolves in aqua regia, forming $SbCl_3$ or $SbCl_5$, according to the degree of concentration of the acids and the duration of the action.

These compounds do not dissolve in water unless free hydrochloric or tartaric acid is present.

For the reactions use a solution of $SbCl_3$.

1. **Water,** added in excess, precipitates white antimony oxychlorid, $SbOCl$. Soluble in tartaric acid, so that if much of this acid is present the precipitation may not take place.

2. **Sodium Hydroxid** precipitates white $SbOOH$. Soluble in excess of the reagent, with formation of sodium metantimonite, $NaSbO_2$.

3. **Ammonium Hydroxid, or Sodium or Ammonium Carbonate,** precipitates the same. Insoluble in excess of the reagent.

4. **Hydrogen Sulfid** precipitates orange-red Sb_2S_3. Insoluble in $(NH_4)_2CO_3$ [See Arsenic 1] and in dilute acids. Soluble in warm concentrated HCl. Soluble also in $(NH_4)_2S$, forming ammonium sulfantimonite, $(NH_4)_3SbS_3$, and in $(NH_4)_2S_x$, forming ammonium sulfantimonate, $(NH_4)_3SbS_4$. HCl precipitates from these solutions Sb_2S_3 and Sb_2S_5 respectively.

5. **Metallic Zinc,** in solutions containing free HCl, precipitates the antimony as a black powder. If a piece of platinum foil is placed in the solution, in contact with the zinc, the antimony will be precipitated on the foil as a black stain.

Antimony, in its pentavalent relations, is acid in its properties. From such compounds the antimony may be precipitated by hydrogen sulfid as orange-red Sb_2S_5. This dissolves in warm concentrated HCl, forming $SbCl_3$ and precipitating sulfur.

TIN (Stannous), Sn''

Tin forms both stannous (Sn'') and stannic (Sn'''') compounds. It dissolves in HCl, forming $SnCl_2$; and in H_2SO_4, forming $SnSO_4$. With very dilute HNO_3 it forms $Sn(NO_3)_2$, some of the acid being reduced forming NH_4NO_3. Thus:

$$4\,Sn + 10\,HNO_3 = 4\,Sn(NO_3)_2 + NH_4NO_3 + 3\,H_2O.$$

With concentrated HNO_3 it forms white stannic acid, H_2SnO_3. It dissolves in aqua regia, forming $SnCl_4$.

For the reactions use a solution of $SnCl_2$.

1. **Sodium Hydroxid** precipitates white $Sn(OH)_2$. Soluble in excess of the reagent, forming sodium stannite, Na_2SnO_2.

2. **Ammonium Hydroxid, or Sodium or Ammonium Carbonate,** precipitates the same. Insoluble in excess of the reagent.

3. **Hydrogen or Ammonium Sulfid** precipitates dark brown SnS. Insoluble in $(NH_4)_2CO_3$ [See Arsenic 1], and in $(NH_4)_2S$ if free from $(NH_4)_2S_x$. Soluble in NaOH, in HCl, and in $(NH_4)_2S_x$, forming with the latter ammonium sulfostannate, $(NH_4)_2SnS_3$. From this solution HCl precipitates yellow stannic sulfid, SnS_2.

Stannous chlorid, and all other stannous compounds, are easily oxidized to stannic compounds. They act, therefore, as powerful reducing agents when in the presence of reducible compounds. Silver salts are reduced to metallic silver, and mercury salts to metallic mercury. [See Silver 13, Mercurous 9, and Mercuric 8.] Bismuth compounds are reduced to metallic bismuth. [See Bismuth 8.] Ferric compounds are changed to ferrous compounds. [See Ferric 10.] Potassium chromate, K_2CrO_4, and potassium permanganate, $KMnO_4$, are reduced to chromium chlorid and manganese chlorid respectively.

$$2\,K_2CrO_4 + 16\,HCl + 3\,SnCl_2 = 4\,KCl + 2\,CrCl_3 + 3\,SnCl_4 + 8\,H_2O.$$

Many other compounds give a similar reaction.

TIN (Stannic), Sn''''

Stannic compounds decompose on standing and precipitate $Sn(OH)_4$. If stannous chlorid be acidified with HCl, a few crystals of potassium chlorate added, and the whole boiled until the chlorous odors are driven away, the $SnCl_4$ thus formed may be used for the following reactions.

1. **Sodium Hydroxid** precipitates white stannic acid, H_2SnO_3. Soluble in excess of the reagent, forming sodium stannate, Na_2SnO_3. Soluble also in the mineral acids.

2. **Ammonium Hydroxid, or Sodium or Ammonium Carbonate,** precipitates the same. Insoluble in excess of the reagent.

3. **Hydrogen Sulfid** precipitates from solutions which do not contain too large an excess of HCl, yellow SnS_2. Soluble in concentrated HCl, and in $(NH_4)_2S$, forming ammonium sulfostannate, $(NH_4)_3SnS_3$. Insoluble in $(NH_4)_2CO_3$. [See Arsenic 1.]

4. If a solution of stannic chlorid is boiled in the presence of some neutral salt, such as sodium sulfate or ammonium nitrate, metastannic acid, $H_{10}Sn_5O_{15}$, is precipitated. This compound is a polymeric form of stannic acid, and is insoluble in HNO_3 or H_2SO_4.

ALUMINUM, Al'''

Aluminum dissolves easily in HCl, with some difficulty in H_2SO_4, and scarcely at all in HNO_3. It dissolves also in NaOH and in KOH, liberating hydrogen.

For the reactions use a solution of $Al_2(SO_4)_3$.

1. **Sodium Hydroxid** precipitates white $Al(OH)_3$. Easily soluble in excess of the reagent, forming sodium aluminate, $NaAlO_2$. From this solution it is reprecipitated by NH_4Cl. Soluble in all mineral acids and in acetic acid.*

2. **Ammonium Hydroxid** precipitates the same. Very slightly soluble in excess of the reagent, but reprecipitated by boiling. If NH_4Cl is present the precipitate is not dissolved in excess of the reagent.*

3. **Sodium or Ammonium Carbonate** precipitates the same, liberating CO_2.*

4. **Ammonium Sulfid** precipitates the same, liberating H_2S.*

---

* The presence of non-volatile organic substances, such as tartaric acid, citric acid, sugar, etc., prevents this precipitation.

5. **Acid Sodium Phosphate** precipitates white $AlPO_4$. Soluble in mineral acids and in NaOH. From the solution in NaOH, NH_4Cl precipitates the aluminum as $Al(OH)_3$.

6. **Sodium Acetate** gives no precipitate if the solution is cold, but if added in large excess and boiled the aluminum is completely precipitated as basic aluminum acetate, $Al(OH)_2(C_2H_3O_2)$. The solution must be neutral. If acid, neutralize with Na_2CO_3 or NaOH.

7. **Barium Carbonate** precipitates white $Al(OH)_3$, liberating CO_2.

CHROMIUM, Cr'''

[illegible]

Chromium dissolves in HCl and H_2SO_4, but is not soluble in HNO_3.

For the reactions use a solution of $Cr_2(SO_4)_3$.

1. **Sodium Hydroxid** precipitates gray-green $Cr(OH)_3$. Soluble in excess of the reagent, giving a dark green solution and forming sodium chromite, $NaCrO_2$. Reprecipitated by boiling or by the addition of NH_4Cl.

2. **Ammonium Hydroxid** precipitates the same. The precipitate is slightly soluble in excess of the reagent when cold and concentrated, giving a reddish color to the solution. Reprecipitated by boiling or by the addition of NH_4Cl.

3. **Sodium or Ammonium Carbonate** precipitates the same, liberating CO_2. The precipitate often contains some basic chromium carbonate of variable composition.

4. **Ammonium Sulfid** precipitates the same, liberating H_2S.

5. **Acid Sodium Phosphate** precipitates gray-green $CrPO_4$. Soluble in the mineral acids and in NaOH.

6. **Sodium Acetate** gives no precipitate unless iron or aluminum salts are present, in which case the chromium is partially precipitated by boiling.

7. **Barium Carbonate** precipitates gray-green $Cr(OH)_3$, liberating CO_2.

All chromium compounds, when treated with suitable oxidizing agents, are converted into compounds of chromic acid. A common method of oxidation is to heat the compound on a piece of platinum foil with a mixture of Na_2CO_3 and KNO_3, which gives the following result.

$$2\,Cr(OH)_3 + 3\,KNO_3 + 2\,Na_2CO_3 = 2\,Na_2CrO_4 + 3\,KNO_2 + 3\,H_2O + 2\,CO_2.$$

The reactions for chromic acid will be given with those of the other acids.

IRON (Ferrous), Fe″

Iron forms both ferrous (Fe″) and ferric (Fe‴) compounds. It dissolves easily in HCl or in H_2SO_4, forming $FeCl_2$ and $FeSO_4$ respectively. It dissolves in HNO_3, forming $Fe(NO_3)_3$, and in aqua regia, forming $FeCl_3$.

For the reactions use a solution of $FeCl_2$ or $FeSO_4$.

1. **Sodium Hydroxid** precipitates white $Fe(OH)_2$. Insoluble in excess of the reagent. The white color of the precipitate may be seen in a freshly reduced solution, but only for a moment, since it absorbs oxygen from the air, changes first to a dirty green, and then to a red-brown color, forming $Fe(OH)_3$. If ammonium salts are present the precipitation is not complete.

2. **Ammonium Hydroxid** partially precipitates the iron as $Fe(OH)_2$. If ammonium salts are present no precipitate appears at first; but on standing the iron is precipitated as red-brown $Fe(OH)_3$.

3. **Sodium or Ammonium Carbonate** precipitates, under the same conditions as above, white $FeCO_3$. This loses CO_2, oxidizes very easily, and is slowly changed to $Fe(OH)_3$.

4. **Hydrogen Sulfid** gives no precipitate in acidified solutions. In a neutral solution it gives a partial precipitation of the iron

as black FeS. If the solution contains sodium acetate the precipitation is nearly complete.

5. **Ammonium Sulfid** precipitates black FeS. Easily soluble in the mineral acids. Difficultly soluble in acetic acid. The precipitate oxidizes easily when exposed to the air, forming $FeSO_4$ and a basic ferric sulfate.

6. **Potassium Cyanid** precipitates light brown $Fe(CN)_2$. Soluble in excess of the reagent, forming $Fe(CN)_2(KCN)_4$ or $K_4Fe(CN)_6$.

7. **Potassium Sulfocyanate** gives no coloration unless ferric salts are present. [See Ferric 6.]

8. **Potassium Ferrocyanid** precipitates bluish-white potassium ferrous ferrocyanid, $K_2Fe''_3[Fe''(CN)_6]_2$. This absorbs oxygen from the air and quickly becomes blue. [See Ferric 7.]

9. **Potassium Ferricyanid** precipitates "Turnbull's blue," $Fe''_3[Fe'''(CN)_6]_2$. Insoluble in HCl. Decomposed by NaOH, forming $Fe(OH)_2$, which oxidizes very rapidly, giving $Fe(OH)_3$.

10. **Barium Carbonate** does not precipitate iron from ferrous solutions. [See Ferric 9.]

IRON (Ferric), Fe'''

When iron is dissolved in HNO_3, or in aqua regia, or when ferrous salts are acted upon by oxidizing agents, such as HNO_3, or $KClO_3$ and HCl, ferric compounds are formed.

$$6\ FeCl_2 + KClO_3 + 6\ HCl = KCl + 3\ H_2O + 6\ FeCl_3.$$

For the reactions use a solution of $FeCl_3$.

1. **Sodium or Ammonium Hydroxid** precipitates red-brown $Fe(OH)_3$. Insoluble in excess of the reagent. Soluble in any mineral acid. [If any non-volatile organic substance, such as tartaric acid, is present, NH_4OH gives no precipitate.]

2. **Sodium or Ammonium Carbonate** precipitates the same, liberating CO_2. The precipitation is only complete after boiling.

3. **Hydrogen Sulfid** reduces ferric salts to ferrous salts, giving a light-colored precipitate of sulfur.

4. **Ammonium Sulfid** reduces ferric salts to ferrous salts, and precipitates black FeS and sulfur. The FeS is soluble in HCl, the sulfur remaining undissolved.

5. **Acid Sodium Phosphate** precipitates yellowish-white $FePO_4$. Soluble in HCl. Insoluble in acetic acid.

6. **Potassium Sulfocyanate** produces a blood-red coloration in the solution, owing to the formation of $Fe(SCN)_3$. [A very delicate reaction.] This action does not take place in the presence of sodium acetate unless HCl is added in excess. [See Ferrous 7.]

7. **Potassium Ferrocyanid** precipitates "Prussian" or "Berlin blue," $Fe'''_4[Fe''(CN)_6]_3$. [A very characteristic reaction.] Insoluble in the mineral acids. Decomposed by NaOH, forming red-brown $Fe(OH)_3$.

8. **Sodium Acetate** produces a red coloration caused by the formation of $Fe(C_2H_3O_2)_3$. [If mineral acids are present they must be neutralized. This can be done best with Na_2CO_3.] On diluting this solution and boiling, the iron is completely precipitated as red-brown basic ferric acetate, $Fe(OH)_2(C_2H_3O_2)$.

9. **Barium Carbonate** precipitates red-brown $Fe(OH)_3$, liberating CO_2. [See Ferrous 10.]

10. **Stannous Chlorid**, or any other reducing agent, reduces ferric salts to ferrous salts.

NICKEL, Ni''

Nickel forms nickelous (Ni'') and a few nickelic (Ni''') compounds. It dissolves slowly in HCl and in H_2SO_4, forming $NiCl_2$ and $NiSO_4$ respectively, and readily in HNO_3, forming $Ni(NO_3)_2$.

For the reactions use a solution of $Ni(NO_3)_2$.

1. **Sodium Hydroxid** precipitates apple-green $Ni(OH)_2$. Insoluble in excess of the reagent. Soluble in NH_4Cl. If sodium hypochlorite, $NaOCl$, or bromin water with excess of $NaOH$, is added to this precipitate, it is oxidized to black $Ni(OH)_3$.

2. **Ammonium Hydroxid** precipitates the same from a neutral solution. Easily soluble in excess of the reagent to a light blue solution. If ammonium salts are present, or some free acid, by neutralizing which ammonium salts would be formed, no precipitate appears.

3. **Sodium or Ammonium Carbonate** precipitates an apple-green basic carbonate of variable composition. Soluble in $(NH_4)_2CO_3$ to a blue solution.

4. **Hydrogen Sulfid** gives no precipitate if the solution contains a free mineral acid. If the solution is neutral it gives a partial precipitation of black NiS. Sodium acetate added in excess to the nickel solution forms nickel acetate, from which solution H_2S precipitates all the nickel as black NiS.

5. **Ammonium Sulfid** precipitates the same. Slightly soluble in excess of the reagent to a dark brown solution, from which the NiS can be reprecipitated by boiling or by the addition of acetic acid. Insoluble in dilute HCl or acetic acid. Soluble in warm HNO_3 or in aqua regia.

6. **Acid Sodium Phosphate** precipitates apple-green $Ni_3(PO_4)_2$. Easily soluble in dilute acids.

7. **Potassium Cyanid** precipitates yellow-green $Ni(CN)_2$. Soluble in excess of the reagent, forming $Ni(CN)_2(KCN)_2$, and reprecipitated from this solution by dilute HCl. If $NaOH$ is added to the latter solution, and then bromin water in excess, black $Ni(OH)_3$ is precipitated, liberating cyanogen bromid, $CNBr$. (Poison! Work under a hood.) [See Cobalt 7.]

8. **Potassium Ferrocyanid** precipitates green $Ni_2Fe(CN)_6$. Insoluble in dilute acids.

9. **Potassium Ferricyanid** precipitates yellow-brown $Ni_3[Fe(CN)_6]_2$. Insoluble in dilute acids.

10. **Potassium Nitrite** gives no precipitate in a nickel solution. [See Cobalt 10.]

COBALT, Co″

Cobalt in its chemical relations very closely resembles nickel. It dissolves in the mineral acids, forming the corresponding salts. These in solution, or when they contain water of crystallization, are red, but on losing water become blue.

For the reactions use a solution of $Co(NO_3)_2$.

1. **Sodium Hydroxid** precipitates a blue basic salt. If excess of the reagent is added, and the whole boiled, the precipitate is changed to red $Co(OH)_2$. On standing, this slowly oxidizes to brown $Co(OH)_3$. Sodium hypochlorite and bromin water give reactions similar to those with nickel.

2. **Ammonium Hydroxid** precipitates from a neutral solution a blue basic salt. Soluble in excess of the reagent to a red-brown solution. If ammonium salts are present no precipitate appears, but the solution becomes red brown.

3. **Sodium or Ammonium Carbonate** precipitates a red-lilac basic carbonate of variable composition. Soluble in excess of the $(NH_4)_2CO_3$ to a red solution, which slowly becomes brown by oxidation. If acid sodium carbonate is used as the reagent it precipitates normal cobalt carbonate, $CoCO_3$.

4. **Hydrogen Sulfid** gives no precipitate if the solution contains a free mineral acid. In a neutral or alkaline solution, or in one containing sodium acetate, it precipitates black CoS.

5. **Ammonium Sulfid** precipitates black CoS. Insoluble in excess of the reagent, in dilute HCl, and in acetic acid. Soluble in warm HNO_3 and in aqua regia.

6. **Acid Sodium Phosphate** precipitates blue $Co_3(PO_4)_2$. Soluble in the mineral acids and in NH_4OH.

7. Potassium Cyanid precipitates red-brown $Co(CN)_2$. Soluble in excess of the reagent, forming $Co(CN)_2(KCN)_4$, and reprecipitated from this solution by dilute HCl. If the solution in KCN is boiled for some time potassium cobalticyanid, $K_3Co(CN)_6$, is formed. [Analogous to potassium ferricyanid.] HCl gives no precipitate in this solution.

If NaOH and bromin water are added to the solution in KCN the same compound, $K_3Co(CN)_6$, is formed, and cobalt is not precipitated. [See Nickel 7.] (Since the commercial cobalt salts often contain traces of nickel, a very slight precipitate will generally be formed.)

8. Potassium Ferrocyanid precipitates bluish-green $Co_2Fe(CN)_6$. Soluble in concentrated HCl to a blue-green solution.

9. Potassium Ferricyanid precipitates brown $Co_3[Fe(CN)_6]_2$. Insoluble in HCl.

10. Potassium Nitrite, added in excess to a cobalt solution which has been previously acidified with acetic acid, precipitates yellow cobaltic-potassium nitrite, $Co(NO_2)_3(KNO_2)_3$. The reaction is represented by the following equation:

$$Co(NO_3)_2 + 7\ KNO_2 + 2\ H(C_2H_3O_2) = \\ Co(NO_2)_3(KNO_2)_3 + 2\ KNO_3 + 2\ K(C_2H_3O_2) + H_2O + NO.$$

The precipitate forms slowly in dilute solutions, and so should be allowed to stand some time. The precipitate is somewhat soluble in pure water, but insoluble in the presence of KNO_2. [See Nickel 10.]

MANGANESE, Mn''

Manganese forms four classes of compounds, two in which it is basic, and two in which it is acid. These are the manganous (Mn'') and manganic salts (Mn'''), manganates (Mn^{vi}) and permanganates (Mn^{vii}). It dissolves easily in most acids, forming manganous salts, which are the common ones.

For the reactions use a solution of $MnSO_4$.

1. **Sodium Hydroxid** precipitates white $Mn(OH)_2$. Insoluble in excess of the reagent. Soluble in NH_4Cl. The precipitate oxidizes slowly in the air, forming brown $Mn(OH)_3$.

2. **Ammonium Hydroxid** precipitates the same in a neutral solution. In a solution containing ammonium salts, or a free acid, no precipitate is formed at first; but on standing, the solution soon oxidizes, and all the manganese is finally precipitated as brown $Mn(OH)_3$.

3. **Sodium or Ammonium Carbonate** precipitates white $MnCO_3$. Boiling makes the precipitation complete.

4. **Hydrogen Sulfid** gives no precipitate in either neutral or acid solutions.

5. **Ammonium Sulfid** precipitates flesh-colored MnS. Soluble in dilute mineral acids and in acetic acid. Insoluble in NH_4Cl, in the presence of which the precipitation is complete.

6. **Acid Sodium Phosphate** precipitates white $Mn_3(PO_4)_2$. Soluble in the mineral acids and in acetic acid. If the precipitate is dissolved in HCl, an excess of NH_4OH added, and the whole boiled, a light rose-colored crystalline precipitate of $MnNH_4PO_4$ is formed.

7. **Potassium Ferrocyanid** precipitates white $Mn_2Fe(CN)_6$. Easily soluble in H_2SO_4 and in HNO_3, and with difficulty in HCl.

8. **Potassium Ferricyanid** precipitates brown $Mn_3[Fe(CN)_6]_2$.

9. If a manganese compound is heated on a piece of platinum foil with a mixture of Na_2CO_3 and KNO_3 it will be oxidized, forming green sodium manganate, Na_2MnO_4. Thus:

$$MnSO_4 + 2\ Na_2CO_3 + 2\ KNO_3 = Na_2MnO_4 + Na_2SO_4 + 2\ KNO_2 + 2\ CO_2.$$

If the green mass is dissolved in water with the addition of a few drops of acetic acid, the color of the solution will change to red, owing to the formation of sodium permanganate, $NaMnO_4$, and dark brown MnO_2 will be precipitated.

10. If a small quantity of red lead, Pb_3O_4, is placed in a test-tube with 2 cc. of concentrated HNO_3, a few drops of the manganese solution added, and the whole carefully warmed, the solution becomes red from the formation of permanganic acid.

$$2\ MnSO_4 + 5\ Pb_3O_4 + 26\ HNO_3 = \\ 2\ HMnO_4 + 2\ PbSO_4 + 13\ Pb(NO_3)_2 + 12\ H_2O.$$

11. Manganic and permanganic acids and their salts are easily reduced to manganous salts in the presence of reducing agents, such as H_2SO_3, H_2S, or nascent hydrogen.

ZINC, Zn''

Zinc dissolves easily in most acids, forming the corresponding salt. It also dissolves in NaOH, forming sodium zincate, Na_2ZnO_2.

For the reactions use a solution of $ZnSO_4$.

1. Sodium Hydroxid precipitates white $Zn(OH)_2$. Easily soluble in excess of the reagent, forming sodium zincate, Na_2ZnO_2.

2. Ammonium Hydroxid precipitates the same. Easily soluble in excess of the reagent, forming $ZnSO_4(NH_3)_4$. Ammonium salts prevent the precipitation.

3. Sodium Carbonate precipitates a white basic carbonate of variable composition, but usually $Zn_2(OH)_2CO_3$. Boiling makes the precipitation complete. If acid sodium carbonate is used as the reagent it precipitates normal zinc carbonate, $ZnCO_3$.

4. Ammonium Carbonate precipitates the same. Soluble in excess of the reagent. Ammonium salts prevent the precipitation.

5. **Hydrogen Sulfid** gives no precipitate in solutions containing a free mineral acid. In a neutral or alkaline solution, or one acidified with acetic acid, it precipitates white ZnS.

6. **Ammonium Sulfid** precipitates the same from any solution. If NH_4Cl is present the precipitation is complete.

7. **Acid Sodium Phosphate** precipitates white $Zn_3(PO_4)_2$. Soluble in dilute acids and in NH_4OH.

8. **Potassium Cyanid** precipitates white $Zn(CN)_2$. Soluble in excess of the reagent, forming $Zn(CN)_2(KCN)_2$. From this solution $(NH_4)_2S$ precipitates white ZnS.

9. **Potassium Ferrocyanid** precipitates white $Zn_2Fe(CN)_6$. Insoluble in dilute acids and in NH_4OH.

10. **Potassium Ferricyanid** precipitates brownish-yellow $Zn_3[Fe(CN)_6]_2$. Soluble in HCl and in NH_4OH.

MAGNESIUM, Mg″

Magnesium dissolves easily in all acids, forming the corresponding salts. If heated in the air it takes fire quite easily, and burns with an intensely white light, forming MgO.

For the reactions use a solution of $MgSO_4$.

1. **Sodium Hydroxid** precipitates white $Mg(OH)_2$. Soluble in NH_4Cl. The presence of ammonium salts prevents the precipitation.

2. **Ammonium Hydroxid** gives a partial precipitation of the same in a neutral solution. If an ammonium salt or a free acid is present no precipitate appears.

3. **Sodium Carbonate** precipitates a white basic carbonate of variable composition. If the precipitate is boiled it has the composition $Mg_3(OH)_2(CO_3)_2$. If ammonium salts are present no precipitate is formed.

4. **Ammonium Carbonate** gives no precipitate if ammonium salts are present.

5. **Acid Sodium Phosphate** precipitates white $MgHPO_4$, which by boiling changes to $Mg_3(PO_4)_2$. If NH_4Cl is added to the solution, and then NH_4OH in excess, the reagent precipitates white crystalline $MgNH_4PO_4$. This precipitate forms slowly in a dilute solution and is complete only after standing some hours.

6. **Ammonium Oxalate** gives no precipitate in dilute solutions. In concentrated solutions it gives a white precipitate of MgC_2O_4. Soluble in NH_4Cl. [See Calcium 6.]

BARIUM, Ba''

The metal barium has little practical value and is very difficult to obtain in the metallic state.

It oxidizes easily in the air and decomposes water at the ordinary temperature.

Its salts are easy to form and many of them are soluble in water.

For the reactions use a solution of $BaCl_2$.

1. **Sodium Hydroxid** precipitates, if the solution is not too dilute, white $Ba(OH)_2$. Somewhat soluble in cold water, much more so in hot.

2. **Ammonium Hydroxid** gives no precipitate in barium solutions.

3. **Sodium or Ammonium Carbonate** precipitates white $BaCO_3$. Somewhat soluble in NH_4Cl. Soluble in water containing CO_2, forming the acid carbonate, $BaH_2(CO_3)_2$. The precipitation can be made complete by adding NH_4OH in slight excess and boiling.

4. **Acid Sodium Phosphate** precipitates a white acid phosphate, $BaHPO_4$. If NH_4OH is present it forms $BaNH_4PO_4$. Soluble in dilute acids and reprecipitated by NH_4OH.

5. **Potassium Chromate** precipitates yellow $BaCrO_4$. Soluble in HCl and HNO_3. Insoluble in NaOH [See Lead 8], and in acetic acid [See Strontium 5].

6. **Sulfuric Acid,** or any soluble sulfate, precipitates white $BaSO_4$. This precipitation takes place even in extremely dilute solutions. Insoluble in all acids and alkalies. [See Strontium 6.]

7. **Ammonium Oxalate** precipitates, if the solution is not too dilute, white BaC_2O_4. Dilute solutions give no precipitate. [See Calcium 6.] Soluble in HCl and HNO_3.

8. **Hydrofluosilicic Acid** precipitates white $BaSiF_6$. Somewhat soluble in water. Insoluble in alcohol and in dilute acids. [See Strontium 8.]

9. If a barium compound is heated on a platinum wire in an oxidizing flame it imparts a pale green color to the flame. If the compound is a chlorid, or is moistened with HCl, the color is more distinct.

STRONTIUM, Sr''

Strontium very closely resembles barium in its chemical properties.

For the reactions use a solution of $SrCl_2$.

1. **Sodium Hydroxid** precipitates white $Sr(OH)_2$. Somewhat soluble in water, but less so than $Ba(OH)_2$.

2. **Ammonium Hydroxid** gives no precipitate.

3. **Sodium or Ammonium Carbonate** precipitates white $SrCO_3$. Its properties are like those of $BaCO_3$. [See Barium 3.]

4. **Acid Sodium Phosphate** precipitates white $SrHPO_4$. Like $BaHPO_4$. [See Barium 4.]

5. **Potassium Chromate** gives no precipitate at first, but after a time, if the solution is neutral and not too dilute, yellow $SrCrO_4$

is precipitated. Insoluble in alcohol even when dilute, so that if alcohol is added to the solution the precipitate appears at once. Soluble in acetic acid. [See Barium 5.]

6. **Sulfuric Acid,** or any soluble sulfate, precipitates white $SrSO_4$. Slightly soluble in water, so that if the solution is very dilute the precipitate does not appear immediately. [See Barium 6 and Calcium 5.] A concentrated solution of Na_2CO_3 or $(NH_4)_2CO_3$ converts it into $SrCO_3$.

7. **Ammonium Oxalate** precipitates white SrC_2O_4. Somewhat soluble in water, but less so than BaC_2O_4.

8. **Hydrofluosilicic Acid** gives no precipitate in moderately dilute solutions. [See Barium 8.]

9. If a strontium compound is heated on a platinum wire in an oxidizing flame it imparts a crimson color to the flame. If the compound is a chlorid, or is moistened with HCl, the color is more distinct.

CALCIUM, Ca''

Calcium very closely resembles strontium and barium in its chemical properties.

For the reactions use a solution of $CaCl_2$.

1. **Sodium Hydroxid** precipitates white $Ca(OH)_2$. Slightly soluble in water, but much less so than $Sr(OH)_2$ or $Ba(OH)_2$.

2. **Ammonium Hydroxid** gives no precipitate.

3. **Sodium or Ammonium Carbonate** precipitates white $CaCO_3$. Its properties are like those of $BaCO_3$. [See Barium 3.]

4. **Acid Sodium Phosphate** precipitates white $CaHPO_4$. If NH_4OH is present the normal salt, $Ca_3(PO_4)_2$, is precipitated. Soluble in dilute acids and reprecipitated by NH_4OH.

5. **Sulfuric Acid,** or any soluble sulfate, precipitates white $CaSO_4$. Somewhat soluble in water, so that if the solution

is very dilute no precipitate appears. A concentrated solution of Na_2CO_3 or $(NH_4)_2CO_3$ converts it into $CaCO_3$.

6. **Ammonium Oxalate** precipitates, even from very dilute solutions, white CaC_2O_4. Soluble in HCl or HNO_3. Insoluble in water and acetic acid. [See Barium 7.] The presence of NH_4OH hastens the precipitation, which, if the solution is cold and dilute, is complete only after long standing.

7. **Hydrofluosilicic Acid** gives no precipitate even if alcohol is added. [See Barium 8.]

8. If a calcium compound is heated on a platinum wire in an oxidizing flame it imparts a yellowish-red color to the flame. If the compound is a chlorid, or is moistened with HCl, the color is more distinct.

THE ALKALI METALS

Potassium and sodium are the common elements belonging to the alkali group of metals. They are very strong bases, and form salts with every acid known. The salts are all soluble in water to some extent, and so form no precipitates with the common reagents, most of which are compounds of these metals. There are a few compounds which are difficultly soluble in water, and these are precipitated when they are produced in sufficiently concentrated solutions. Most of the salts of these metals are either insoluble, or difficultly soluble, in alcohol, so that the addition of this reagent often helps the formation of a precipitate. The compound radical ammonium, NH_4, forms a series of compounds analogous to those of potassium and sodium.

POTASSIUM (Kalium), K′

For the reactions use a solution of KCl.

1. **Acid Sodium Tartrate,** $HNa(C_4H_4O_6)$, precipitates, if the solution is not too dilute, white crystalline $HK(C_4H_4O_6)$. The

precipitate forms slowly, but may be hastened by shaking. [See Ammonium 2.]

2. **Hydrofluosilicic Acid** precipitates, if the solution is not too dilute, white K_2SiF_6. Insoluble in dilute acids and in alcohol.

3. If to 2 cc. of a solution of sodium nitrite there are added 1 cc. of acetic acid and 5 drops of a solution of cobalt nitrate a deep orange-yellow liquid is formed. This precipitates from the potassium solution yellow cobaltic-potassium nitrite, $Co(NO_2)_3(KNO_2)_3$. [See Cobalt 10.]

4. **Platinum Chlorid** * precipitates from neutral or slightly acid solutions yellow K_2PtCl_6. Soluble in 100 parts of water. Insoluble in alcohol.

All potassium salts, when heated on a platinum wire in an oxidizing flame, impart a reddish-violet color to the flame. This color appears red when seen through a blue glass.

SODIUM (Natrium), Na′

For the reactions use a solution of NaCl.

1. **Hydrofluosilicic Acid** precipitates, after long standing if the solution is dilute, or upon addition of alcohol, white Na_2SiF_6.

2. **Acid Potassium Pyroantimonate,** $K_2H_2Sb_2O_7$, precipitates, in neutral solutions which do not contain other metals, white $Na_2H_2Sb_2O_7$. The precipitation is slow, but may be hastened by shaking.

3. All sodium salts, when heated on a platinum wire in an oxidizing flame, impart a bright yellow color to the flame. This color is not seen through blue glass. A crystal of potassium bichromate appears colorless in this yellow light.

---

* The reactions with platinum chlorid may be omitted.

AMMONIUM, $(NH_4)'$

For the reactions use a solution of NH_4Cl.

1. **Sodium Hydroxid,** or any soluble base, when heated with an ammonium compound, decomposes it, liberating NH_3. This may be recognized by its characteristic odor, or by the white clouds of NH_4Cl which are formed if a rod moistened with HCl is held in the escaping gas.

2. **Acid Sodium Tartrate** precipitates, if the solution is not too dilute, $HNH_4(C_4H_4O_6)$. The precipitation may be hastened by shaking. [See Potassium 1.]

3. **Platinum Chlorid** precipitates, from neutral or slightly acid solutions, yellow $(NH_4)_2PtCl_6$. Soluble in 170 parts of water. Insoluble in alcohol.

4. **Nessler's Reagent,** a solution of $HgI_2(KI)_2$ with an excess of KOH, precipitates, even from extremely dilute solutions, brown $Hg_2I(NH_2)O$. This reaction is best shown by filling a test-tube nearly full of water, adding two or three drops of the ammonium solution, and then the reagent.

REACTIONS FOR THE ACID RADICALS IN SOLUTION

For the reactions for the acid radicals it is better to use solutions of the salts derived from the acids rather than the acids themselves, although the latter may sometimes be used. The salts are usually neutral in their action on litmus paper, while the acids and most acid salts turn the blue litmus paper red. The free acids may be further distinguished by leaving no residue when a few drops are evaporated to dryness on a piece of platinum foil.

The reactions are similar to those for the metals except that the solutions which were then used for the reactions now become the reagents, and the reagents then used are now the solutions for the reactions. In testing for the acid radicals, therefore, only a few of the more characteristic reactions will be given. For other reactions the student is referred to those given under the different metals.

The student must always consider the nature not only of the reagent used but also of the substance in the solution. If either is reducing in its action this will manifest itself in the precipitation. [See Silver 13, Mercurous 9, Bismuth 8, etc.] The relation which the metal in each bears to the acid radical in the other must also be considered. If the metal in the unknown solution forms a precipitate with the acid radical of the reagent no information regarding the acid radical of the unknown substance can be obtained by this particular reaction. This does not often occur, but when it does the other reactions must be relied upon for proving the constitution of the acid radical.

HYDROCHLORIC ACID, HCl

For the reactions use a solution of NaCl.

1. **Lead Acetate** precipitates white $PbCl_2$. Soluble in boiling water or in a large quantity of cold water, so that if the solution is very dilute the precipitate may fail to appear.

2. **Silver Nitrate** precipitates white AgCl. Easily soluble in NH_4OH and in KCN, and reprecipitated from these solutions by HNO_3.

3. **Mercurous Nitrate** precipitates white HgCl. By the addition of NH_4OH this precipitate becomes black, owing to the formation of amido-mercuric chlorid, $HgNH_2Cl$, mixed with finely divided mercury.

The changing of this precipitate from white to black by the addition of NH_4OH is characteristic of mercurous compounds rather than of chlorids.

HYDROBROMIC ACID, HBr

For the reactions use a solution of KBr.

1. **Lead Acetate** precipitates white $PbBr_2$. Somewhat soluble in water, but not as easily soluble as $PbCl_2$.

2. **Silver Nitrate** precipitates yellowish-white AgBr. Soluble with some difficulty in NH_4OH, but easily soluble in KCN. Insoluble in dilute acids.

3. **Mercurous Nitrate** precipitates yellowish-white HgBr. The precipitate becomes black on adding NH_4OH.

4. **Chlorin Water** liberates bromin from many of its compounds, coloring the solution red brown. If a little carbon disulfid, CS_2, is added to the solution, and the whole well shaken, the bromin dissolves in the CS_2 and colors it red brown.

HYDRIODIC ACID, HI

For the reactions use a solution of KI.

1. **Lead Acetate** precipitates yellow PbI_2. Soluble in boiling water, from which solution it crystallizes, on cooling, in golden yellow scales.

2. **Silver Nitrate** precipitates light yellow AgI. Only very slightly soluble in NH_4OH, but easily soluble in KCN. Insoluble in HNO_3.

3. **Mercurous Nitrate** precipitates yellowish-green HgI. [See Mercurous 5.]

4. **Mercuric Chlorid** precipitates scarlet-red HgI_2. Soluble in KI. [See Mercuric 5.]

5. **Bismuth Nitrate** precipitates brown BiI_3.

6. **Copper Sulfate** precipitates white Cu_2I_2 together with free iodin, which colors the precipitate brown. If H_2SO_3 is added the precipitate appears white.

7. **Chlorin or Bromin Water** liberates iodin from most of its compounds. If a little CS_2 is added to the solution and the whole well shaken, the iodin dissolves in the CS_2 and colors it violet. If starch paste is added to the solution, the iodin colors it deep blue.

HYDROFLUORIC ACID, HF

For the reactions use a solution of KF.

1. **Lead Acetate** precipitates white PbF_2. Soluble in HNO_3.

2. **Silver Nitrate** gives no precipitate. (Distinction between fluorids and the other halogen salts.)

3. **Barium Chlorid** precipitates white BaF_2. Soluble in HCl or in HNO_3.

4. **Calcium Chlorid** precipitates white CaF_2. Scarcely soluble in any dilute acid.

5. All fluorids are decomposed by concentrated H_2SO_4, liberating HF. This acid unites with the silicon in glass, forming SiF_4. Hence if a fluorid, together with some concentrated H_2SO_4, is heated for a moment in a clean test-tube, and the tube then emptied and cleaned, it will be found to have been etched. To show this reaction the solution must be fairly concentrated.

HYDROCYANIC ACID, HCN

For the reactions use a solution of KCN.

1. **Lead Acetate** precipitates white $Pb(CN)_2$. Insoluble in KCN.

2. **Silver Nitrate** precipitates white AgCN. Soluble in KCN and in NH_4OH, and reprecipitated from these solutions by HNO_3.

3. **Copper Sulfate** precipitates greenish-yellow $Cu(CN)_2$. Soluble in KCN, from which solution H_2S will not precipitate the copper.

4. **Cadmium Nitrate** precipitates white $Cd(CN)_2$. Soluble in KCN, from which solution H_2S precipitates yellow CdS.

5. If a few drops of $(NH_4)_2S_x$ are added to a solution of KCN, and the solution boiled for a moment, potassium sulfocyanate, KSCN, is formed. If HCl is now added in excess, ferric chlorid will produce a blood-red coloration, owing to the formation of $Fe(SCN)_3$.

6. If a small quantity of NaOH is added to a solution of KCN, then three or four drops each of $FeSO_4$ and $FeCl_3$, and finally HCl in excess, Prussian blue is formed. [See Ferric 7.]

SULFOCYANIC OR THIOCYANIC ACID, HSCN

For the reactions use a solution of KSCN.

1. **Silver Nitrate** precipitates white AgSCN. Soluble in NH_4OH.

2. **Mercurous Nitrate** produces a gray precipitate, which is a mixture of Hg and $Hg(SCN)_2$, with perhaps some HgSCN.

3. **Mercuric Nitrate** precipitates white $Hg(SCN)_2$.

4. **Copper Sulfate** precipitates, from a concentrated solution, black $Cu(SCN)_2$. If the solution is dilute, an emerald-green coloration is produced. If H_2SO_3 in excess is added to this solution, and the whole boiled, the copper is reduced and white $Cu_2(SCN)_2$ is precipitated. [See Copper 8.]

5. **Ferric Chlorid** produces a blood-red coloration in the solution, owing to the formation of $Fe(SCN)_3$. This is a very characteristic reaction.

HYDROFERROCYANIC ACID, $H_4Fe(CN)_6$

For the reactions use a solution of $K_4Fe(CN)_6$.

1. **Lead Acetate** precipitates white $Pb_2Fe(CN)_6$.

2. **Silver Nitrate** precipitates white $Ag_4Fe(CN)_6$. Insoluble in dilute NH_4OH.

3. **Copper Sulfate** precipitates red-brown $Cu_2Fe(CN)_6$. This reaction can be shown in a very dilute solution.

4. **Ferric Chlorid** precipitates Prussian blue, $Fe_4[Fe(CN)_6]_3$. Decomposed by NaOH, forming red-brown $Fe(OH)_3$.

HYDROFERRICYANIC ACID, $H_3Fe(CN)_6$

For the reactions use a solution of $K_3Fe(CN)_6$.

1. **Silver Nitrate** precipitates red-brown $Ag_3Fe(CN)_6$. Soluble in NH_4OH.

2. **Ferrous Sulfate** precipitates Turnbull's blue, $Fe_3[Fe(CN)_6]_2$. Insoluble in HCl.

3. **Ferric Chlorid** gives a red-brown solution but no precipitate.

4. **Zinc Sulfate** precipitates brownish-yellow $Zn_3[Fe(CN)_6]_2$. Soluble in HCl and in NH_4OH.

HYPOCHLOROUS ACID, HClO

All hypochlorites are soluble in water, and so the acid radical cannot be precipitated. If a concentrated solution of a hypochlorite is boiled, oxygen is liberated. If a dilute acid is added to the solution, chlorin is liberated.

For the reactions use a solution of NaClO.

1. **Lead Acetate**, to which NaOH has been added until the precipitate first formed is dissolved, precipitates brown PbO_2.

$$Pb(C_2H_3O_2)_2 + 2\,NaOH + NaClO = PbO_2 + 2\,NaC_2H_3O_2 + NaCl + H_2O.$$

The precipitation is hastened by boiling.

2. **Silver Nitrate** gives a white precipitate of AgCl, silver chlorate being formed at the same time.

$$3\,AgNO_3 + 3\,NaClO = 2\,AgCl + AgClO_3 + 3\,NaNO_3.$$

3. If a piece of litmus paper is moistened with a few drops of the solution and then exposed to acid fumes, the color will be bleached. If the moistened paper is breathed upon, the CO_2 in the breath will effect the same change.

CHLORIC ACID, $HClO_3$

The chlorates are all soluble in water and so form no precipitates.

For the reactions use a solution of $KClO_3$.

1. **Silver Nitrate** gives no precipitate with a chlorate, but if H_2SO_3 is added to the solution, the chlorate is reduced to a chlorid, and $AgNO_3$ then gives a white precipitate of AgCl.

2. **Hydrochloric Acid** decomposes the chlorates, giving chlorin peroxid and chlorin. Thus:

$$2\,HCl + KClO_3 = KCl + H_2O + ClO_2 + Cl.$$

The chlorin peroxid and chlorin dissolve in the solution, coloring it yellow; but if the solution is boiled these gases will pass off, giving what is called a "chlorous odor." This mixture possesses great oxidizing power.

HYDROGEN SULFID (Hydrosulfuric Acid), H_2S

For the reactions use a solution of H_2S or $(NH_4)_2S$.

1. **Lead Acetate** precipitates black PbS. Soluble in warm dilute HNO_3.

2. **Silver Nitrate** precipitates black Ag_2S. Soluble in warm dilute HNO_3.

3. **Antimony Chlorid** precipitates orange-red Sb_2S_3. Soluble in $(NH_4)_2S$ and reprecipitated by HCl.

4. All soluble sulfids, and most insoluble ones, are decomposed by warm H_2SO_4, liberating H_2S, which may be detected by its odor; also by the brown or black stain on a piece of paper moistened with lead acetate and held in the escaping gas.

THIOSULFURIC ACID, $H_2S_2O_3$

The salts of this acid, which are called thiosulfates, were formerly called hyposulfites. The free acid does not exist.

For the reactions use a solution of $Na_2S_2O_3$.

1. **Lead Acetate** precipitates white PbS_2O_3. Soluble in an excess of $Na_2S_2O_3$. Decomposed by boiling, forming PbS. [See Sulfurous Acid 1.]

2. **Silver Nitrate** precipitates white $Ag_2S_2O_3$. Easily soluble in an excess of $Na_2S_2O_3$, forming the double salt, $AgNaS_2O_3$.

The precipitate quickly becomes black, especially if warm, being reduced to Ag_2S.

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

3. **Barium Chlorid** precipitates, from a concentrated solution, white BaS_2O_3. Soluble in a large quantity of water. Decomposed by HCl, liberating sulfur dioxid and sulfur.

4. **Ferric Chlorid** produces a violet color in the solution. The color is not permanent and the solution soon becomes cloudy, owing to the reduction to $FeCl_2$ and the liberation of sulfur.

5. **Hydrochloric Acid** decomposes the thiosulfates, liberating SO_2 and giving a precipitate of free sulfur. [See Sulfurous Acid 4.]

SULFUROUS ACID, H_2SO_3

This is a weak acid and exists only in a dilute solution. It easily decomposes when heated, forming SO_2 and H_2O. Its salts are much more stable, but are all decomposed by dilute acids. A solution of a sulfite, on standing, becomes partially oxidized, forming a sulfate.

For the reactions use a solution of Na_2SO_3.

1. **Lead Acetate** precipitates white $PbSO_3$, which is not decomposed by boiling. [See Thiosulfuric Acid 1.] Soluble in dilute HNO_3.

2. **Silver Nitrate** precipitates white Ag_2SO_3, which is decomposed by boiling, forming black metallic silver.

3. **Barium Chlorid** precipitates white $BaSO_3$. Easily soluble in dilute HCl. The solution in HCl is often incomplete, owing to the presence of sulfates, which precipitate insoluble $BaSO_4$.

4. **Hydrochloric Acid** decomposes the sulfites, liberating SO_2. If a little potassium permanganate, $KMnO_4$, is now added, it is at once decolorized, owing to reduction. Thus:

$$2\ KMnO_4 + 5\ SO_2 + 2\ H_2O = 2\ MnSO_4 + K_2SO_4 + 2\ H_2SO_4.$$

Most other mineral acids give a similar reaction.

5. If a solution of H_2SO_3 is boiled with a little stannous chlorid and HCl it is first reduced to H_2S, the $SnCl_2$ being oxidized to $SnCl_4$. The H_2S then precipitates yellow SnS_2.

SULFURIC ACID, H_2SO_4

For the reactions use a solution of Na_2SO_4.

1. **Lead Acetate** precipitates white $PbSO_4$. Easily soluble in ammonium tartrate or ammonium acetate. [See Lead 11.]

2. **Barium Chlorid** precipitates white $BaSO_4$. Insoluble in all dilute acids.

3. **Calcium Chlorid** precipitates, in not too dilute solutions, white $CaSO_4$. A concentrated solution of Na_2CO_3 or $(NH_4)_2CO_3$ converts the precipitate into $CaCO_3$, which dissolves in dilute HCl, liberating CO_2.

CHROMIC ACID, H_2CrO_4

Chromium, p. 14

Chromium ordinarily acts like the metals, forming compounds with the acid radicals. It may be oxidized by fusion with Na_2CO_3 and KNO_3, forming a compound with the metal, in which chromium is found in the acid radical. [See page 15.]

For the reactions use a solution of K_2CrO_4.

1. **Lead Acetate** precipitates yellow $PbCrO_4$. Soluble in NaOH. Insoluble in acetic acid.

2. **Silver Nitrate** precipitates red-brown Ag_2CrO_4. Soluble in HNO_3 and in NH_4OH.

3. **Mercurous Nitrate** precipitates brick-red Hg_2CrO_4. Soluble in HNO_3.

4. **Barium Chlorid** precipitates yellow $BaCrO_4$. Insoluble in NaOH and in acetic acid.

5. Take a dilute solution of hydrogen dioxid, H_2O_2, acidify with HCl, add a little ether (about half an inch deep in the test-tube), then two or three drops of the chromate solution, and shake. A portion of the chromate will be oxidized by the H_2O_2, forming an unstable blue compound, which is supposed to be perchromic acid, $HCrO_4$. This dissolves in the ether, which rises to the surface, giving it a rich blue color.

6. **Nitric Acid** converts the yellow K_2CrO_4 into red potassium dichromate, $K_2Cr_2O_7$. This salt, which may be regarded as an acid chromate, gives in most cases the same reactions as the normal chromate.

[illegible] $2HNO_3$ = [illegible] Cr_2O [illegible]

7. The chromates, and especially the dichromates, when treated with H_2SO_4, form sulfates and liberate oxygen. They are therefore powerful oxidizing agents, and are used as such, especially in organic chemistry.

$K_2Cr_2O_7 + 4H_2SO_4$ = [illegible] $SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

NITROUS ACID, HNO_2

This acid does not exist in the free state. Even when liberated in a dilute solution it is easily decomposed, giving nitric acid, nitric oxid, and water. Its salts, the nitrites, are quite stable, but they are all decomposed by dilute acids, forming HNO_3 and liberating NO.

For the reactions use a solution of KNO_2.

1. **Silver Nitrate** precipitates, in a concentrated solution, white $AgNO_2$.

2. **Cobalt Nitrate,** to which has been added acetic acid, precipitates in an excess of the solution, yellow $Co(NO_2)_3(KNO_2)_3$. [See Cobalt 10.]

Sodium nitrite does not give this reaction.

3. If KI is added to a solution of a nitrite, together with a little starch paste and a few drops of dilute H_2SO_4, iodin is liberated, which colors the starch paste blue.

4. If a little $FeSO_4$ is added to a solution of a nitrite, and then a few drops of dilute acetic acid, the whole becomes brown, from the NO which is liberated dissolving in the $FeSO_4$. [See Nitric Acid 1.]

5. Nitrous acid is capable of oxidation to nitric acid in the presence of oxidizing agents. If $KMnO_4$ is added to a solution of a nitrite acidified with H_2SO_4, it is decolorized, owing to its reduction. Thus:

$$4\,KMnO_4 + 10\,KNO_2 + 11\,H_2SO_4 = 7\,K_2SO_4 + 4\,MnSO_4 + 10\,HNO_3 + 6\,H_2O.$$

NITRIC ACID, HNO_3

All nitrates are soluble in water, and so form no precipitates with the metals. They are all decomposed by H_2SO_4, liberating HNO_3. Nitric acid is an oxidizing agent, and the tests which indicate its presence are connected with an oxidizing action.

For the reactions use a solution of KNO_3.

1. Mix some of the nitrate solution with an equal volume of $FeSO_4$. Incline the tube a little and carefully pour down the side some concentrated H_2SO_4, and where the mixture meets the surface of the acid a brown ring of color will appear. The brown compound, which is due to a solution of NO in $FeSO_4$, is decomposed by heat, liberating the NO. [See Nitrous Acid 4.]

The action is threefold: (1) the liberation of HNO_3 by the action of H_2SO_4 on the nitrate; (2) the oxidation of $FeSO_4$ by the HNO_3, liberating NO; and (3) the absorption of NO by $FeSO_4$, forming the unstable brown compound.

2. If concentrated H_2SO_4 is mixed with the nitrate solution, a few fragments of copper added, and the whole boiled, NO is liberated, which, combining with the oxygen in the air, forms red-brown fumes of NO_2. These will be more easily seen by looking down through the mouth of the tube. The action is analogous to that in the first test.

PHOSPHORIC ACID, H_3PO_4

For the reactions use a solution of Na_2HPO_4.

1. **Lead Acetate** precipitates white $Pb_3(PO_4)_2$. Easily soluble in HNO_3.

2. **Silver Nitrate** precipitates yellow Ag_3PO_4. Soluble in NH_4OH and in HNO_3.

3. **Barium Chlorid** precipitates white $BaHPO_4$. Soluble in dilute HCl and reprecipitated by NH_4OH.

4. **Magnesium Sulfate,** to which has been added NH_4Cl and then NH_4OH in excess, precipitates white crystalline $MgNH_4PO_4$. This precipitate forms slowly, and in a dilute solution is complete only after standing some hours.

5. **Ammonium Molybdate,** $(NH_4)_2MoO_4$, with an excess of HNO_3 precipitates yellow ammonium phospho-molybdate, $(NH_4)_3PO_4(MoO_3)_{12}$. Soluble in NH_4OH and in excess of Na_2HPO_4. The precipitation is hastened by warming.

ARSENIOUS ACID, H_3AsO_3

We have already learned that arsenic may be precipitated as a sulfid. [See Arsenic 1.] It forms no other salts in which it acts as a metal, but acts like an acid, forming salts with the metals. The alkaline salts only are soluble in water. These may be formed by dissolving the oxid, As_2O_3, in a solution of an alkaline hydroxid.

For the reactions use a solution of K_3AsO_3 or Na_3AsO_3.

1. **Silver Nitrate** precipitates, in a neutral solution, yellow Ag_3AsO_3. Soluble in NH_4OH, in HNO_3, and in NH_4NO_3. If the ammoniacal solution is boiled for some time, metallic silver is precipitated, a portion of the arsenite being oxidized to an arsenate.

2. **Copper Sulfate** precipitates Scheele's green, $CuHAsO_3$. Soluble in NH_4OH and in acids.

If an excess of NaOH is added to a solution of an arsenite, then a few drops of $CuSO_4$, and the whole boiled, red Cu_2O is precipitated, a portion of the arsenite being oxidized to an arsenate. (Distinction from arsenates.) [See Arsenic Acid 2.]

3. **Reinsch's Test.** If a piece of metallic copper is placed in an arsenite solution acidified with HCl and warmed, a gray film of copper arsenid, Cu_5As_2, is formed on the surface of the copper.

4. **Stannous Chlorid,** to which has been added at least two volumes of concentrated HCl, and then warmed, precipitates black metallic arsenic.

5. **Hydrogen or Ammonium Sulfid** gives no precipitate in a neutral or alkaline solution of an arsenite. If the solution is acid, or is rendered acid, yellow As_2S_3 is precipitated. [See Arsenic 1.]

ARSENIC ACID, H_3AsO_4

Salts of this acid are derived from As_2O_5 or by oxidation of the arsenites.

The reactions for arsenic acid are very closely analogous to those for phosphoric acid.

For the reactions use a solution of Na_3AsO_4.

1. **Silver Nitrate** precipitates, in a neutral solution, red-brown Ag_3AsO_4. Soluble in NH_4OH and in HNO_3.

2. **Copper Sulfate** precipitates light blue $CuHAsO_4$. Soluble in NH_4OH. Not decomposed by boiling in an alkaline solution. [See Arsenious Acid 2.]

3. **Magnesium Sulfate,** to which has been added NH_4Cl and then NH_4OH in excess, precipitates white crystalline $MgNH_4AsO_4$. The precipitate forms slowly, especially in a dilute solution, but may be hastened by shaking. Soluble in HCl and reprecipitated

by NH_4OH. If $(NH_4)_2S$ or H_2S is added to the solution in HCl, the arsenate is reduced and yellow As_2S_3 mixed with free sulfur is precipitated. The action is hastened by warming. (Distinction from phosphates.)

4. **Ammonium Molybdate** gives no precipitate in the cold. If the solution is warmed, yellow ammonium arseno-molybdate, $(NH_4)_3AsO_4(MoO_3)_{12}$, is formed. Insoluble in NH_4OH.

5. **Hydrogen or Ammonium Sulfid** in a solution acidified with HCl reduces an arsenate to an arsenite, and then precipitates yellow As_2S_3 mixed with free sulfur. [See Arsenic 1.]

BORIC ACID, H_3BO_3

This is a weak acid. Only a few salts are known, and most of these are from the derivatives, — metaboric acid, HBO_2, and pyroboric acid, $H_2B_4O_7$.

For the reactions use a solution of borax, $Na_2B_4O_7$.

1. **Lead Acetate** precipitates, in not too dilute solutions, white $Pb(BO_2)_2$. Soluble in excess of the reagent.

2. **Silver Nitrate** precipitates white $AgBO_2$. If the solution is too dilute, the precipitate is yellow or brown, from the presence of Ag_2O.

3. **Barium Chlorid** precipitates, in not too dilute solutions, white $Ba(BO_2)_2$. Soluble in excess of the reagent and in NH_4Cl.

4. If a little alcohol is added to a solution of a borate in a small porcelain dish, then a little concentrated H_2SO_4, and the whole warmed, ethyl borate (boric ether) is formed. This is inflammable, and so the mixture may be ignited, when it will be seen to burn with a green-bordered flame.

CARBONIC ACID, H_2CO_3

This is a weak acid, existing only in a dilute solution. Its salts are common and quite stable.

For the reactions use a solution of Na_2CO_3.

1. **Lead Acetate** precipitates white $PbCO_3$ or, if the solution is hot, a white basic carbonate.

2. **Silver Nitrate** precipitates light yellow Ag_2CO_3. Soluble in NH_4OH and in $(NH_4)_2CO_3$.

3. **Barium Chlorid** precipitates white $BaCO_3$. Soluble in water containing CO_2, forming $BaH_2(CO_3)_2$, and reprecipitated by boiling. To show this solubility fill a large test-tube containing the precipitate with water, shake the mixture, pour out about one half, and lead CO_2 through the liquid until the precipitate dissolves.

4. All carbonates, whether soluble or insoluble in water, are decomposed with effervescence by dilute HCl and other acids, liberating CO_2. The presence of the CO_2 may be confirmed by decanting the heavy gas into a test-tube containing a little lime-water, $Ca(OH)_2$. On shaking with the gas, the lime-water becomes milky, owing to the precipitation of $CaCO_3$. Baryta-water, $Ba(OH)_2$, may be used in place of the lime-water.

SILICIC ACID, H_4SiO_4

This acid exists only in a dilute solution. On attempting to concentrate the solution, it loses a molecule of water and forms metasilicic acid, H_2SiO_3. This in turn decomposes on heating to 130°, forming H_2O and SiO_2. The silicates occurring in nature are generally salts of the polysilicic acids. Only the alkaline silicates are soluble in water.

For the reactions use a solution of Na_4SiO_4.

1. **Hydrochloric Acid** (concentrated) precipitates, in not too dilute solutions, white gelatinous H_4SiO_4. In dilute solutions this precipitate will appear only after long standing. It is somewhat soluble in water and in HCl, so that a portion of it remains in the solution.

2. **Ammonium Carbonate** or **Ammonium Chlorid** precipitates the same.

3. **Barium Chlorid** precipitates white Ba_2SiO_4.

4. **Calcium Chlorid** precipitates white Ca_2SiO_4.

ACETIC ACID, $H(C_2H_3O_2)$

This and the following acids belong to the division known as Organic Chemistry. They are, however, frequently used in the process of analysis, and it is therefore desirable to know how to recognize them.

Acetic acid is a liquid, boiling, when pure, at 119°. It has a characteristic pungent odor like that of vinegar. It is a monobasic acid, and its salts are all soluble in water, although one or two of them may be partly precipitated if the solutions are sufficiently concentrated.

For the reactions use a solution of $Na(C_2H_3O_2)$.

1. **Silver Nitrate** precipitates, from concentrated solutions, white $Ag(C_2H_3O_2)$. Soluble in NH_4OH.

2. **Ferric Chlorid** gives, in a neutral solution, a deep red coloration, but no precipitate. If this solution is now boiled, a precipitate of red-brown basic ferric acetate, $Fe(OH)_2(C_2H_3O_2)$, appears and the solution becomes colorless.

3. **Sulfuric Acid** gives no precipitate, but liberates acetic acid, which may be recognized by its odor.

4. If a few drops of alcohol are added to a solution of an acetate, then a little concentrated sulfuric acid, and the whole warmed, ethyl acetate (acetic ether) is formed. This is a volatile, ethereal liquid, having an agreeable and characteristic odor somewhat like that of apples.

OXALIC ACID, $H_2C_2O_4$

Oxalic acid is a white crystalline solid, soluble in water. It is a dibasic acid. The oxalates of the alkalies are soluble in water, while most of the others are insoluble.

For the reactions use a solution of $(NH_4)_2C_2O_4$.

1. **Lead Acetate** precipitates white PbC_2O_4. Soluble in HNO_3.

2. **Silver Nitrate** precipitates white $Ag_2C_2O_4$. Soluble in HNO_3 and in NH_4OH.

3. **Barium Chlorid** precipitates, in not too dilute solutions, white BaC_2O_4. Somewhat soluble in water. Soluble in HCl and in acetic acid.

4. **Calcium Chlorid** precipitates white CaC_2O_4. Insoluble in water, in acetic acid, and in NH_4OH. Soluble in HCl.

TARTARIC ACID, $H_2(C_4H_4O_6)$

Tartaric acid is a white crystalline solid, soluble in water. It is a dibasic acid. The normal tartrates of the alkalies are easily soluble in water, while the acid salts dissolve with difficulty. Most of the other tartrates are insoluble in water, but many of them dissolve in excess of the alkaline tartrates, forming double salts.

For the reactions use a solution of sodium potassium tartrate (Rochelle salt), $NaK(C_4H_4O_6)$.

1. **Lead Acetate** precipitates white $Pb(C_4H_4O_6)$. Soluble in HNO_3 and in NH_4OH.

2. **Silver Nitrate** precipitates white $Ag_2(C_4H_4O_6)$. Soluble in HNO_3 and in NH_4OH.

3. **Barium Chlorid,** when added in excess, precipitates white $Ba(C_4H_4O_6)$. Soluble in acetic acid.

4. **Calcium Chlorid,** when added in excess, precipitates white $Ca(C_4H_4O_6)$. Soluble in all acids and in NH_4Cl. Insoluble in NH_4OH.

5. If a few drops of silver nitrate are added to a solution of a tartrate in a carefully cleaned test-tube, then NH_4OH added drop by drop until the precipitate first formed is nearly dissolved, and the whole gently warmed, the silver tartrate will be reduced and metallic silver deposited as a brilliant mirror upon the glass. (A very characteristic reaction.)

PART II

REACTIONS FOR DRY SUBSTANCES

BLOWPIPE ANALYSIS

Matter, at the ordinary temperature, nearly always exists in the solid state. For purposes of analysis it is much more convenient to have it in the liquid condition. This may be obtained by solution or fusion. Since the latter often requires a very high temperature the former is almost universally employed.

In obtaining a solution of a given substance, it sometimes happens that a change in composition occurs, since solution may be attended by chemical change. In order to know the original composition of a substance we may have to analyze it in its original condition. The methods employed for this purpose belong to that part of analytical chemistry known as Blowpipe Analysis, and, while it is not desirable to present an exhaustive treatise at this time, a knowledge of the simpler operations belonging to this part of the subject is indispensable to the chemist.

By these methods all simple inorganic substances and many organic compounds may be completely analyzed, and many important facts about the more complex compounds may be learned. Some of the phenomena, while perfectly evident, are so slight as to be easily overlooked, unless carefully observed. They are, however, simple and easy to follow, and if carefully observed the results are accurate and conclusive. This part of the work, therefore, is of great value in developing the powers of observation.

Nearly all of the results are produced by heat, either alone or with reagents. The operations should be carried on systematically and the student taught to make the proper deductions from each operation before going on to the next.

For the heat a Bunsen lamp is employed. This is supplemented by an instrument called a blowpipe. The lamp should be furnished with an inner tube to be inserted for use with the blowpipe. The latter is used for producing both the oxidizing and reducing flame. The proper manner of using the blowpipe, and the ability to produce both the oxidizing and reducing flame, should be thoroughly mastered.

The operation, which is not very difficult, but is apt to puzzle the student at first, is as follows. Insert the blowpipe tube in the Bunsen lamp and turn down the flame so that it will be from four to five centimeters in length. Bring the tip of the blowpipe into the flame about a third part of the width of the flame and near the end of the inner tube. If a fairly strong current of air is now sent through the blowpipe, a long, pointed, blue, oxidizing flame is produced. This flame is used for fusion and oxidation. The hottest part of the flame is about midway between the point of the inner blue cone and the extreme tip of the flame. The point of maximum oxidation is at the extreme tip of the flame, or even just beyond this if the temperature is found to be sufficiently high.

If the tip of the blowpipe is held just outside the gas flame, and a gentle stream of air is sent through the blowpipe, the inner blue cone will be surrounded by a luminous mantle, forming the reducing flame. The point of maximum reduction is just within the point of the luminous mantle. The reducing flame is not nearly so hot as the oxidizing flame.

The proper use of the blowpipe can best be learned by practice under the guidance of a competent instructor. The other apparatus, as well as the reagents to be used, will be described as they are employed.

I. THE EFFECT OF HEAT ALONE

The substance is heated in a piece of hard glass tubing closed at one end. It should be heated in the Bunsen flame, at first gently, then strongly.

A. Water is given off. This is recognized by its condensation in small drops in the upper part of the tube, and indicates the following about the substance.

(*a*) *It is a deliquescent salt.* A deliquescent substance is one which absorbs moisture from the atmosphere. The water is driven off at a comparatively low temperature, and usually in small quantities.

(*b*) *It contains enclosed water.* The substance often decrepitates, or crackles, when heated. This is caused by the bursting of the particles. The amount of water is usually small.

This reaction is particularly characteristic of NaCl and certain other halogen salts; also of other salts which do not contain water of crystallization.

(*c*) *It contains chemically combined water.* The substance may be an hydroxid, an acid salt (generally of a volatile acid or one easily decomposed), an ammonium salt, or an organic compound. The steam, as it passes out of the tube, should be tested with a piece of moistened litmus paper. A neutral reaction usually indicates an hydroxid; an acid reaction, an acid salt; an alkaline reaction, an ammonium salt. The compound often shows a permanent change of color. If it blackens and gives off empyreumatic odors, it indicates an organic substance.

This action may require a fairly high temperature. The amount of water varies, but is usually not very great.

(*d*) *It contains water of crystallization.* A portion of the water comes off at or below 100°, but the last portion may require a much higher temperature. The amount of water is usually relatively large. Some alums, borates, and phosphates swell up considerably while giving off their water.

B. A gas is given off. This may consist of one or more of the following gases.

(*a*) *Oxygen.* This is recognized by the igniting of a glowing splinter when introduced into the tube. It indicates that the substance was a nitrate, a peroxid, or some highly oxidized salt, such as a chlorate, bromate, iodate, dichromate, or permanganate.

(*b*) *Ammonia.* This is easily recognized by its odor and the white fumes of NH_4Cl which are formed when a glass rod moistened with HCl is held in the escaping gas. It indicates an ammonium salt.

(*c*) *Carbon dioxid.* This is recognized by the turbidity which is caused when lime-water [$Ca(OH)_2$] is exposed to the gas. It indicates a carbonate or an organic compound. The latter usually blackens by heating. All carbonates give this except normal carbonates of the alkali metals. These, especially the commercial carbonates, sometimes contain, as impurity, small quantities of the acid carbonates, which give this reaction. A convenient instrument for showing this is made from a piece of glass tubing drawn out at one end to a capillary and bent like a siphon. This is attached to the closed tube by a piece of rubber tubing, the capillary end being placed in the lime-water and the closed tube heated.

(*d*) *Carbon monoxid.* This gas burns with a bright blue flame, by which it may be recognized. This indicates an oxalate or a formate. The latter blackens when heated.

The flame of carbon monoxid does not always appear blue, because of the presence of some impurity (such as sodium). It may also fail to appear because of the presence of water in the form of steam.

(*e*) *Sulfur dioxid.* This may be recognized by its odor, that of burning sulfur. It indicates a sulfate or a sulfite.

(*f*) *Hydrogen sulfid.* This is recognized by its odor, and by blackening a piece of paper moistened with lead acetate. It indicates a sulfid containing water.

(*g*) *Nitrous oxid.* This supports combustion nearly as well as oxygen and may be recognized by the same test. It indicates ammonium nitrate.

(*h*) *Nitrogen trioxid or tetroxid.* These gases may be recognized by their brownish-red color and a peculiar odor which is like that of nitric acid. They usually indicate a nitrate or nitrite of the heavy metals. The alkaline salts do not give this reaction.

(*i*) *Chlorin.* This is recognized by its yellow color and its odor; also by its bleaching action. It indicates certain chlorids and hypochlorites.

(*j*) *Bromin.* This is recognized by its red-brown color and its odor, which is much like that of chlorin. It indicates certain bromids, and other bromin compounds.

(*k*) *Iodin.* This is recognized by its deep violet-colored vapor. It indicates iodin, an iodid, or some other iodin compound.

(*l*) *Cyanogen.* This is recognized by its odor (Poison!), which is like that of KCN, and by the crimson color of its flame. It indicates a cyanid of one of the less basic metals.

(*m*) *Organic gases.* These may usually be recognized by their inflammability, the flame being more or less luminous. They indicate an organic substance.

C. A sublimate is formed. Some substances when heated pass directly from the solid to the gaseous state. When this gas comes in contact with the colder surface of the upper part of the tube it condenses again to a solid, forming a sublimate. This usually begins to form at a distance of one or more centimeters from the substance, and the line of formation is usually a sharp one, the sublimate shading off gradually above it. Sometimes when a substance fuses, a film of the melted material may extend up the tube for some distance from the substance. This must not be mistaken for the sublimate. The sublimates vary much in color.

1. A white sublimate is formed by the following substances.

(*a*) *Ammonium salts.* If two or three drops of a solution of NaOH are placed in the tube with the substance and warmed (the original substance may be treated this way in a test-tube), ammonia is given off, which may be recognized by its odor.

(*b*) *Mercurous chlorid.* The sublimate is yellow while hot, but becomes white on cooling.

(*c*) *Mercuric chlorid.* This is much like the mercurous chlorid, but fuses before it sublimes.

(*d*) *Arsenic trioxid.* This gives a sublimate of octahedral crystals. If a bit of charcoal is placed in the tube with the substance and heated, a black mirror of arsenic is produced.

2. A colored sublimate is formed by the following substances.

(*a*) *Arsenic.* This gives a black shining mirror, and may be formed by the element itself, or by its compounds in the presence of a reducing agent, like carbon. The vapor has a peculiar garlic-like odor.

(*b*) *Antimony sulfid.* This sublimes only at a very high temperature, the sublimate being black when hot, and reddish brown when cold.

(*c*) *Mercuric sulfid.* This forms a black sublimate which shows red when rubbed with a glass rod.

(*d*) *Iodin.* This gives a black sublimate and a deep violet-colored vapor.

(*e*) *Arsenic sulfid.* This is dark reddish brown while hot, and yellowish red when cold.

(*f*) *Sulfur.* This may come from free sulphur or from certain sulfids. The sublimate is brownish yellow while hot, and sulfur yellow when cool. It burns easily, giving off sulfur dioxid.

(*g*) *Mercuric iodid.* This forms a yellow sublimate, which soon changes to red, especially if rubbed with a glass rod.

D. The substance changes color. Many substances, upon heating, do not change in composition, but change in appearance. Upon cooling, the original color appears.

Many salts decompose on heating, leaving an oxid of the metal which may have a bright color. This may exhibit some of the phenomena given below, and thus give a clew to the original substance. The following are characteristic.

(*a*) *The substance is white*, becomes yellow when hot, and white again on cooling. This indicates zinc oxid, ZnO.

(*b*) *The substance is white*, becomes yellowish brown when hot, and is a dirty pale yellow on cooling. At a high temperature it is infusible and luminous. It indicates stannic oxid, SnO_2.

(*c*) *The substance is orange or light yellow*, becomes brown red when hot, and yellow when cold. It is fusible at a high temperature. It indicates lead oxid, PbO.

(*d*) *The substance is yellow*, becomes orange yellow or red brown when hot, and yellow when cold. It is fusible at a high temperature. It indicates bismuth oxid, Bi_2O_3.

(*e*) *The substance is red or red brown*, becomes a very dark red brown, almost black, when hot, and red when cold. It is infusible. It indicates ferric oxid, Fe_2O_3.

(*f*) *The substance is yellowish red*, becomes dark brown or black when hot, and red when cold. It decomposes when strongly heated, forming a black or gray sublimate, and giving off oxygen. It indicates mercuric oxid, HgO.

E. The substance fuses without decomposition. This generally indicates that the substance is an alkaline salt, though a very few other salts do this.

F. The substance carbonizes. Water is usually given off together with gases having a characteristic odor. This indicates an organic compound. Only a few organic compounds can be completely determined by these actions. They are the more common acids, and metallic salts of organic acids.

(*a*) *Acetates.* These give off aceton, which has a characteristic odor somewhat suggestive of vinegar.

(*b*) *Formates.* These give off CO, which burns with a bright blue flame.

(*c*) *Tartrates.* These give an odor like that of burnt sugar.

These salts of metallic bases and organic acids in decomposing by heat always leave a carbonate of the metal, which by further heating will form an oxid of the metal, unless the latter belongs to the alkali group. The carbonate may be recognized by the effervescence when a drop of HCl is added.

II. THE SUBSTANCE IS HEATED ON CHARCOAL

This gives the effect of heat in the presence of a strong reducing agent, the hot charcoal. A shallow cavity is made in a piece of soft-wood charcoal, the substance is placed in this, and heated with the blowpipe flame, at first gently, afterwards strongly. It is best to hold the charcoal somewhat inclined toward the flame, so that in case an incrustation should be formed it may be observed more readily. If the substance is very light and dry, so that it is liable to be blown away, it may be moistened with water, or, in some cases, a small piece of borax may be fused with the substance.

A. The substance fuses easily without decomposition, and sinks into the charcoal. This indicates a salt of the alkali metals or some of the salts of the alkaline earths.

B. The substance yields a metallic bead without any incrustation.

(*a*) *The bead is white.* This indicates tin, aluminum, or silver. Tin is very easily fusible (232°), aluminum requires quite a high temperature (655°), and silver fuses only with great difficulty (960°).

(*b*) *The bead is red.* This indicates copper and requires a very high temperature (1080°) and often long-continued heating. The bead is malleable, which distinguishes it from CuO, which is red, but brittle.

(*c*) *The bead is yellow.* This indicates gold and requires a very high temperature (1061°).

C. The substance yields a metallic bead with an incrustation.

(*a*) The bead is white, soft, and malleable. The incrustation is yellow and volatile. This indicates lead.

(*b*) The bead is white, soft, and malleable. The incrustation is red brown and volatile. This indicates cadmium.

(*c*) The bead is white, rather hard, and malleable. It is pretty well covered with the incrustation, which is yellow when hot, and white when cold. This indicates zinc.

(*d*) The bead is white, hard, and brittle. The incrustation is white and volatile. This indicates antimony.

(*e*) The bead is white, hard, and brittle. The incrustation is yellow and volatile. This indicates bismuth.

D. The substance is infusible, dark brown or black in color, gives no incrustation, and is more or less easily attracted by a magnet.

This indicates iron, chromium, nickel, cobalt, or manganese. These may be distinguished by the borax bead. [See Coloration of the Borax or Microcosmic Bead.]

Molybdenum, tungsten, and some of the platinum metals are infusible, and would be found here. They are not magnetic.

E. The substance deflagrates, or burns up quickly. This indicates a nitrate, or some highly oxidized salt, such as a chlorate, bromate, or iodate. Only the alkaline salts show this action in a marked degree; other salts are scarcely to be recognized by this test.

F. The substance decrepitates. This indicates a crystalline salt, which may contain enclosed water but does not usually contain water of crystallization. Sodium chlorid and other halogen salts show this action best.

G. The substance volatilizes.

(*a*) It forms a white, very volatile incrustation, and has a strong garlic odor. This indicates arsenic or some of its compounds. (Poison!)

(*b*) Those substances which form a sublimate in the closed tube are volatile on charcoal, and some of them give an incrustation which is volatile and similar in color to the sublimate.

H. The substance burns.

(*a*) The substance is a metal which burns with a brilliant white light, leaving a white infusible oxid. This indicates magnesium.

(*b*) The substance is a metal which burns with bright scintillations, leaving a dark brown or black oxid, which is magnetic. This indicates iron.

(*c*) The substance is a metal which burns with a bright white light, leaving an oxid which is yellow while hot, and white when cold. This indicates zinc.

(*d*) The substance burns with a blue flame, giving off SO_2, which may be recognized by its odor. This indicates sulfur.

I. The substance is infusible, white, and highly luminous when strongly heated. It should be allowed to cool somewhat, and the residue then moistened with a drop or two of a solution of $Co(NO_3)_2$, and again ignited strongly. The mass, on cooling, should then show a characteristic color as follows.

(*a*) *Blue.* This indicates aluminum oxid and alkaline phosphates or borates. Silicon dioxid and certain silicates when heated very strongly show this same reaction.

(*b*) *Flesh color.* This indicates magnesium oxid.

(*c*) *Green.* This, if yellowish green, indicates zinc oxid; if bluish green, tin oxid; if a dirty dark green, antimony oxid.

(*d*) *Violet.* This indicates magnesium arsenate, borate, or phosphate. The latter is fusible.

(*e*) *Red brown* while hot, colorless when cold. This indicates barium oxid. The residue gives an alkaline reaction with litmus paper.

(*f*) *Gray.* This indicates an oxid of calcium, or strontium, the latter being dark gray. The residue gives an alkaline reaction with litmus paper.

III. THE SUBSTANCE IS HEATED ON CHARCOAL WITH SODIUM CARBONATE

Very often the addition of sodium carbonate (soda) assists in the reduction of a compound, and hence some of the preceding reactions are more easily seen when this reagent is used. The silicates are reduced, barium and strontium salts form fusible compounds which sink into the charcoal, while calcium and magnesium salts are not changed. The salts of most of the other metals are reduced to oxids, or, in many cases, to the metal itself, by the combined action of the soda and the charcoal.

(*a*) If a compound containing sulfur in any form is strongly heated with sodium carbonate on charcoal, it is reduced to sodium sulfid, Na_2S. If a portion of the fused mass is placed on a clean silver coin and moistened with water, a dark brown or black stain of silver sulfid is produced. The particular way in which the sulfur is combined in the compound is not indicated by this action but may be determined by the action of sulfuric acid on the compound, and by special tests. [See VIII, (*d*).]

IV. COLORATION OF THE FLAME

Many substances, especially the alkali and alkaline earth salts, impart a characteristic color to the non-luminous flame. In the case of the alkali salts any compound may be used. The chlorids being most easily volatilized give the best results, and so, in case of other salts, it is often better to moisten the compound with HCl.

In the examination a platinum wire is used. It should be cleaned by ordinary methods, and then heated until no color is imparted to the flame. This may often be hastened by first dipping the wire in HCl. If the wire has been used with some difficultly volatile salt, it may be necessary to heat in a blast flame.

The sodium flame is nearly always visible, and very persistent, and not infrequently conceals any other color that may be present. Thus if sodium and potassium compounds occur together, the color due to potassium cannot be seen. The yellow color due to sodium compounds is entirely absorbed if the flame is observed through a piece of blue glass. The colors of the other compounds may be somewhat modified by this, but can all be seen. For very exact work a spectroscope should be used. This shows the color as a combination of colored lines, which occupy a certain position on a scale, and thus determine with certainty the presence or absence of any element. For the scope of the present work, however, this is not necessary. The following are the most characteristic colors produced.

(*a*) *A yellow flame.* This indicates sodium. The color disappears when observed through blue glass.

(*b*) *A violet flame.* This indicates potassium, and the color is nearly the same when observed through blue glass.

(*c*) *A red flame.* This indicates lithium if bright red; strontium if carmine red; calcium if orange red.

(*d*) *A green flame.* This indicates barium or boric acid if yellowish green (the latter, if in a salt, should first be moistened with H_2SO_4), copper if emerald green, thallium if bright grass-green. Phosphates, if warmed with a drop or two of H_2SO_4, show a transient bluish-green flame.

(*e*) *A blue flame.* This indicates copper chlorid, lead, antimony, or arsenic. Copper chlorid and lead give an azure blue, the former, after heating a short time, changing to green; antimony a greenish blue; arsenic a light blue.

V. COLORATION OF THE BORAX OR MICROCOSMIC BEAD

Many metallic oxids dissolve in fused borax or microcosmic salt, imparting a characteristic color to the fused mass. Compounds with sulfur, arsenic, or antimony must first be roasted to change them to oxids. This may be done on charcoal. Most other salts are changed to oxids by heat, and so show this action.

A platinum wire is used, the operation being as follows. Make a small loop at the end (not more than two millimeters in diameter), heat to redness, and, while hot, plunge it into the borax or microcosmic salt, as the case may be. Usually enough of the salt will adhere the first time; if not, after heating, the action should be repeated. Heat the salt in the non-luminous flame until the water of crystallization is driven off and the whole forms a clear, colorless bead in the loop. Bring the bead into contact with the substance for examination, taking care that only a very small quantity adheres to it, heat strongly in the oxidizing flame, and observe the color. It should afterwards be heated in the reducing flame, and the color observed.

Either salt may be used, although the borax will usually be found to be the more convenient, the microcosmic salt having a tendency to fall off from the wire. In a few cases, however, the latter must be used. The difference in color is very slight. The color of the bead while hot is sometimes characteristic. The following are the most important oxids which give colored beads.

(*a*) *Iron oxid.* In the oxidizing flame the bead is yellow or deep red when hot, and colorless to yellow when cold. In the reducing flame it is green when hot, and bottle-green when cold.

(*b*) *Chromium oxid.* In the oxidizing flame the bead is yellowish green when hot, and grass-green when cold. In the reducing flame it is a fine emerald green.

(*c*) *Nickel oxid.* In the oxidizing flame the bead is violet red when hot, and brown when cold. In the reducing flame it is gray or opaque from the reduced nickel, but by long heating it becomes colorless.

(*d*) *Cobalt oxid.* In both the oxidizing and reducing flame the bead is bright blue.

(*e*) *Manganese oxid.* In the oxidizing flame the bead is reddish violet (amethyst color). In the reducing flame it is colorless.

(*f*) *Copper oxid.* In the oxidizing flame the bead is bluish green. In the reducing flame it is brown; by long heating, red brown.

(*g*) *Bismuth oxid.* In the oxidizing flame the bead is yellow when hot, and colorless or opalescent when cold. In the reducing flame it is gray or opaque from the presence of reduced metal.

(*h*) *Silicon dioxid.* This dissolves in borax and gives a colorless bead with either flame. In the microcosmic salt it gives an insoluble, opaque mass, which floats about in the bead and is known as the "silica skeleton."

VI. THE SUBSTANCE IS FUSED ON PLATINUM FOIL WITH SODIUM CARBONATE AND POTASSIUM NITRATE

This may be done by mixing the substance with three or four times as much sodium carbonate, together with a small quantity of potassium nitrate (saltpeter), and heating on a piece of platinum foil until the mixture is completely fused.

Only the salts of manganese and chromium are to be tested for in this way, and they should have been indicated with more or less certainty by some of the preceding tests. The compounds of these metals will be strongly oxidized by the potassium nitrate, and the residue will have a characteristic color.

(*a*) *The residue is green.* This indicates a manganese compound which has been oxidized to a manganate. The green mass is decomposed by boiling water, and brown manganese oxid is precipitated.

(*b*) *The residue is yellow.* This indicates a chromium compound which has been oxidized to a chromate. If the color of the fused mass should not be very distinct, the presence of the chromate may be confirmed by dissolving the mass in warm water, adding acetic acid in excess to decompose the excess of sodium carbonate, and precipitating the chromic acid with lead acetate. [See Lead 8.]

VII. THE SUBSTANCE IS ACTED UPON BY SULFURIC ACID

The action of sulfuric acid upon a salt is primarily to liberate the acid from which the salt was derived. It quite often happens that the acid thus liberated is unstable and decomposes, setting free some gas which is easily recognized and which is characteristic. A few salts, such as sulfates, phosphates, arsenates, etc., are not volatile, and so yield negative results when treated in this way. These will have been detected by some of the previous actions, so that the negative result will be characteristic.

Whenever a metal is acted upon by any acid the primary result is the liberation of hydrogen. If the acting acid is concentrated sulfuric acid, and the temperature is high, the hydrogen which is formed will immediately reduce some of the acid, forming sulfur dioxid, which is recognized by its odor.

The concentrated acid is quite generally used, though the dilute acid may sometimes have to be employed. In the latter case the results are usually the same if any action takes place. The differences, and the cases where it is necessary to use the dilute acid, will be noted as they occur. In a few cases explosive gases may be liberated, and in order to avoid accidents it is best to proceed as follows.

Place in a test-tube a small quantity of concentrated sulfuric acid (not more than a centimeter in depth), and heat to about 100°. Do not heat much if any higher than this, or the acid itself may begin to decompose and give off gases which will obscure the desired result.

At this temperature any explosive gases which may be generated will be decomposed as fast as formed, and so can never accumulate in sufficient quantities to become dangerous. Add the substance under examination slowly and in small quantities, and carefully observe the results.

The following are the more important gases given off by this action. When not otherwise stated they may be recognized as given on page 51, or by special tests.

(*a*) *Oxygen.* This indicates that the substance was a peroxid or some highly oxidized salt, such as a chromate or permanganate.

(*b*) *Carbon dioxid.* This indicates a carbonate, an oxalate, or some organic compound. The latter generally blackens, and gives empyreumatic odors. [Compare Carbonic Acid 4.] Sulfur dioxid is also formed from the presence of carbon. [See (*j*).]

(*c*) *Carbon monoxid.* This indicates a formate, oxalate, cyanid, ferrocyanid, ferricyanid, or some organic substance. Oxalic acid gives both CO and CO_2.

(*d*) *Hydrochloric acid.* This is recognized by its suffocating odor, and the white fumes when a glass rod dipped in ammonia is held in the escaping gas. It indicates a chlorid.

(*e*) *Hydrobromic and hydriodic acids.* These present properties very much like hydrochloric acid, but in addition are more or less completely decomposed by the heat, giving bromin or iodin. They indicate a bromid or iodid respectively.

(*f*) *Hydrofluoric acid.* This indicates a fluorid. It is liberated as a colorless fuming gas, which has a suffocating odor and is very corrosive. If breathed in more than minute quantities, it may prove dangerous. This acid etches glass, and so when a fluorid is heated in a clean test-tube with concentrated H_2SO_4 the sides of the tube will be etched.

If a glass rod moistened with water is held in the escaping gas, it is at once coated with gelatinous silica, because of the decomposition of the SiF_4 which is present.

(*g*) *Hydrocyanic acid.* This is recognized by its odor, which is similar to that of KCN. It is exceedingly poisonous and burns with a violet flame. It indicates a cyanid or a sulfocyanate. The ferrocyanids heated with dilute H_2SO_4 also give HCN.

(*h*) *Hydrogen sulfid.* This indicates a sulfid. Dilute sulfuric acid shows this reaction and gives even better results than the concentrated acid, for in the presence of certain reducing agents concentrated H_2SO_4 may be reduced to H_2S, especially at a high temperature. [See VIII, (*c*).]

(*i*) *Hydrogen.* This gas is inflammable, and when mixed with air is explosive, so that when a flame is brought to the mouth of the test-tube in which it is being generated a sharp explosion often occurs (not dangerous) and a flame runs down the tube. This indicates a metal, and the reaction is best observed with dilute sulfuric acid; for if the acid is concentrated the hydrogen may reduce it, forming sulfur dioxid.

(*j*) *Sulfur dioxid.* This indicates a sulfite or a thiosulfate, the latter giving in addition a yellow precipitate of sulfur. This action is also given by dilute sulfuric acid. Certain elements, such as lead, copper, mercury, carbon, etc., when heated with the concentrated acid also give sulfur dioxid. [See (*i*).]

(*k*) *Nitrogen peroxid.* This indicates a nitrate or a nitrite. The nitrites are decomposed by cold dilute sulfuric acid, giving the red fumes of nitrogen peroxid at once, while the nitrates give nitric acid. [See (*l*).]

(*l*) *Nitric acid.* This indicates a nitrate. The nitric acid formed in this way has much the appearance of hydrochloric acid, but may be recognized by adding a small piece of metallic copper, when red fumes of nitrogen peroxid are given off. [See Nitric Acid 1.] The latter are also produced by boiling, which decomposes the nitric acid.

(*m*) *Chlorin.* This indicates a hypochlorite, from which it is also liberated by dilute sulfuric acid.

(*n*) *Chlorin peroxid.* This is a heavy yellowish-green gas, which smells something like chlorin and is very explosive. It indicates a chlorate. By decomposition it forms chlorin and oxygen.

(*o*) *Bromin.* This indicates a bromid. [See (*e*).]

(*p*) *Iodin.* This indicates some iodin compound, usually an iodid. [See (*e*).]

(*q*) *Acetic acid.* This may be recognized by its pungent odor, which is like that of vinegar. It indicates an acetate.

VIII. SPECIAL TESTS

In testing substances systematically, as in the preceding sections, we sometimes find two or three compounds which resemble each other so closely as to make it difficult to determine what we have. In order to distinguish such substances we may subject them to some special and characteristic test. The following are the most important substances to be distinguished in this way.

(*a*) *Hydrochloric acid.* This gas fumes in the air and has a suffocating odor. It is in this respect quite like hydrobromic, hydrofluoric, and nitric acids. If to the mixture of warm sulfuric acid and a chlorid [see VII, (*d*)] a little MnO_2 is added, chlorin will be liberated, which may be recognized by its yellow color and its peculiar odor.

(*b*) *Hydrobromic acid.* If a mixture of sulfuric acid and a bromid be treated with MnO_2, bromin will be liberated, which may be recognized by its red-brown color and its odor, which is similar to that of chlorin.

(*c*) *Hydriodic acid.* This is also a fuming gas with a suffocating odor; but when liberated from an iodid with sulfuric acid it is more or less decomposed, and iodin set free. The latter is recognized by its violet-colored vapor. Since hydriodic acid is a reducing agent, if the temperature is high and the sulfuric acid concentrated, the latter may be reduced and hydrogen sulfid liberated. [See VII, (*h*).]

(*d*) *Sulfur compounds.* These all give the test for sulfur as shown under III, (*a*). Having thus determined that the compound contains sulfur in some form, we have to determine further what compound we have. The following are the most important compounds of sulfur and the way to distinguish them. Treat them with warm concentrated sulfuric acid as under VII. In most cases dilute sulfuric acid will give the same reaction.

Sulfids will yield hydrogen sulfid, which may be recognized by its odor.

Sulfites will yield sulfur dioxid, which may be recognized by its odor.

Thiosulfates will yield sulfur dioxid, together with a yellow precipitate of sulfur, which remains undissolved in the acid.

Sulfates are entirely unaffected by both concentrated and dilute sulfuric acid, and so may be distinguished by this negative action.

If a sulfate is strongly heated in a closed tube with a small piece of magnesium wire, the latter becomes incandescent, a vigorous action takes place, MgS is formed, and SO_2 is liberated. After the tube is cool, if a little dilute acid is added to the contents, H_2S is liberated.

Sulfocyanates (called also sulfocyanids) give free sulfur, and HCN, which may be recognized as under VII, (*g*).

[The rare elements selenium and tellurium resemble sulfur very closely and give a similar reaction when heated on charcoal with sodium carbonate. Selenium when thus treated gives an odor of rotten horseradish. Tellurium does not give an odor, but in the closed tube gives a white sublimate which is fusible but not volatile.]

(*e*) *Boric acid.* If a borate is placed in a test-tube with concentrated sulfuric acid, a little alcohol added, and the whole warmed, ethyl borate is formed, which burns with a characteristic green flame. If the amount is small the flame may appear yellow with a green border.

(*f*) *Acetic acid.* If an acetate is treated with sulfuric acid, acetic acid is liberated. [See VII, (*q*).] If alcohol is also added ethyl acetate is formed, which may be recognized by its apple-like odor.

(*g*) *Phosphoric acid.* The phosphates are not easily decomposed and so the tests already given are not altogether satisfactory. [See II, I, (*a*) and IV, (*d*).] If a phosphate is strongly heated in a closed tube with a small piece of magnesium wire, the latter becomes incandescent, a vigorous action takes place, and magnesium phosphid is formed. After the tube is cool, if the contents are moistened with a drop or two of water, phosphin is liberated, which has a characteristic and disagreeable odor something like rotten fish. If the amount of phosphin is sufficient, it may take fire spontaneously. Hypophosphites when heated alone in a closed tube will give phosphin.

(*h*) *Arsenic.* Most arsenic compounds when heated on charcoal give the characteristic garlic odor. [See II, G, (*a*).] Arsenic compounds which do not give this when heated alone should be mixed with potassium oxalate or potassium cyanid and heated, when the odor is given.

Most compounds of arsenic heated in a closed tube with a little charcoal give the characteristic arsenic mirror. [See I, C, 2, (*a*).] All compounds of arsenic will give this if previously mixed with equal parts of sodium carbonate and potassium cyanid.

(*i*) *Peroxids.* In addition to the reactions already given [see I, B, (*a*) and VII, (*a*)], peroxids and all highly oxidized compounds when heated with concentrated hydrochloric acid give free chlorin.

PART III

SYSTEMATIC EXAMINATION FOR METALS IN SOLUTION

SIMPLE COMPOUNDS

This section of the work has for its aim instruction in the general scheme for qualitative analysis, and is given here because it is advisable that the analysis of simple compounds should precede that of complex bodies.

By simple compounds we mean those which contain but one metal and one acid radical, the salts being usually normal. In actual analysis there are few simple compounds, and often the substance to be analyzed is quite complex, containing several metals and more than one acid radical.

In the systematic analysis of substances, certain reagents are used to separate the metals into groups, and are therefore known as group reagents. The groups are then subdivided by other reagents until a single metal is separated from the others. The separated metal is then tested by methods given under Part I.

This particular section, which treats of simple compounds, is therefore valuable in learning the groups and group reagents and how to use them, as well as the methods for further subdividing the groups. The next section will treat of the analysis of mixed compounds.

Group 1

The solution should first be tested with litmus paper to see whether it is neutral, acid, or alkaline. If it is found to be alkaline, it must first be rendered acid by hydrochloric acid. If it is neutral or acid, add two or three drops of HCl and observe whether or not a precipitate is formed. If no precipitate forms, silver, mercurous, and probably lead compounds, which constitute Group 1, are absent, in which case pass on to Group 2. If a precipitate forms, add more HCl until the metal has been completely precipitated.

[Certain basic salts of antimony or bismuth may be precipitated by the first drops of HCl. These dissolve easily on the addition of more acid and will then appear in their proper place in the next group.]

Take about one-half of the white precipitate, add a little water, and boil. If the precipitate dissolves, it is lead chlorid. Confirm by adding K_2CrO_4 or H_2SO_4.

[These and all the following confirmatory tests are given under the respective metals in Part I, and should be referred to by the student in testing.]

To the other half add NH_4OH. If the precipitate dissolves, it is silver chlorid. Confirm by reprecipitating with HNO_3.

If on the addition of the NH_4OH the precipitate becomes black, it is mercurous chlorid. Confirm by testing the original solution with $SnCl_2$.

Group 2

If no precipitate was formed by the addition of HCl, add to this acid solution hydrogen sulfid until, after stirring or shaking, the solution distinctly smells of this reagent. (If the liquid becomes only slightly turbid by the addition of the H_2S, heat nearly to boiling, add more H_2S, and allow it to stand for a short time.)

If no precipitate is formed, pass on to Group 3. Group 2 consists of lead, mercuric, bismuth, copper, cadmium, arsenic, antimony, and tin compounds, and the precipitate, which is a sulfid of one of these metals, may be yellow, orange red, brown, or black. If the solution should be strongly acid, or contain some easily reducible compound, a milky appearance, due to the separation of free sulfur, may be produced by the reagent.

(*a*) *The precipitate is yellow.* Take a portion of the precipitate, add equal volumes of NH_4OH and $(NH_4)_2S$, and warm. If the precipitate does not dissolve, it is cadmium sulfid. Confirm by testing the original solution with NaOH.

If the yellow precipitate dissolves in $(NH_4)_2S$, it is arsenic or stannic sulfid. Test the original solution with NaOH. If no precipitate is formed, it is arsenic; if a precipitate forms which is soluble in excess of the reagent, it is stannic.

(*b*) *The precipitate is orange red.* It is antimony sulfid. Confirm by diluting the original solution with water, when a white basic compound will be precipitated.

(*c*) *The precipitate is brown.* It is stannous or bismuth sulfid. Take a portion of the precipitate and treat it with a little $(NH_4)_2S_x$. If it dissolves, it is stannous. Confirm by testing the original solution with $HgCl_2$.

If the precipitate is insoluble in $(NH_4)_2S_x$, it is bismuth. Confirm by testing the original solution with water or with K_2CrO_4. As bismuth sulfid is dark brown it may be mistaken for black, but the confirmatory test will reveal its identity.

(*d*) *The precipitate is black.* It is lead, mercuric, or copper sulfid. Take a portion of the precipitate, add an equal volume of water and a few drops of concentrated HNO_3, and boil for a moment. If it remains undissolved, it is mercuric. Confirm by testing the original solution with KI or $SnCl_2$.

If it dissolves, it is lead or copper. Add to this solution NH_4OH in excess. A light blue precipitate, easily soluble in the NH_4OH to a deep blue solution, indicates copper. This needs no further confirmation.

If the addition of the NH_4OH above produces a white precipitate, insoluble in excess of the reagent, it indicates lead. This will have been shown under Group 1, unless the solution is very dilute. Confirm by testing the original solution with KI or K_2CrO_4.

[Gold and platinum, which are precipitated by H_2S as black sulfids, as well as the rare elements in other groups, are not usually found in an elementary course, and so are omitted.]

Group 3

If no precipitate is formed by the addition of H_2S, take a portion of the original solution, add an equal volume of NH_4Cl, and then NH_4OH until it is distinctly alkaline. If no precipitate is formed, pass on to Group 4. If a precipitate is formed it is an hydroxid of either aluminum, chromium, or iron.

(*a*) *The precipitate is white.* It is aluminum hydroxid. Confirm by testing the original solution with NaOH, which should give a white precipitate, soluble in excess of the reagent.

(*b*) *The precipitate is gray green.* It is chromium hydroxid. Confirm by dissolving in a few drops of HNO_3, boiling, and adding NaOH in excess, which forms a gray-green precipitate.

(*c*) *The precipitate is greenish white or dirty green*, changing to reddish brown by exposure to the air. It is ferrous hydroxid. Confirm by dissolving in HNO_3, boiling, and adding NH_4OH, when red-brown ferric hydroxid is precipitated.

(*d*) *The precipitate is red-brown.* It is ferric hydroxid. Confirm by dissolving the precipitate in a few drops of HCl and testing with $K_4Fe(CN)_6$.

[The presence of non-volatile organic substances, such as tartaric or citric acid, sugar, etc., prevents the precipitation of this group by NH_4OH. These may be removed by evaporating to dryness and igniting.]

If the solution contains phosphoric, oxalic, boric, or hydrofluoric acid, combined with either barium, strontium, calcium, or magnesium, the metal, with its corresponding acid, will be precipitated by the addition of ammonia, and appear as a white precipitate in the third group. These acids must be removed before the metal can be determined. This is a somewhat complicated operation and will be given under Group 3 of mixed compounds.

Group 4

If no precipitate is formed by the addition of NH_4OH, add to this alkaline solution a slight excess of $(NH_4)_2S$ and heat to boiling. If no precipitate is formed, pass on to Group 5. If a precipitate is formed, it is a sulfid of either nickel, cobalt, manganese, or zinc.

If hydrogen sulfid gas is passed through the solution containing NH_4OH, it forms $(NH_4)_2S$, and the metals of this group will be precipitated as above. This method is to be preferred in many cases, since it insures having freshly prepared $(NH_4)_2S$, which is likely to decompose on standing and so become worthless.

(*a*) *The precipitate is black.* It is either nickel or cobalt sulfid. Take a portion of the original solution and add NaOH. If the precipitate is apple green, it is nickel. Confirm by testing with KCN. If the precipitate is blue and turns red by boiling, it is cobalt. Confirm by testing with KCN or with KNO_2.

(*b*) *The precipitate is flesh colored.* It is manganese sulfid. Confirm by testing the original solution with NaOH or NH_4OH.

(*c*) *The precipitate is white.* It is zinc sulfid. Confirm by adding NH_4OH to the original solution until the precipitate first formed dissolves, and then adding H_2S, when a white precipitate is formed.

Group 5

If no precipitate is formed by $(NH_4)_2S$, add to a portion of the original solution an equal volume of NH_4Cl, enough NH_4OH to render it alkaline, and then $(NH_4)_2CO_3$ to slight excess.

If a precipitate is formed, it is a carbonate of either barium, strontium, or calcium. The precipitate should be white.

Dissolve the precipitate in acetic acid. To a portion of this solution add K_2CrO_4. If a yellow precipitate is formed, it is barium chromate. Confirm by testing the original solution, considerably diluted with water, with H_2SO_4 or by the coloration of the flame.

To another portion add $CaSO_4$. If a white precipitate is formed, it is strontium sulfate. Confirm by testing the original solution, diluted with an equal volume of water, with H_2SO_4. A precipitate should appear after standing a short time. The coloration of the flame may also be used.

To another portion add $(NH_4)_2C_2O_4$. If a precipitate is formed at once, it is calcium oxalate. Confirm by testing the original solution with H_2SO_4 after diluting with a considerable quantity of water. If the solution is sufficiently diluted, no precipitate will appear. The coloration of the flame may also be used.

Group 6

This group includes all those metals which are not precipitated by the preceding group reagents. It consists of magnesium and the alkali metals, and their presence must be determined by special tests.

If no precipitate is formed by $(NH_4)_2CO_3$, add to this alkaline solution some Na_2HPO_4. If a white precipitate is formed, it is magnesium-ammonium phosphate. Confirm the presence of magnesium in the original solution by any of the tests for that metal.

To the original solution add a little concentrated NaOH, and boil. The odor of ammonia, together with an alkaline reaction in the steam passing off, indicates an ammonium compound.

Add to the original solution some acid sodium tartrate, and shake vigorously for a minute. A white crystalline precipitate indicates a potassium compound. If the solution is too dilute, it must be concentrated by boiling, or the precipitate may not appear. Confirm by the coloration of the flame.

Add to the original solution some acid potassium pyroantimonate, and shake well. A white precipitate indicates sodium. If the solution is too dilute, it must be concentrated by boiling, or the precipitate may not appear. Confirm by the coloration of the flame.

EXAMINATION FOR ACID RADICALS

In the examination for acid radicals in solution we have no simple method of determination by successive elimination as in the examination for metals. The acids may be grouped together, but the same acid is generally found in more than one group. The determination of the metal should always precede that of the acid radical, and the presence of certain metals in the solution will often eliminate certain acid radicals. Thus if barium is present the solution cannot contain sulfuric acid, or if silver is present in a neutral or acid solution, the halogen acids, with the exception of hydrofluoric acid, must be absent.

In the analysis of simple compounds, therefore, we first find what metal is present. Knowing this we may generally avoid the necessity of looking for many of the acid radicals. Those remaining may be determined by the special reactions given in Part I.

SYSTEMATIC EXAMINATION FOR METALS IN SOLUTION

MIXED COMPOUNDS

In the analysis of simple compounds in solution the method of procedure is largely a matter of convenience. We now take up the analysis of solutions containing more than one simple compound, and our method of procedure must be systematic. The precipitation and analysis of the different groups must be taken up in their regular order; for while the group reagents will precipitate and so separate the metals of any group from those of the succeeding groups, they will not separate them from the preceding groups but will generally precipitate more or less completely the metals of those groups.

It is of course understood that work of this kind should always be carried on under the direction of a competent teacher, who should give personal instruction in the various analytical processes. The few general directions given here will, if carefully observed, save much time and trouble.

In beginning an analysis take a sufficient quantity of the solution for the purpose (50 cc. of the solution will with proper care be found sufficient for most analyses). Do not take more than is necessary, or the different operations will require more time, and the results will not only be no better but often not so clear.

In using the group reagents be sure that the group is completely precipitated, but avoid using a large excess of the reagent.

Before precipitating any group always test the liquid with the group reagent of the preceding group, to be sure that the latter has been completely precipitated.

In using any reagent for the further division of the group, or in testing for a particular metal, always avoid using a large excess, unless this is expressly required, since a large excess may so modify the results as to render them untrustworthy.

Take care that all the analytical processes — precipitation, filtration, washing the precipitate, solution, etc. — are carefully performed. Many an analysis is spoiled through incomplete precipitation or incomplete washing of the precipitate. When results are not what they should be it is certain that something is wrong. Try to find the cause of the trouble at once; failing in this, ask the instructor.

All the different parts of the analysis should be kept properly labeled so that the analyst may know what he is doing and so be sure of his results. A preliminary test will often show the absence of some metal in a group. This will save time which would otherwise be spent in trying to separate the metal from the rest of the group.

Always bear in mind that the analyst, if he is successful, must be careful in little things. Careful work will always give satisfactory results, but careless work is valueless.

PRELIMINARY EXAMINATION

Before beginning the work of separation, test the solution with litmus paper to determine its condition. It should be either neutral or acid. If this is the case, pass on to the precipitation of Group 1. If the solution is neutral, neither phosphates, borates, nor oxalates will be found in the precipitate of Group 3.

Occasionally an alkaline solution may be found, in which case it should be acidified with HCl. In doing this a number of substances held in the alkaline solution may be precipitated, the following being those most likely to occur.

If a white precipitate appears which does not dissolve in an excess of the acid, it usually belongs to Group 1 and may be determined as given under that group.

If the solution contains a soluble silicate (only the alkaline silicates are soluble), and is not too dilute, the addition of HCl will cause a partial precipitation of silicic acid. This has none of the characteristics of the compounds found in Group 1, and is gelatinous in appearance, by which it may generally be recognized. To determine what metals may be present with silicic acid, the whole solution, with an excess of HCl, must be evaporated to dryness, the dried mass extracted with water and a little HCl, and the metals, which will be found in the solution, separated in the regular way.

If a white precipitate appears which dissolves in excess of the HCl, the metal belongs to Group 2 or to some subsequent group and will appear in its proper place.

If a yellow or reddish-colored precipitate is formed, the solution contained a sulfo-salt of arsenic, antimony, or tin, and these may be separated and determined as given under Group 2, Subdivision B.

If the solution contains an alkaline sulfid, the addition of HCl will liberate H_2S and produce a yellowish-white, finely divided precipitate of sulfur.

In a few other cases compounds may be found dissolved in an alkaline solution, which give off some characteristic gas when acidified with HCl. The gas will distinguish the acid in the compound, the metal usually passing into solution to reappear in its proper place. In exceptional cases the precipitate formed may be filtered off, dried, and tested as given under Blowpipe Analysis.

Group 1

To this group belong **Lead, Silver,** and **Mercury(ous).**

The metals are precipitated from a neutral or acid solution by HCl, forming chlorids, which are insoluble in dilute acids.

The lead chlorid, being somewhat soluble, even in cold water, is not completely precipitated. The part remaining in the solution will be precipitated in the second group.

may [illegible] [illegible]

If the solution for any reason contains much free nitric acid, any mercurous salt originally contained in the solution may be partially or entirely oxidized to a mercuric compound, and so be found with the metals of Group 2.

Take about 30 cc. of the solution in a beaker of convenient size, test it with litmus paper and, if found to be neutral or acid, add to the cold solution a few drops of dilute HCl. (For treatment of the solution if found alkaline, see Preliminary Examination, page 77.) If no precipitate appears, pass on to Group 2.

If a precipitate is formed, add slowly 2 or 3 cc. of the reagent, stirring the whole constantly with a glass rod. As the amount of the reagent which it is necessary to use depends upon the relative strength of reagent and solution, and also upon the number of metals to be precipitated, add the reagent as directed and then allow the precipitate to subside. After the supernatant liquid becomes clear, add two or three drops of the reagent, allowing them to run down the inside of the beaker, and notice if the liquid becomes cloudy. If it does, the operation must be repeated as above until, after testing, the supernatant liquid remains clear, showing that the precipitation is complete.

The precipitate, which should be white, consists of the chlorids of some or all of the metals of the group, and should next be filtered to separate it from the surrounding liquid which contains the metals of the remaining groups. The liquid which passes through the filter is called the filtrate. This is set aside for later examination, and the precipitate examined for Group 1.

After transferring the precipitate to the filter, wash it twice with cold water. This wash water may be thrown away.

Heat about 10 cc. of water to boiling, and pour upon the precipitate on the filter. If lead chlorid is present, it will dissolve in the hot water and pass through the filter. This last filtrate may be tested for lead by K_2CrO_4 or H_2SO_4. [See Part I, Lead.]

If lead is found, wash the precipitate several times with hot water to remove it, throwing away the wash water, and then add to the precipitate on the filter some NH_4OH. If silver chlorid is present, it will dissolve in the ammonia and pass through the filter. By adding HNO_3 in excess to this alkaline filtrate the white silver chlorid is reprecipitated.

If mercurous chlorid is present, it is changed by the ammonia into a black compound which is a mixture of amido-mercuric chlorid, $HgNH_2Cl$, and finely divided mercury. This is generally regarded as sufficient proof of the presence of mercurous chlorid, but a further confirmation may be obtained by dissolving the precipitate in a few drops of aqua regia, and testing the mercuric chlorid thus formed with $SnCl_2$.

Group 2

To this group belong **(Lead), Mercury(ic), Bismuth, Copper, Cadmium, Arsenic, Antimony,** and **Tin.**

H_2S The metals are precipitated from an acid solution by hydrogen sulfid, forming sulfids, which are insoluble in dilute acids. see These sulfids are of two kinds, as shown by their action when treated with ammonium sulfid. These form the two subdivisions of the group.

Subdivision A includes the sulfids of *(Lead)*, *Mercury(ic)*, *Bismuth*, *Copper*, and *Cadmium*. These compounds, which are basic in character, and so sometimes called sulfo-bases, are insoluble in ammonium sulfid.

Subdivision B includes the sulfids of *Arsenic*, *Antimony*, and *Tin*. These compounds, which are acid in character, and so sometimes called sulfo-acids, are soluble in ammonium sulfid, the latter compound, which is strongly basic in character, uniting with these sulfo-acids to form soluble sulfo-salts.

Inasmuch as the analysis of this group is attended with considerable difficulty, it is best to make a preliminary test of the solution to see if any members of the group are present.

Take a small quantity of the acid filtrate from Group 1, or of the acid solution from which Group 1 is absent, place it in a test-tube and treat it with hydrogen sulfid. If no precipitate is formed, or if only a milky, white precipitate is formed (which is free sulfur, and caused by an excess of acid in the solution), the contents of the test-tube may be thrown away and the remainder of the solution treated as if it were the filtrate from Group 2.

If the solution contains nitrates or free nitric acid, the H_2S will be partially oxidized to H_2SO_4, and members of Group 5, if present, will be precipitated. The presence of Group 5 may be shown by adding a drop or two of H_2SO_4 to a few drops of the solution in a test-tube. If a precipitate is formed, the above action may be partially obviated by adding Na_2CO_3 to the filtrate from Group 1 until a precipitate begins to form. Dissolve this precipitate in HCl and then proceed.

If a precipitate was formed in the test-tube, the whole of the solution should be warmed to about 70° and a slow stream of hydrogen sulfid gas (not more than two hundred bubbles per minute) passed through the warm liquid. If the solution has not become sufficiently diluted, enough warm water should be added to make the total volume 100 to 150 cc. before the precipitation. The treatment with H_2S should be continued until, after blowing off the excess of the gas from the surface of the liquid, the latter distinctly smells of the reagent. This will usually take about ten minutes.

Allow the precipitate to settle. If it does not do so readily, boil the whole for a moment. Decant the clear solution through a filter, and set aside this group filtrate for the following groups. The precipitate is again treated with boiling water, and after it has settled the whole is filtered and washed with hot water, the wash water being thrown away.

Next make another preliminary test to see if both subdivisions of the group are present. This is done by placing a small portion of the precipitate in a test-tube, adding a few drops of $(NH_4)_2S_x$, and gently warming. If the precipitate is all dissolved, only Subdivision B can be present. If some of the precipitate remains undissolved, it belongs to Subdivision A, in which case, in order to tell whether anything has been dissolved, filter, dilute with a little water, and add to the filtrate a slight excess of dilute HCl. A white, finely divided precipitate is only sulfur and shows that Subdivision B is absent, while its presence is shown by a more or less yellow or orange-colored flocculent precipitate.

If both subdivisions are found to be present, place the whole precipitate in a porcelain dish, add enough $(NH_4)_2S_x$ to cover the precipitate, warm gently for ten minutes (do not let the mixture boil), and filter. Wash two or three times with hot water, adding each time a few drops of the yellow ammonium sulfid to the precipitate on the filter. The precipitate now contains Subdivision A, and the filtrate Subdivision B.

Group 2, Subdivision A

Transfer the precipitate containing Subdivision A to a porcelain dish or a beaker. Add enough concentrated HNO_3 diluted with an equal volume of water to cover the precipitate, and boil as long as anything dissolves.

The sulfids of lead, bismuth, copper, and cadmium are dissolved in the nitric acid, while the mercuric sulfid, being insoluble in HNO_3, remains as a heavy black precipitate. If the acid used is too concentrated and the boiling is continued for some time, the black precipitate may be changed to a white basic compound. [See Part I, Mercurous 4.] In the decomposition of the sulfids some sulfur is set free. This appears as a more or less dark-colored mass floating on the surface of the liquid. If lead is present in the original solution, most of it will have been removed in Group 1. A portion of that remaining, which was precipitated by H_2S, may be oxidized by the

HNO_3, and be found as $PbSO_4$ mixed with the insoluble mercuric sulfid, the remainder being dissolved.

The black precipitate of HgS, or the white basic compound as noted above, may be dissolved on the filter with a few drops of warm aqua regia. Dilute this acid solution with water and confirm the presence of mercury by $SnCl_2$ or KI.

Hg

The acid filtrate from the HgS, which may contain nitrates of lead, bismuth, copper, and cadmium, should be evaporated nearly to dryness to remove the excess of HNO_3 and then dissolved in water. If in dissolving in water a precipitate appears, add HNO_3 drop by drop until the precipitate (probably $BiONO_3$) disappears. If lead was found in the first group, add a little (1 cc.) dilute H_2SO_4 and filter off the precipitated $PbSO_4$.

To this last filtrate, or to the previous one if lead was not present, add an excess of NH_4OH. Bismuth is precipitated as white bismuth hydroxid, $Bi(OH)_3$, while copper and cadmium, which are first precipitated, are dissolved in excess of the reagent.

The precipitate containing the bismuth hydroxid should be washed once or twice with water. To confirm the presence of bismuth add to the precipitate on the filter a few drops of dilute HCl, and allow the acid solution to filter into a large test-tube filled with cold water. A white precipitate of bismuth oxychlorid, BiOCl, confirms the presence of bismuth.

If the alkaline filtrate, after precipitating the bismuth, is blue, it conclusively proves the presence of copper, and may contain cadmium. If colorless, it can only contain cadmium. In the latter case the presence of cadmium may be confirmed by treatment with H_2S, when yellow cadmium sulfid, CdS, is precipitated.

If the solution is blue, in order to determine the presence or absence of cadmium add KCN to the solution until the blue color disappears, and then treat with H_2S, when a yellow precipitate proves the presence of cadmium.

[It sometimes happens that the precipitate of CdS obtained in this way is dark colored. This may be due to different causes, such as traces of silver or mercury compounds due to incomplete separation of the first group, or failure completely to remove members of succeeding groups by washing. In any case any considerable quantity of the precipitate may be regarded as evidence of the presence of cadmium.]

Group 2, Subdivision B

The alkaline filtrate from Subdivision A is treated with dilute HCl until the solution is acid.

This decomposes the sulfo-salts, the metals being precipitated as sulfids, together with more or less free sulfur. These are filtered, washed with hot water, and the filtrate and wash water thrown away.

It has already been observed that the metals which constitute Subdivision B exist in two states of valence and so form two series of compounds. [See the respective metals in Part I.] If compounds of these metals in the lower form are found in the solution, the corresponding sulfids are precipitated by H_2S. These sulfids when dissolved by the yellow ammonium sulfid, $(NH_4)_2S_x$, are oxidized (or sulfurized) and, after decomposition of the sulfo-salts by HCl, appear as the higher sulfids. This can best be seen in the case of tin, in which the stannous sulfid is brown, while the stannic sulfid is yellow.

The precipitate obtained by the decomposition of the sulfo-salts by HCl, or the whole group precipitate if Subdivision A was found absent by the preliminary test, is placed in a porcelain dish well covered with concentrated HCl and heated to boiling. (This last operation should be carried on under a hood on account of the large amount of hydrochloric acid gas which is given off.) The whole should be kept at or near the boiling temperature for five minutes and filtered while hot. It is better to dilute the solution with a little water before filtering. As. Arsenic sulfid remains as a yellow precipitate, while the tin and antimony sulfids are dissolved, forming chlorids.

Dissolve the arsenic sulfid by adding a little concentrated HCl (2 or 3 cc.) and a few crystals of $KClO_3$. This oxidizes the arsenic compound to arsenic acid. The excess of HCl should be removed by evaporating nearly to dryness. Dissolve the nearly dry mass in a little water (filter if necessary), add an equal volume of NH_4Cl, then NH_4OH to excess, and finally $MgSO_4$, when white crystalline $MgNH_4AsO_4$ is formed. [See Part I, Arsenic Acid 3.]

The presence of arsenic may also be shown by mixing a little of the yellow precipitate with Na_2CO_3 and KCN and then heating in a closed tube, when the "arsenic mirror" will be formed. [See Part II, VIII, (*h*).]

The acid filtrate from the arsenic sulfid, which may contain both antimony and tin in the form of chlorids, must first be tested to see if antimony is present. This can often be determined by the color of the precipitate of Subdivision B, since the orange-red color of the antimony sulfid is characteristic. A small quantity may, however, be overlooked, and so, to make sure, place a drop of the acid solution on a clean platinum foil and put into it a bit of metallic zinc. If antimony is present, a black spot of metallic antimony is immediately formed on the foil. This is soluble in HNO_3.

Sb +

Sb.

If antimony is found to be present, place the whole of the acid solution in a porcelain dish, put into it a piece of clean platinum foil and a piece of zinc in such a way that the two metals shall be in contact.

The antimony which is present in the solution as the chlorid, $SbCl_3$, will be reduced to metallic antimony and form a black deposit upon the platinum foil.

The tin, which, if present, is in the solution as stannic chlorid, $SnCl_4$, will be reduced to stannous chlorid, $SnCl_2$, or, if the action is continued long enough, to metallic tin. The latter will be found as a gray deposit on and about the zinc. Filter and test the filtrate with $HgCl_2$. A white precipitate indicates tin. [See Part I, Mercuric 8.]

Sn.

If the action is allowed to continue until all the tin in the solution is reduced to the metallic state, the white precipitate will not appear. If this should be the case, as a further precaution pour off the solution as carefully as possible from the deposited metals, remove any zinc which may remain undissolved, add to the metallic mixture a little concentrated HCl, and warm. If tin is present, it will dissolve, forming stannous chlorid, which may be filtered from the undissolved antimony and tested as above.

[If it is desirable to know whether the tin was originally present as a stannous or a stannic compound, take a few drops of the original solution, remove any of the metals of Group 1 which may have been present, and add a little $HgCl_2$. A white or gray precipitate, insoluble in concentrated HCl, proves the tin to be stannous.]

Group 3

To this group belong **Aluminum**, **Chromium**, and **Iron**.

If phosphates, oxalates, silicates, borates, or fluorids are present in the solution, the corresponding salts of **Barium**, **Strontium**, **Calcium**, and **Magnesium** may be precipitated with this group.

The presence of these salts very materially complicates the whole treatment of the group, and so, in making up solutions for an elementary analytical course, they should be omitted until the student has become familiar with the separations without them. The method of treatment when these salts are present will be found on page 90.

The metals of this group are precipitated by ammonium hydroxid, in the presence of ammonium chlorid, forming hydroxids.

In addition to the metals of this group mentioned above, if manganese is present in the solution, traces of it are always found in this group precipitate. This is due to the fact that manganese, while not immediately acted upon by NH_4OH in the presence of NH_4Cl, gradually becomes oxidized and is then more or less completely precipitated by the NH_4OH, especially after long standing. [See Part I, Manganese 2.]

Before precipitating Group 3 the filtrate from Group 2 must be boiled until the H_2S remaining in the solution has been completely expelled. If this is not done, the NH_4OH, which is used to precipitate Group 3, will form $(NH_4)_2S$ with the H_2S, and any metals belonging to Group 4 which may be present will be precipitated by it. The boiling must be continued until the odor of H_2S entirely disappears, or, better, until a piece of filter paper moistened with lead acetate, when held in the escaping steam, remains unchanged, it being blackened by H_2S. If Group 2 was not present, the solution need only be heated to the boiling point.

If iron is present, it may have been in the original solution either as a ferrous or a ferric compound, but before precipitation in this group it must always be in the ferric state, since most ferrous compounds are unstable and not completely precipitated by the group reagent. Furthermore, whatever may have been the condition of the iron in the original solution, if it has been acted upon by H_2S, as it must have been if the second group was present, all of the iron will now be in the ferrous condition, because of the reducing action of the H_2S, and so it will always have to be oxidized before precipitation. [See Part I, Ferric 3.]

A preliminary test for iron should be made by taking a few drops of the solution in a test-tube, adding two or three drops of HNO_3, boiling, and then testing with $K_4Fe(CN)_6$. A blue precipitate indicates iron. [See Part I, Ferric 7.]

If iron is found, add to the hot solution a little concentrated HNO_3 (not more than 1 or 2 cc.) and boil. If the solution becomes dark colored, continue adding the HNO_3 to the hot solution drop by drop until it becomes clear, when the oxidation will be complete.

[Be careful not to add more HNO_3 than is necessary, since manganese, if present, will also be oxidized, and will then be precipitated with Group 3.]

Add to the solution an equal volume of NH_4Cl, to keep metals belonging to Group 4 from precipitating, and then NH_4OH to slight but distinct excess. Boil for a moment and filter as soon as the precipitate settles. The filtrate, which contains the metals of the succeeding groups, is set aside for further examination. The precipitate contains the hydroxids of the metals of the third group, together with certain phosphates, oxalates, etc., if these salts were present in the solution.

PHOSPHATES, OXALATES, ETC., ARE ABSENT

If the color of the precipitate is white, it can consist of aluminum hydroxid only. If it is gray green, chromium hydroxid, and perhaps aluminum hydroxid, is present. If it is dark red-brown, all of the metals of the group may be present.

Dissolve the precipitate in warm dilute HCl, avoiding a large excess of the acid. Add an excess of a concentrated solution of sodium hydroxid and heat to boiling, keeping the whole at that temperature for a short time.

All the metals of the group are precipitated as hydroxids, but the aluminum hydroxid is dissolved in excess of the reagent, forming sodium aluminate, $NaAlO_2$. Filter and wash the precipitate with hot water.

Add to the alkaline filtrate HCl until it is distinctly acid, and then add NH_4OH until it is alkaline. An almost transparent, flocculent precipitate, which at first usually rises to the surface of the liquid, indicates the presence of aluminum.

[If the original solution contains tin in the form of stannous chlorid, and too much HCl was added before precipitation of the second group, some of the stannous sulfid there precipitated may have been dissolved, forming stannous chlorid. This will appear in the solution with the aluminum and be precipitated with it. [See Part I, Stannous 2.] In order to detect the tin, heat a small portion of the alkaline filtrate to boiling and then add a drop or two of a solution of $Bi(NO_3)_3$. A black precipitate of metallic bismuth shows the presence of the stannous chlorid. [See Part I, Bismuth 8.] Instead of the alkaline filtrate a little of the aluminum hydroxid precipitate may be dissolved in NaOH and then treated as above.

If tin is found by this test, in order to determine whether aluminum is present, render the whole alkaline filtrate very slightly acid with HCl; or dissolve the white precipitate in a very slight excess of HCl, dilute to about 100 to 150 cc., and precipitate the tin with H_2S. If the solution is sufficiently dilute, the stannous sulfid will not dissolve in the HCl. Filter off the precipitate, if any, and treat the filtrate as before to detect the presence of aluminum.]

The precipitate formed by NaOH may contain both iron and chromium, and possibly traces of manganese.

If the precipitate has a dark red-brown color, this is usually considered sufficient evidence that iron is present. If further proof of its presence is desired, dissolve a small portion of the precipitate in HCl, and test the solution with $K_4Fe(CN)_6$ or KSCN.

The presence of chromium may be shown by fusing a small portion of the precipitate, mixed with sodium carbonate and potassium nitrate, on a piece of platinum foil. This oxidizes the chromium to a chromate, which appears as a yellow mass on the foil. [See Part II, VI.]

If manganese is present, it will also become oxidized to a manganate, forming a green mass on the foil. Since the green manganate entirely conceals the yellow chromate, in order to show the presence of chromium when manganese is also present, dissolve the fused mass in warm water, filter if necessary, add an excess of acetic acid, and boil to decompose the sodium carbonate. The green manganate is more or less completely decomposed, while the chromate dissolves unchanged. If lead acetate is now added to the acid solution, yellow lead chromate, $PbCrO_4$, is precipitated, which confirms the presence of chromium.

[It is often desirable to know whether the iron is present as a ferrous or ferric compound. To determine this, take a little of the original solution and, if acid, nearly or quite neutralize it with a concentrated solution of Na_2CO_3. If a slight precipitate forms, dissolve it with a drop or two of HCl. Add to the neutral or very slightly acid solution freshly prepared barium carbonate, $BaCO_3$ (which should be previously shaken), in sufficient quantity to precipitate any aluminum, chromium, or ferric iron which may be present. The operation is best carried on in a flask, which should be loosely corked. Shake the mixture occasionally for ten minutes, allow the precipitate to settle, and filter. The filtrate now contains all the ferrous iron, and the precipitate all the ferric.]

PHOSPHATES, OXALATES, ETC., ARE PRESENT

If the original solution was neutral or alkaline, none of these salts can be present. If it was acid, any or all of them may be present.

Precipitate the group as given above when these salts are absent, observing all the precautions there mentioned. Filter and set aside this, the original group filtrate, for later examination, since, if the amount of phosphates, oxalates, etc., is small, it may contain metals belonging to each of the succeeding groups. Preliminary tests should then be made for each acid before making the separation.

Phosphoric acid is best shown by taking a small portion of the precipitate in a test-tube, dissolving in a little concentrated HNO_3, adding ammonium molybdate, and warming. A yellow precipitate, insoluble in HNO_3, indicates phosphoric acid. [See Part I, Phosphoric Acid 5.]

Oxalic acid is best shown by dissolving a small portion of the precipitate in HNO_3, adding an excess of a concentrated solution of Na_2CO_3, and boiling. The metals present are all precipitated, and the oxalic acid combines with the reagent to form sodium oxalate. Filter, add to the filtrate acetic acid in excess, boil to expel the CO_2, and add $CaCl_2$. A white precipitate, insoluble in acetic acid, indicates oxalic acid. [See Part I, Oxalic Acid 4.]

The three other acids are not likely to be met with in an elementary course; in more advanced practical work they are quite often found, especially silicic acid, which is found in nearly all minerals.

Silicic acid may be shown by making a microcosmic bead and introducing a bit of the precipitate. A "silica skeleton" indicates silicic acid. [See Part II, V, (*h*).]

Boric acid is best shown by the flame test. Take a small portion of the precipitate in a porcelain dish, add concentrated H_2SO_4 and a little alcohol, warm, and ignite. A green or green-bordered flame indicates boric acid. [See Part II, VIII, (*e*).]

Hydrofluoric acid is best shown by the etching of glass. [See Part II, VII, (*f*).]

Having shown the presence of any of these acids, before separating the metals they must be removed.

The whole group precipitate is dissolved in a slight excess of HCl and then reprecipitated by concentrated NaOH. The aluminum precipitate, whether present in the form of hydroxid or phosphate, is dissolved in excess of the reagent, and its presence confirmed as before. [See page 88.]

Silicic acid will rarely be found in a solution intended for an elementary analytical course. If, however, it should be found, it must be removed first of all.

To remove silicic acid, dissolve the original group precipitate in HNO_3, and evaporate the whole to complete dryness on a water bath. This changes any silicic acid which may be present into silicon dioxid, SiO_2, which is insoluble in water and in acids. Add to the dried mass hot water and a little HNO_3. The metals, which are now in the form of nitrates, will dissolve, while the silicon dioxid will remain undissolved. Filter off the insoluble silicon dioxid, which may be tested and then thrown away, but keep the acid filtrate. If either phosphoric or oxalic acid was found by the preliminary tests, it must next be removed. [See below.] If neither of these acids was found to be present, add NH_4Cl to the acid filtrate, precipitate the group with NH_4OH, and separate the metals as already given. The filtrate from this last precipitation should be added to the original group filtrate for further examination.

To remove phosphoric acid, take the acid filtrate after removing the silicic acid, or if silicic acid was not present, take the NaOH precipitate, and after dissolving it in a little concentrated HNO_3 in a porcelain dish, add a sufficient quantity of pure tin foil (a piece about four inches square will generally be sufficient), and heat to boiling. Allow the hot mass to stand a few minutes, dilute with an equal volume of water, and filter. The concentrated HNO_3 acts upon the tin, forming metastannic acid, which combines with the phosphoric acid, forming a compound of somewhat doubtful composition. This latter compound is insoluble in HNO_3, and so all the phosphoric acid will be found in the precipitate. The filtrate should now be tested to see if phosphoric acid is still present. If found, the operation must be repeated until it has been entirely removed. If oxalic acid was found by the preliminary test, it must now be removed. If no oxalic acid is present, add NH_4Cl to the acid filtrate, precipitate the group with NH_4OH, and separate the metals as before. The filtrate from this last precipitation, which may contain metals belonging to the succeeding groups, should be added to the original group filtrate for further examination.

To remove oxalic acid, take the acid filtrate after removing the phosphoric acid, or if phosphoric acid was not present, take the NaOH precipitate, and after dissolving it in a little HNO_3 add a concentrated solution of Na_2CO_3 in slight excess, and boil for a moment. The oxalates are all decomposed and form soluble sodium oxalate, the metals all being found in the precipitate in the form of carbonates or hydroxids. Filter and wash with hot water. The filtrate contains the sodium oxalate, and after it has been tested may be thrown away. Dissolve the precipitate in HCl, add NH_4Cl, precipitate the group with NH_4OH, and separate the metals as before. The filtrate from this last precipitation should be added to the original group filtrate for further examination.

Boric and hydrofluoric acids are very difficult to separate. They are found in small quantities in a large number of minerals, but will hardly be found in an elementary analytical course. The method of removing them belongs therefore to a more advanced course and so will be omitted here.

Group 4

To this group belong **Nickel, Cobalt, Manganese,** and **Zinc.**

The metals are precipitated from a solution containing NH_4Cl and an excess of NH_4OH, by means of hydrogen or ammonium sulfid, forming sulfids. These are all insoluble in alkalies, but a part of them are easily soluble in acids.

Since the precipitation and separation of the metals of this group is attended with considerable difficulty, it is always best to make a preliminary test to see if any of them are present. This is best done by adding a few drops of $(NH_4)_2S$ to a small portion of the solution. If a precipitate forms, some of the metals of the group are present, and the whole solution must be treated in a somewhat similar way.

The filtrate from Group 3 usually contains enough NH_4Cl. Add NH_4OH, if necessary, until the liquid smells strongly of the reagent, and pass a slow stream of hydrogen sulfid gas through the liquid until it is saturated.

Instead of the H_2S, colorless ammonium sulfid, $(NH_4)_2S$, is very commonly used to precipitate this group. This reagent decomposes on standing, and often contains notable quantities of the yellow ammonium sulfid, $(NH_4)_2S_x$. For these reasons hydrogen sulfid is recommended as the better and more convenient reagent to use. This forms $(NH_4)_2S$ with the excess of NH_4OH in the solution, and so the final result is the same whichever reagent is used.

After precipitation the whole should be boiled in a flask until the excess of $(NH_4)_2S$ has been decomposed and the liquid no longer smells of the reagent, or at most only slightly. This may take some minutes, but should always be done. The precipitate should now settle quickly, leaving a clear solution above. [Sometimes the liquid above the precipitate appears dark brown in color. This is due to the fact that NiS is slightly soluble in $(NH_4)_2S$, giving a dark brown solution. [See Part I, Nickel 5.] If this is the case, or if the precipitate does not settle quickly, continue the boiling for a little time, adding water and a little NH_4OH to replace that lost by evaporation, until the precipitate settles quickly and the solution becomes clear.]

Filter quickly while hot, and preserve the filtrate for further examination, after testing it with $(NH_4)_2S$ to see if the group has been completely precipitated. The precipitate is washed with hot water, and the wash water thrown away.

The sulfids, particularly those of nickel and cobalt, have a tendency to oxidize on the filter and thus form sulfates. The latter are soluble in water and so pass through with the wash water. If the boiling is continued long enough, and in a flask, and if the filtering takes place while the solution is still hot, the sulfids will not usually oxidize enough to do any harm. If oxidation should take place (and this can usually be noted by the grayish film which appears on the surface of the black precipitate), a little H_2S water or $(NH_4)_2S$ added to the filter will stop it.

If the precipitate is white, it consists of zinc sulfid only. If it is flesh colored, it contains manganese sulfid, and perhaps zinc sulfid. If it is black, all the metals of the group may be present.

Make a hole through the bottom of the filter in the funnel and wash the contents into a beaker. Add to the sulfids in the beaker about 20 to 30 cc. of dilute HCl, warm for five minutes without boiling, filter, and wash. The manganese and zinc sulfids are easily dissolved by the dilute acid and will be found in the filtrate as chlorids, while the nickel and cobalt sulfids, being insoluble in the dilute acid, remain in the precipitate. [If the acid used is too concentrated, a very little of the cobalt sulfid may dissolve and give a faint pink color to the solution. This will do no harm.]

The black precipitate, which may contain both nickel and cobalt sulfids, is next examined with the borax bead to see if cobalt is present. A blue bead confirms the presence of cobalt. Dissolve the precipitate in a small quantity of aqua regia, evaporate nearly to dryness, and dissolve the nearly dry mass in water. If no cobalt was found by the borax bead, the nickel is now precipitated from the solution with NaOH, forming apple-green $Ni(OH)_2$. If cobalt was found by the borax bead, take a portion of the solution, add KCN until the precipitate first formed dissolves in excess, and boil for a minute. Next add a little NaOH, and finally bromin water in excess. A black precipitate indicates nickel, since cobalt does not give this reaction. [See Part I, Nickel 7 and Cobalt 7.]

These preliminary tests for the presence of nickel and cobalt are usually sufficient for a qualitative analysis.

If it is desirable to separate the two, add to the aqueous solution, after having dissolved the sulfids in aqua regia, acetic acid, and then potassium nitrite in excess. The whole should be warmed and allowed to stand several hours. The cobalt is completely precipitated as yellow $Co(NO_2)_3(KNO_2)_3$, the nickel remaining in solution. [See Part I, Nickel 10 and Cobalt 10.]

Filter and precipitate the nickel from the filtrate with NaOH. Confirm the presence of nickel in the last precipitate by means of the borax bead. [See Part II, V, (*c*).]

The acid filtrate, containing the manganese and zinc in the form of chlorids, should be boiled, if necessary, until no more H_2S is given off, and then treated with a slight excess of concentrated NaOH. Both metals are precipitated as hydroxids, but the zinc hydroxid dissolves in excess of the reagent. Filter and examine the filtrate with H_2S. A white precipitate of ZnS confirms the presence of zinc.

The precipitate of manganese hydroxid, which should at first be white, may be dark colored from a trace of cobalt dissolved by the HCl. In any case it becomes dark brown after standing a few minutes. This is caused by oxidization and the formation of manganic hydroxid, $Mn(OH)_3$, which is usually considered sufficient proof of the presence of manganese. [See Part I, Manganese 1.] A further confirmatory proof of the presence of manganese may be obtained by fusing a portion of the precipitate on a piece of platinum foil with Na_2CO_3 and KNO_3, forming a green manganate.

Group 5

To this group belong **Barium, Strontium,** and **Calcium.**

The metals are precipitated from a solution containing an excess of NH_4OH by means of ammonium carbonate, forming carbonates.

The filtrate from Group 4 should be boiled until all the $(NH_4)_2S$ in the solution has been decomposed. Add to the solution enough NH_4OH to give a strong alkaline reaction. If a precipitate should form with the NH_4OH, add NH_4Cl until it dissolves. The group is now precipitated with an excess of ammonium carbonate $(NH_4)_2CO_3$, boiled for a moment, and filtered, care being taken that an excess of NH_4OH is always present. The carbonates thus precipitated are somewhat soluble in ammonium chlorid, which is always present in this solution from the preceding groups. The boiling tends to make the precipitate crystalline and less soluble in the NH_4Cl. The filtrate is set aside for further examination, the precipitate containing all the metals of this group which may be present. This precipitate need not be washed.

Make a preliminary test to see if barium is present by taking a small portion of the precipitate, dissolving it in a drop or two of acetic acid, and adding potassium chromate, K_2CrO_4. A yellow precipitate indicates barium.

If barium is found to be present, dissolve the whole precipitate in acetic acid, add K_2CrO_4 in a sufficient excess to make the whole solution decidedly yellow, filter, and wash. All the barium is precipitated, while the strontium and calcium remain in the filtrate. Confirm the presence of barium by dissolving some of the yellow precipitate in HCl, diluting with water, and adding some dilute H_2SO_4, when white $BaSO_4$ will be precipitated.

The pale green color which a barium compound imparts to the non-luminous flame may also be used as a confirmatory test.

The strontium and calcium remaining in the filtrate are again precipitated with $(NH_4)_2CO_3$, after adding an excess of NH_4OH, the whole boiled for a moment, filtered, and washed until all the yellow color disappears from the precipitate, and the filtrate comes through colorless. This last filtrate may be thrown away.

The last precipitate, containing the carbonates of strontium and calcium, or the original group precipitate if barium is absent, is then dissolved in dilute HCl.

Make a preliminary test to see if strontium is present, by taking a small portion of this solution and adding a little calcium sulfate, $CaSO_4$. A white precipitate shows the presence of strontium. This preliminary test should be thrown away.

[The coloration of the non-luminous flame is often employed as a preliminary test to show the presence of strontium. Since strontium and calcium both give colored flames, the former a carmine red and the latter an orange or brick red, unless great care is used there is danger of error. A comparison of the two colored flames will easily show the difference. It is therefore best, especially for one using this test who is not perfectly familiar with the two colors, to compare the color of the flame of the unknown substance with that produced by calcium chlorid.]

If strontium is found to be present, add a dilute solution of ammonium sulfate $(NH_4)_2SO_4$. [A solution of the proper strength is made by dissolving two grams of $(NH_4)_2SO_4$ in 100 cc. of water.] The precipitation takes place slowly and is complete only after standing some time. This precipitates the strontium as sulfate, while the calcium sulfate remains in the dilute solution, it being quite soluble in water.

The calcium remaining in the solution, which if it is not already so should be made alkaline with NH_4OH, is then precipitated by ammonium oxalate as white calcium oxalate, CaC_2O_4.

[If too large an excess of NH_4Cl is found in the solution after precipitating the third and fourth groups, it will interfere with the complete precipitation of the fifth group, the metals of which will then be precipitated in the sixth group with any magnesium which may be present. To avoid this the filtrate from Group 4 may be evaporated to dryness, ignited, and the ammonium compounds volatilized by heat. The residue is dissolved in water, adding a drop or two of HCl if necessary. The solution is then made alkaline with NH_4OH, and the group precipitated with $(NH_4)_2CO_3$.]

Group 6

To this group belong **Magnesium, Potassium, Sodium,** and the compound radical **Ammonium.**

There is no special group reagent and there are few insoluble compounds except those of magnesium. This group therefore includes all metals not precipitated by the preceding group reagents.

On account of the difficulty in making a complete determination of the alkali metals, potassium and sodium, they are not always sought for in a qualitative analysis, especially since their determination in a quantitative analysis occurs after all the other metals, including magnesium, have been removed, and when the solution can contain nothing else.

If it is desirable to determine their presence or absence, the filtrate from Group 5 must be subjected to a preliminary test at this point. Their presence is shown by the coloration which they give to the non-luminous flame.

The flame test for sodium is so delicate that unless the characteristic yellow flame is quite brilliant it is probably due to an accidental impurity.

The violet flame, due to potassium, is entirely concealed by the yellow flame if sodium is present. It can then be seen through a blue glass, which cuts off all the yellow light. [See Part II, IV.]

If sodium is absent, the filtrate from Group 5 is made strongly alkaline with NH_4OH. If a precipitate should occur on the addition of the NH_4OH, add NH_4Cl until the precipitate dissolves. Add acid sodium phosphate, Na_2HPO_4, in excess, and allow the whole to stand for some hours in a warm place. The magnesium is all precipitated as white crystalline $MgNH_4PO_4$, which is soluble in acetic acid.

[It sometimes happens that some metals of the preceding groups, particularly aluminum and the fifth-group metals, have not been completely precipitated. These will be precipitated here as phosphates, and appear at once as a white flocculent precipitate. If this precipitate is filtered at once, enough of the magnesium will remain in the filtrate to appear after a time as a white crystalline precipitate, adhering more or less closely to the sides of the beaker. This can always be seen if the inside of the beaker is rubbed with a glass rod, the crystals forming where the glass is rubbed.]

If sodium is present, the magnesium must be precipitated by some other reagent to avoid introducing sodium into the solution. This may be done by ammonium phosphate, or, better, by a saturated solution of barium hydroxid, $Ba(OH)_2$. The reagent is added in excess, the precipitate filtered off, and the excess of $Ba(OH)_2$ removed by $(NH_4)_2CO_3$. The barium carbonate is then filtered off, the filtrate evaporated to dryness in a porcelain dish, and cautiously ignited to expel the ammonium salts.

The residue, containing the potassium and sodium salts, is dissolved in a very small quantity of water, filtered, if necessary, and divided into two portions.

To one portion add an excess of acid sodium tartrate, $NaH(C_4H_4O_6)$, and allow it to stand for some time with occasional shaking. A white crystalline precipitate of $KH(C_4H_4O_6)$ indicates potassium.

[A better test, although not often employed in a qualitative analysis on account of the cost of the reagent, is to add a few drops of platinum chlorid, $PtCl_4$, and evaporate to dryness on a water bath. The residue is then moistened with water, and a little alcohol added. A heavy, yellow crystalline precipitate, insoluble in alcohol, is potassium chloroplatinate, K_2PtCl_6, and indicates potassium.]

To the other portion add acid potassium pyroantimonate, $K_2H_2Sb_2O_7$, and allow it to stand some time. A white precipitate indicates sodium.

The presence of ammonium is shown by adding concentrated NaOH to the original solution and warming. Any ammonium compound present is decomposed, and ammonia, NH_3, is liberated, which is recognized by its characteristic odor.

SYSTEMATIC EXAMINATION FOR ACID RADICALS IN SOLUTION

PRELIMINARY EXAMINATION

We have already noted (page 75) that there is no simple method for the determination of the acid radicals by successive elimination, as there is in the examination for the metals. Fortunately, in most cases only a few acids need be looked for in mixed compounds in solution, since the presence of any metals, except those of the alkali group, proves conclusively the absence of one or more of the acid radicals.

As an illustration of this fact we may note that if silver is found in an acid solution, it would be impossible for any hydrochloric acid to be present; or, if a solution contains barium, sulfuric acid could not be present; or, if a neutral solution contains lead, only nitric and acetic need be looked for, since all other lead salts are insoluble in water. If the student will bear in mind the above examples, and many similar ones which will readily suggest themselves, he will be saved much useless labor.

The first step in analyzing a solution is, therefore, to determine what metals are present. Having done this we know that all those acids which form insoluble compounds with any of the metals which are present must be absent, and we may then proceed to determine the acids that are present. [The word "acid," as used in this connection, does not necessarily mean free acid, but is used to denote the acid radical which is combined with a metal to form the salt.]

A number of salts which are insoluble in water are kept in solution by the presence of some free acid. When the latter is neutralized in the examination for the metals, not only the metal but often the acid will be precipitated; so that a number of the acids, if present, will be discovered during the examination for the metals. Thus, if phosphoric, oxalic, silicic, boric, or hydrofluoric acid is present, together with certain members of Groups 3, 4, 5, or 6 (Mg), it will remain in solution as long as free acids are present, but will be precipitated with Group 3, and can be detected as given on page 90.

PREPARATION OF THE SOLUTION

First Method. After having determined what metals are present, a solution must be carefully prepared before examining for the acids. For this purpose take a portion of the original solution (50 cc.) and heat nearly to boiling. Add to the hot solution a very slight excess of Na_2CO_3, boil for a moment, and filter. Preserve some of the precipitate for a future test.

The filtrate, which contains all the acid radicals, and which should be alkaline from the excess of Na_2CO_3, must now be neutralized, and the excess of the sodium carbonate removed. In order to do this, while the liquid is kept boiling add HNO_3 carefully and slowly, at the last drop by drop, as long as the carbon dioxid continues to escape.

After the carbonate is thus decomposed, boil for a moment, and then test with litmus paper. The liquid should now be slightly acid. Next add to the liquid dilute NH_4OH drop by drop, stirring all the while, until it is exactly neutral. If very much of an excess of acid has been added, it is better to very nearly neutralize this with NaOH, completing the operation with the NH_4OH. The reason for this is that the presence of ammonium salts in any but minute quantities interferes with the precipitation of some of the acid radicals. Great care should therefore be taken in the preparation of this solution, since much of the success in the determination of the acid radicals depends upon the care with which this solution has been prepared.

Second Method. If only members of the first and second groups of the metals were found in the original solution, they may be removed by means of H_2S instead of Na_2CO_3.

To prepare the solution by this method, saturate the original solution with H_2S, heat the whole to boiling, and filter. Boil the filtrate until all the H_2S has been expelled. The solution should now be slightly acid. Carefully neutralize the acid as in the first method, and the solution is ready for use.

Arsenic, when present, usually belongs with the acid radical. In the examination for the metals, arsenic acid, when present, is reduced to arsenious acid by H_2S. [See Part I, Arsenic.]

In the preparation of the solution for acids by the first method the arsenic is not precipitated by the Na_2CO_3, and so, if found in the examination for metals, may now be looked for among the acids.

If the second method for preparing the solution for acids is employed, the arsenic will be precipitated with the metals and so will not be found among the acids.

CLASSIFICATION OF THE ACID RADICALS

The classification of the acid radicals is based upon the solubility or insolubility of certain of their salts, which are precipitated by certain reagents. They are thus divided into certain arbitrary groups, as in the case of the metals, but the methods of treatment for these acid groups are quite different. These groups can be subdivided only to a limited extent, so that in most cases each acid has to be detected by a special test. The group reagents are therefore employed to ascertain the presence or absence ot any of the members of a group rather than to separate them from one another.

In the classification of the acid radicals we recognize three main groups, the grouping being based upon the insolubility of their barium and silver salts. Only the comparatively common acids will be treated here. For the detection of the rare acids the student should consult some large work like Fresenius' *Manual of Qualitative Chemical Analysis.*

Group 1 contains those acid radicals whose barium salts are precipitated from a neutral solution by means of barium chlorid.

Group 2 contains those acid radicals whose silver salts are precipitated from a solution acidified with nitric acid by means of silver nitrate.

Group 3 contains the remaining acid radicals; that is, those whose barium salts are soluble in water, and whose silver salts are soluble in water or in nitric acid, or in both.

Acids: Group 1

The neutral solution prepared for the examination for acids as described above is treated with barium chlorid, filtered, and the filtrate preserved for some tests in the next group. The barium salts of the following acids may be found in the precipitate, viz.:

Sulfuric acid, H_2SO_4,
Sulfurous acid, H_2SO_3,
Phosphoric acid, H_3PO_4,
Arsenic acid, H_3AsO_4,
Arsenious acid, H_3AsO_3,
Boric acid, H_3BO_3,
Hydrofluoric acid, HF,
Carbonic acid, H_2CO_3,
Silicic acid, H_4SiO_4 or H_2SiO_3,
Chromic acid, H_2CrO_4,
Oxalic acid, $H_2C_2O_4$,
Tartaric acid, $H_2(C_4H_4O_6)$, and
Citric acid, $H_3(C_6H_5O_7)$.

Take a portion of the precipitate and add to it some HCl. If it remains undissolved, sulfuric acid is present. If sulfur dioxid is given off (recognized by its odor), sulfurous acid is present. The sulfites should completely dissolve in HCl, but as they gradually oxidize to sulfates, even by standing, there is usually a small portion which will not dissolve. [See Part I, Sulfurous Acid 3.]

If carbonates are present, they dissolve in HCl with effervescence, which is caused by the liberation of carbon dioxid. The latter can be recognized by the ordinary test with limewater. [See Part I, Carbonic Acid 4.]

If members of Groups 3, 4, 5, or 6 (Mg) of the metals were found in the examination for metals, phosphoric, oxalic, hydrofluoric, boric, and silicic acids, if present, were probably found in the precipitate with Group 3, and recognized by the tests given there. [See page 90.] In any case if it is desirable to test for them here, the tests there given are the ones to be employed.

If arsenic or arsenious acid is present, the arsenic acid will be reduced to arsenious acid by H_2S, and both will be precipitated in Group 2 of the metals.

If chromic acid is present, it will have been reduced by H_2S and precipitated by the ammonium hydroxid in Group 3 of the metals. In this acid separation the presence of chromic acid imparts a yellow color to the solution, and its presence may be confirmed by making the solution strongly acid with acetic acid and adding lead acetate. A yellow precipitate soluble in NaOH is lead chromate. Chromium may also have been present in the original solution as a chromium salt of some acid. To determine whether or not this is so, take a small portion of the precipitate, obtained by boiling the original solution with Na_2CO_3, and dissolve it in HCl. Precipitate this last solution with NH_4OH or NaOH. Filter, wash the precipitate, and test it for chromium as given on page 89.

If a non-volatile organic acid, such as tartaric or citric acid, is present, some of the metals will not be completely precipitated in the preparation of the solution for acids. [See Part I, Aluminum 2, 3, 4, and Ferric 1.] The presence of these metals may interfere with the test for these acids, and so, if present, they must be removed. In order to remove them, take some of the solution prepared for the examination for acids, make it alkaline with NH_4OH, saturate it with H_2S, heat it to boiling, and filter. Make the filtrate slightly acid with HCl and boil until all the H_2S has been expelled. Filter again if necessary. This will remove any metals remaining in the solution except traces of aluminum and chromium, and they will do no harm.

After the solution is cold, add NH_4OH to distinct alkaline reaction, then NH_4Cl, and finally $CaCl_2$. Shake or stir vigorously and allow to stand fifteen minutes. If no precipitate appears, tartaric acid is absent. If a precipitate appears, it may or may not be caused by tartaric acid, but the solution should be allowed to stand two hours for complete precipitation. After this, filter and save the filtrate to test for citric acid. The precipitate is dissolved in cold NaOH, allowed to stand a few minutes with occasional stirring, filtered, and the filtrate boiled. If a precipitate separates by boiling, it indicates tartaric acid, which may now be filtered off and tested as under Part I, Tartaric Acid 5.

Citric acid is not very often found, but, if present, it may be detected in the filtrate after precipitating the tartrates with $CaCl_2$. To do this, add to this filtrate three volumes of alcohol, and after allowing it to stand for a moment, filter and wash the precipitate with alcohol. Dissolve the precipitate on the filter with a little dilute HCl, add NH_4OH to this solution until alkaline, and boil. If no precipitate appears, add a little more $CaCl_2$ and NH_4OH and boil again. A precipitate is calcium citrate and indicates citric acid.

Acids: Group 2

To a second portion of the prepared solution add dilute HNO_3 until distinctly acid, and boil. This decomposes sulfids, sulfites, thiosulfates, and nitrites. These give off H_2S, SO_2, and N_2O_3, respectively, which serves to recognize them. If silver nitrate is now added, the silver salts of the following acids may be precipitated.

Hydrochloric acid, HCl,
Hydrobromic acid, HBr,
Hydriodic acid, HI,
Hydrocyanic acid, HCN,
Hydroferrocyanic acid, $H_4Fe(CN)_6$,
Hydroferricyanic acid, $H_3Fe(CN)_6$,
Sulfocyanic or Thiocyanic acid, $HSCN$.

In addition to these, phosphoric and chromic acids, if present, will be precipitated again in this group, unless too much HNO_3 has been added.

If hydrogen sulfid was present, unless it was completely decomposed when boiled with HNO_3, the precipitate will be black, in which case add a little more dilute HNO_3, boil until all the H_2S is expelled, and filter.

Since the presence of any of the cyanogen acids interferes with the tests for the halogen acids, they must first be removed. The presence or absence of the cyanogen acids is determined in the following way.

Take a little of the prepared solution, add a few drops of HCl and some ferric chlorid. A red solution indicates a sulfocyanate, a blue precipitate, a ferrocyanid. If both are present, the blue color covers up the red, in which case add to the solution about 2 cc. of ether and shake thoroughly. The sulfocyanate, if present, dissolves in the ether and gives it a red color.

Take a little of the filtrate from the first acid group, add a few drops of HNO_3, and then some $AgNO_3$. A red brown precipitate indicates a ferricyanid. [This may also be shown by adding to the solution before preparing it for the acid tests some freshly prepared solution of ferrous sulfate, when Turnbull's blue is formed.]

If neither hydroferrocyanic nor hydroferricyanic acid is present, take a little of the prepared solution, acidify with HCl, and, while cold, add a few drops of both $FeSO_4$ and $FeCl_3$. If the solution is acid, there should be no precipitate. Now add NaOH until the mixture is strongly alkaline, warm a little, and add HCl until acid. A blue precipitate indicates hydrocyanic acid.

If either hydroferrocyanic or hydroferricyanic acid is found to be present, place a small portion of the precipitate, formed by $AgNO_3$ in precipitating acid Group 2, in a small dish, add to it a little dilute H_2SO_4, and warm. Hydrocyanic acid will be liberated and may be recognized by its odor. [Caution! This latter operation should be carried on under a hood with a good draught, and the liberated gas smelled cautiously, as it is very poisonous.]

If any of the cyanogen acids are found in the examination as given above, they must now be removed. This can be done in the following manner.

Take about one half of the group precipitate formed by $AgNO_3$, place it in a porcelain crucible, and ignite for about five minutes over a Bunsen lamp. The silver salts of the cyanogen acids will be decomposed, while the silver salts of the halogen acids will remain unchanged. Add to the ignited residue about four times its weight of $NaKCO_3$ and thoroughly fuse the whole. The fused mass is then digested for some time with warm water and filtered. The chlorids, bromids, and iodids will now be found in the filtrate as alkaline salts, free from cyanogen compounds.

The test for hydrochloric acid in the presence of hydrobromic and hydriodic acids requires some care, but it may be done as follows, with the solution just prepared.

Take about 10 cc. of the solution in a large test-tube and make it distinctly acid with H_2SO_4. Boil to decompose the excess of Na_2CO_3. Add about 3 cc. of a concentrated solution of ferric sulfate and boil again. [Any of the double sulfates, known as the iron alums, may be used. Ferric chlorid may also be used if perfectly free from nitrates.] Test the escaping steam for iodin with starch paper, and, if found, boil until the iodin is all expelled, adding more of the iron solution if necessary.

After the iodin is all expelled, add a solution of $KMnO_4$ to distinct coloration and boil again. Test the escaping steam for bromin with potassium iodid starch paper. [Do not allow the liquid to touch the paper.] If bromin is found, boil until it is expelled, adding enough of the $KMnO_4$ so that the solution will show the purple color after boiling.

The excess of the $KMnO_4$ is removed by adding a few drops of alcohol, boiling a moment, and filtering. The presence of chlorin can now be shown by adding a little HNO_3 and some $AgNO_3$. A white precipitate is silver chlorid. [Instead of $KMnO_4$ a solution of $K_2Cr_2O_7$ may be used.]

If none of the cyanogen acids were found to be present, the halogen acids may be tested for in the following way.

Take some of the group precipitate formed by $AgNO_3$ and place it in a porcelain dish with some dilute H_2SO_4 and a piece of metallic zinc. The nascent hydrogen reduces the silver salts to metallic silver, which may be filtered off. The excess of zinc is removed with Na_2CO_3, as in the preparation of the solution for acids. The alkaline filtrate is then made acid with H_2SO_4, which decomposes the excess of Na_2CO_3. The solution may now be examined for the halogen acids as above.

If nitrous acid was present in the original solution, it will have been decomposed by the nitric acid in the preparation of the solution for this group. Its presence may be confirmed by adding acetic or dilute sulfuric acid to the original solution, when red-brown fumes of N_2O_3 or NO_2 will be liberated.

Acids: Group 3

The only acid radicals found in this group are

Nitric acid, HNO_3,
Chloric acid, $HClO_3$, and
Acetic acid, $H(C_2H_3O_2)$.

These cannot be precipitated under ordinary conditions and so are recognized by special tests.

Nitric acid may be recognized in the original solution by either of the tests already given. [See Part I, Nitric Acid 1 and 2.]

Nitrous acid shows the same result as in the first test for nitric acid referred to above. If, however, a portion of the solution is acidified with dilute H_2SO_4 and boiled, all nitrites will be decomposed and N_2O_3 or NO_2 liberated. Any other dilute acid will produce the same result as H_2SO_4.

Chloric acid is not common in solutions.. When present it may be recognized by evaporating a small quantity of the prepared solution to dryness in a porcelain dish on the water bath, and adding to the residue a small quantity of concentrated H_2SO_4. The heavy, yellow, explosive gas, chlorin peroxid, ClO_2, is liberated, which may be further recognized by its peculiar "chlorous" odor.

Acetic acid may be recognized by its special test. [See Part II, VIII, (*f*).] If a chlorate is present, it should be entirely decomposed by sulfuric acid, as given above, before making this test.

PART IV

SYSTEMATIC EXAMINATION OF COMPLEX SOLIDS

Hitherto we have had for our study the analysis of substances already in solution, or, as in Part II, the study of simple compounds in the solid state. If the analytical chemist could always receive his complex substances in solution, his work would be comparatively simple, and the methods given in Part III would enable him to analyze all ordinary inorganic substances. As a matter of fact, most of the material sent to the chemist for analysis is more or less complex and usually in the solid state, and it is necessary for him to know how to proceed under these conditions.

It often happens that the physical properties of a substance are such that the chemist is able to infer many things as to its nature and composition. His knowledge of the more important reagents and their action upon the different elements and compounds should enable him to determine by a few simple tests whether or not his inference is correct.

It sometimes happens, also, that in a complex body the only knowledge desired is regarding the presence or absence of a single ingredient. The method of procedure in such a case is not very complicated and the result is easily acquired by methods already given.

But if we wish to know all the ingredients to be found in a complex chemical compound or mixture; if we wish to know that it contains certain ingredients and no others; in short, if we wish to make a complete qualitative analysis of the substance, we must employ a systematic course of analysis. We must of course know the common reagents and their action on all kinds of matter, but haphazard testing will not accomplish our purpose. We must know what solvents and reagents to use and in what order they must be applied, and follow this order, or our analysis will be little better than guess work.

A preliminary examination of the substance should always be made, since that will often reveal the absence of some ingredient which will enable the chemist to shorten his work, or the presence of some ingredient which will enable him to take certain precautions, and so avoid some difficulty. In any case, the preliminary examination will always indicate the nature of the substance to be analyzed.

PRELIMINARY EXAMINATION

Since the object of a preliminary examination is to obtain information regarding the nature of the substance to be analyzed, considerable care should be exercised in considering any physical or chemical properties which may be observed, as this may result in the saving of much time and labor.

The substance should first be examined with regard to its physical properties. Note its color and structure, whether it is homogeneous or heterogeneous, crystalline or amorphous; or, if it is a compact mass, whether it is hard or soft; or, if metallic, whether it is malleable or brittle, and whether it has a high or low specific gravity. These are the principal physical properties to note, and the student's knowledge of these properties should give him considerable information about the substance.

Most of the preliminary tests employed to show the chemical properties are included in those reactions which are given under Blowpipe Analysis (Part II), and consist of any or all of the different methods of treatment which are given in that part of the work. It will of course sometimes happen that the tests given there will have little or no value, since in a complex substance two elements may be present which will give conflicting results, and so will modify those results which we should otherwise obtain. Many of the reactions will, however, give important indications. The tests given in Part II should be followed in about the same order in which they are given there, the detail of which need not be repeated here.

The methods here given provide for the recognition of only the common inorganic substances and the salts of a few of the simplest and most common organic acids. If other organic material is found to be present, it may be removed by igniting the substance in a crucible until all the organic matter has been oxidized and driven off.

All solid substances may be divided into two general classes, viz.:

I. Metals and alloys.

II. Substances which are neither metals nor alloys.

A metal or an alloy can usually be recognized as such by its metallic luster, hardness, malleability, and high specific gravity. Only a few of the metals or alloys are brittle, and only a very few have a specific gravity of less than four.

Substances which are neither metals nor alloys usually lack the metallic luster, are more or less brittle, though sometimes very hard, and have a specific gravity less than four. The most of them can be reduced to a powder with comparative ease.

I. THE SUBSTANCE IS A METAL OR AN ALLOY

This class may be further divided into three divisions, according to the action of the different substances when treated with nitric acid. These divisions are:

A. Metals insoluble and unchanged in nitric acid. This division includes gold, platinum and most of the rare metals of the platinum group, and their alloys.

B. Metals which form insoluble oxids by the action of nitric acid. This division includes antimony and tin and their alloys.

C. Metals and alloys soluble in nitric acid. This division includes all the other common metals and their alloys.

Since chemically pure metals are not often found, and, if found, are rarely the object of a qualitative analysis, only the general process of treating alloys will be given here, since that will be sufficient for all cases.

No metals used commercially are ever chemically pure, but all contain greater or less quantities of other metals which have not been completely removed in the process of reducing the metals from their ores. These metals can hardly be classed as alloys, and yet, for analytical purposes, they are such. If an analysis of the impurity in a commercial metal is desired, it is only necessary to employ a larger amount and proceed as in the analysis of an alloy.

Heat a portion (1 or 2 grams) of the alloy with nitric acid of about 1.2 specific gravity (equal parts of concentrated acid and water). After the action, if any, has ceased, if a white residue is left, add an equal volume of water and heat to boiling. [Certain nitrates are not very soluble in nitric acid, and so crystallize out if the solution is too concentrated.] Filter and wash the residue with a little hot water. Test the filtrate by evaporating a small portion on platinum foil to see if anything has dissolved. If a residue remains on the foil, it belongs to division C, and the filtrate must be preserved and tested as given under C.

A. The residue is dark colored, or has a metallic appearance. Dissolve it in aqua regia, evaporate to dryness, add a little concentrated HCl, and evaporate a second time; after which, add some water, and evaporate a third time to remove the excess of acid. Dissolve the residue in water, add oxalic acid, and warm for an hour, when all the gold will be precipitated. Filter off the gold and evaporate the filtrate to dryness. Ignite the dried filtrate in a porcelain crucible, under a hood, to remove the excess of oxalic acid. The platinum will remain in the crucible in the metallic state, and may be dissolved again in aqua regia and subjected to further tests.

B. The residue is white and pulverulent. This generally consists of metastannic acid, $H_{10}Sn_5O_{15}$, or metantimonic acid, $HSbO_3$. If the residue is dark colored, it may consist of both divisions A and B. Fuse this residue in a porcelain crucible, with a mixture of equal parts of dry Na_2CO_3 and sulfur, for five or ten minutes. After the crucible and its contents have become cool, dissolve out the fused mass with hot water, and filter if necessary. A precipitate will consist of division A, and is treated as given above. The solution, or filtrate, should now be acidified with dilute HCl, which precipitates the antimony and tin as sulfids, after which they may be separated, as given in Part III, Group 2, Subdivision B. [See page 84.]

C. The substance is completely dissolved by HNO_3. The filtrates from A and B, or the entire solution if the alloy dissolved completely in HNO_3, should now be evaporated to dryness, and then dissolved in water, a few drops of HNO_3 being added, if necessary, to make a clear solution.

The metals are now in solution as nitrates and may be separated by the methods given under Part III, Mixed Compounds. [See page 76.]

II. THE SUBSTANCE IS NEITHER A METAL NOR AN ALLOY

In this case if the substance is a mixture, the different ingredients are first separated from each other, as far as possible, according to their solubility or insolubility in water and acids. If a residue remains which is insoluble in water and acids, it is subjected to a special course of treatment as given under E.

If the substance for analysis is a complex compound, it may be treated in the same systematic way, but will usually be found to be insoluble in water and acids and will have to be brought into solution by fusion with the alkaline carbonates, as given below under E, (*c*). If the substance is shown by the preliminary examination to be a silicate, and nothing else, we may pass at once to division F, which treats of silicates.

If the substance is not already in that condition, it should be well pulverized before beginning the analysis. From one to three grams should be taken for analysis.

A. The substance is partially or entirely soluble in water. Place the substance in a proper-sized beaker or flask, add to it distilled water, and heat to boiling. Digest the substance at or near the boiling point for a few minutes, stirring or shaking frequently, and filter if it has not all dissolved. If the substance completely dissolves, the solution may now be examined for metals as given in Part III, page 76, and for acid radicals as given on page 101.

If a residue remains undissolved, filter as above directed, and wash it thoroughly with hot water. Evaporate a small portion of the filtrate to dryness on a platinum foil, to see if anything has dissolved. If a residue remains on the foil, the whole filtrate must be examined, as directed above, when all dissolves.

B. The substance is insoluble in water. A small portion of the undissolved residue from A is subjected to a preliminary examination with warm dilute HCl. This may be done in a test-tube. Note carefully if any gases are given off, as these indicate what kind of compounds are being dissolved. A carbonate gives off CO_2; a sulfid gives off H_2S; a peroxid or some highly oxidized salt (such as chromate, etc.) gives off Cl; a sulfite or thiosulfate gives off SO_2; a cyanid gives off HCN (Poison!). These gases may be recognized by the tests already given. Silicic acid sometimes separates out as a white gelatinous mass, indicating a silicate which is decomposed by acids. [See F.]

If no action takes place, test a few drops of the acid liquid on a platinum foil to see if anything has dissolved. If nothing has dissolved, throw away the small portion taken for the preliminary test and then pass on to C. If something has dissolved, treat the whole residue from A with HCl, as above. After all action has ceased, boil for a moment and, if any undissolved residue remains, filter and wash with hot water. [The wash water, after the first washing, should be thrown away.]

The residue is preserved for C and the filtrate evaporated to dryness in a porcelain dish. The dried mass is then dissolved in water and the metals separated, as in Part III.

If cyanids, especially the compound cyanids, are present, they are not all completely dissolved or decomposed by the HCl. They will therefore be found in some of the successive portions. A more complete method of separation under these conditions will be found under G.

C. The substance is insoluble in H_2O and in HCl. The residue from B is next treated with warm dilute HNO_3 (equal parts concentrated HNO_3 and water). Observe carefully if any action takes place. If nitric oxid is given off, shown by the red-brown fumes, oxidation is taking place. Certain sulfids are decomposed by HNO_3, giving off some H_2S, and liberating sulfur, which appears as a dark-colored mass floating on the surface of the liquid. Silicic acid sometimes separates as a white gelatinous mass, indicating a silicate. [Compare B.]

In any case filter, wash with hot water, and evaporate the filtrate to dryness. The undissolved residue, if any, is preserved for D. Dissolve the evaporated filtrate in water and examine for metals, as in Part III.

D. The substance is insoluble in H_2O, and in both HCl and HNO_3. The residue from C is next treated with aqua regia under a hood. After digesting for some minutes, the mass is diluted with an equal portion of water and filtered. Any residue is preserved for E. The filtrate is evaporated to dryness, dissolved in water, and the metals separated as before.

E. The substance is insoluble in H_2O and in all acids. The residue from D may consist of any or all of the following compounds, viz.:

Barium, strontium, and calcium sulfates,
Lead sulfate, and possibly lead chlorid,
Silver chlorid, bromid, iodid, and cyanid,
Silicic acid and many silicates,
Aluminum, and chromium oxids,
Calcium fluorid,
Sulfur, and
Carbon.

In addition to these, a few rare compounds consisting of certain aluminates, phosphates, arsenates, and oxids are insoluble in acids, and so, if present, would be found here.

Preliminary tests may be made to see what compounds are present, although this is not absolutely essential. It is better, however, to test a small portion before each step, provided the amount of material is not too small.

(*a*) Lead and silver salts, if present, must first be removed. The lead salts are removed by heating the whole residue with a concentrated solution of ammonium acetate, which dissolves them. Filter, wash, and test one portion of the filtrate with $BaCl_2$ for sulfuric acid, another portion with H_2S for lead, and a third portion, acidified with HNO_3, with $AgNO_3$ for chlorin.

(*b*) If a residue remains, or if nothing dissolves in the ammonium acetate, digest the residue for some time with a solution of KCN, at a gentle heat, repeating the operation, if necessary, until all the silver salts are dissolved. (If sulfur is present, this operation should be carried on in the cold.)

The whole is now filtered and the precipitate well washed. If the filtrate is acidified with HNO_3 (do this under a hood), the silver salt is precipitated and may be further tested for silver by filtering and fusing a portion of this last precipitate on charcoal with Na_2CO_3, which will give a bead of metallic silver.

(*c*) The residue is now free from lead and silver salts. It is next heated in a covered porcelain crucible until all sulfur, if present, is volatilized. It is then mixed with four parts of $NaKCO_3$ and one part of KNO_3 and heated in a platinum crucible for a half hour, or until it is all thoroughly fused. If the red-hot crucible is placed on a cold metal plate, the fused mass can generally be removed in a cake after it has become cold. Digest the fused mass in hot water for a half hour and then filter, washing the residue once with hot water. The residue should be thoroughly washed, but the wash water, except the first washings, may be thrown away. Preserve the residue for examination under (*d*).

The filtrate now contains the acids which were present in the insoluble compounds, together with those bases which are soluble in the alkaline carbonates. It is examined as follows.

(c_1) Take a small portion of the filtrate, acidify it with HCl, and add $BaCl_2$. A white precipitate indicates a *sulfate.*

(c_2) Take another portion, acidify it with H_2SO_4, heat it to boiling, and, while hot, saturate it with H_2S. A yellow precipitate is As_2S_3 and indicates an *arsenate.*

(c_3) Filter off the yellow arsenic sulfid from (c_2), add to the filtrate enough concentrated HNO_3 to make it strongly acid, and then some ammonium molybdate solution. A yellow precipitate indicates a *phosphate.*

(c_4) To another portion of the filtrate add HCl to decompose the carbonates, and boil until all CO_2 has been driven off. Make the solution alkaline with NH_4OH, filter, and add to the filtrate some $CaCl_2$. If a precipitate forms, it is CaF_2 and indicates a *fluorid*. This may be further tested as in Part I, Hydrofluoric Acid 5.

(c_5) If the filtrate from (*c*) is yellow, it may contain chromates. Acidify a portion with acetic acid and add lead acetate. A yellow precipitate indicates a *chromate*.

(c_6) The remainder of the filtrate is acidified with HCl and evaporated to dryness. It is best to repeat this operation, adding more HCl to insure the complete decomposition of the silicic acid. The dried mass is then treated with hot water, a few drops of HCl being added if necessary.

If silicic acid was present, it will now appear as an insoluble precipitate of silicon dioxid, SiO_2. The metals which were dissolved by the carbonates will now be in solution as chlorids. Filter off the SiO_2. This indicates a *silicate*, and may be tested as in Part II, V, (*h*). Test the filtrate for metals as in Part III.

(*d*) The residue from (*c*) is now washed into a porcelain dish, made acid with HCl, and evaporated to dryness, repeating the operation, as directed above, to insure complete decomposition of any silicic acid present. Dissolve the dried mass in water, add a few drops of HCl, filter off any insoluble silicon dioxid, and examine the filtrate for metals, as given in Part III.

F. The substance is a silicate. If the preliminary examination (see page 112) shows us that the substance is a silicate, most of the preceding steps may be omitted, or at least modified.

All silicates may be divided into two general classes, viz.:

(*a*) Silicates which are completely decomposed by the mineral acids, HCl, H_2SO_4, or HNO_3.

(*b*) Silicates that are not decomposed, or which are only partially decomposed, by acids.

In order to determine to which of these two classes a given silicate belongs, it is first necessary to reduce the substance to a very fine powder. Digest a portion of this powder with some HCl, warming, but not boiling, the liquid. If the acid decomposes the silicate, this will generally be indicated by a change in the color of the solution and the presence of silicic acid, which appears as a white, flocculent, gelatinous, or pulverulent mass in the solution. If HCl fails to decompose it, test another portion with H_2SO_4 (three parts acid to one part water). The indications are the same as with HCl, and if both fail to decompose the silicate, it belongs to the second class.

(*a*) **Silicates decomposed by acids.** The finely powdered silicate is mixed with a little water to a thin paste, in a porcelain dish, and then digested with HCl at a temperature near the boiling point, until it is completely decomposed. Evaporate the whole to dryness, with occasional stirring, add more acid, and evaporate the second time. Treat the dried mass with hot water, adding a few drops of HCl, and filter off the insoluble silica, SiO_2.

The metals will now be in solution as chlorids and may be separated as in Part III.

If lead or silver is found in the silicate, it is better to use HNO_3, the operation being otherwise conducted as above. Sulfuric acid may be used if an aluminum silicate is to be decomposed.

Silicates not infrequently contain small quantities of titanium in the form of TiO_2, and replacing some of the SiO_2. If the solution, after filtering off the silica, is diluted and then boiled for a long time, the TiO_2 is precipitated. (Titanium is a rare element, which need not be looked for in most qualitative analyses.)

(*b*) **Silicates not decomposed by acids.** Take about a gram of the finely powdered silicate and mix it with about four grams of $NaKCO_3$. (A mixture of equal parts of Na_2CO_3 and K_2C_3O will answer.) Place the mixture in a platinum crucible and heat for half an hour, or until it is all in a state of complete fusion. If the crucible is allowed to cool on a metal plate, the fused mass can usually be removed in a lump.

Place this fused mass, or the crucible and its contents, if the contents cannot be easily removed, in a porcelain dish, cover with warm water, and add HCl sufficient to decompose the carbonates. The whole is now evaporated to dryness and treated as in the case of silicates decomposed by acids.

Of course after the addition of both sodium and potassium carbonates, this portion cannot be examined for alkali metals. If these are present, they may be detected as follows.

Take another portion of the finely powdered silicate, mix with it one part of ammonium chlorid and eight parts of precipitated calcium carbonate. Heat this mixture to moderate redness for half an hour in a covered platinum crucible. Place the crucible and its contents in a porcelain dish with water, boil until the whole mass is completely disintegrated, and filter. Add to the filtrate NH_4OH until it is alkaline, then ammonium carbonate to slight excess. See that the mixture now smells strongly of ammonia, allow it to settle, and filter.

The last filtrate will now contain the alkali metals and of course ammonium salts. Evaporate this to dryness and ignite gently until all the ammonium compounds have been decomposed. Dissolve what remains in water, filter if necessary, and examine the solution as in Part III, Group 6.

G. Cyanids are present. The cyanids, and more especially the compound cyanids, if present, are not completely dissolved or decomposed when treated with HCl, as in division B. They will generally be detected by the methods already given, but a much more satisfactory method of treatment when they are present is the following.

A small portion of the residue from A is tested with HCl, which will usually decompose some of the cyanids so as to liberate HCN. If cyanids are found, take the whole residue from

A and boil it with a little concentrated NaOH solution for a short time, add some concentrated solution of Na_2CO_3 and boil again for a few minutes. Dilute with hot water, filter, and wash the residue, if any, with hot water. The residue will now be free from all cyanids, except silver cyanid (which will be found in E), and is treated as given under B.

(*a*) A small portion of the strongly alkaline filtrate is treated with H_2S. (It is best to use a solution of H_2S; or, if the gas itself is used, not to completely saturate the solution, as some of the metals, such as aluminum, etc., may be precipitated, since NaOH is present.) If no precipitate forms, pass on to (*b*). If a precipitate forms, take about one half of the alkaline filtrate and add Na_2S [$(NH_4)_2S$ may be used], avoiding any unnecessary excess. Warm the whole without boiling, filter, and wash with hot water, saving the filtrate for (*b*).

The precipitate, which will contain the metals belonging to Groups 1, 2 (Subdivision A), 3, and 4, is treated with dilute HNO_3. Filter off any insoluble HgS or $PbSO_4$ which may be present and examine for metals, as given in Part III.

(*b*) The filtrate from (*a*) or a portion of the alkaline filtrate, if no precipitate was formed by the Na_2S, is now made acid with dilute H_2SO_4 and saturated with H_2S. If no precipitate forms, pass on to (*c*). If there is a precipitate, it belongs to Group 2, Subdivision B. Examine as given on page 84.

(*c*) The filtrate from (*b*) still contains those metals which form the double cyanogen compounds (ferro- and ferri-cyanids, cobalticyanids, etc.) and aluminum. A portion of the solution may be tested for the acid radicals, as given in Part III.

Evaporate another portion of this filtrate nearly to dryness after acidifying strongly with H_2SO_4, and then heat (under a hood) until most of the excess of H_2SO_4 has been driven off. Dissolve the residue in water and examine the solution for metals of the third and fourth groups, as given in Part III.

Since the ferricyanids are reduced to ferrocyanids by H_2S, and since H_2SO_4 is used in the tests for the other acids and metals, we must test for sulfuric and ferricyanic acids in the remaining portion of the original alkaline solution. This may be done in the usual way after acidifying with HCl or HNO_3. [See the corresponding acids in Part I.]

APPENDIX A

Names, Symbols, and Atomic Weights of the Elements

The non-metallic elements are printed in small capitals.

NAME	SYMBOL	ATOMIC WEIGHT O=16	NAME	SYMBOL	ATOMIC WEIGHT O=16
Aluminum	Al.	27.1	Neodymium	Nd.	143.6
Antimony	Sb.	120.2	NEON	Ne.	20.
ARGON	A.	39.9	Nickel	Ni.	58.7
ARSENIC	As.	75.	NITROGEN	N.	14.
Barium	Ba.	137.4	Osmium	Os.	191.
Bismuth	Bi.	208.5	OXYGEN	O.	16.
BORON	B.	11.	Palladium	Pd.	106.5
BROMIN	Br.	80.	PHOSPHORUS	P.	31.
Cadmium	Cd.	112.4	Platinum	Pt.	194.8
Cæsium	Cs.	133.	Potassium	K.	39.1
Calcium	Ca.	40.1	Praseodymium	Pr.	140.5
CARBON	C.	12.	Radium	Rd.	225.
Cerium	Ce.	140.	Rhodium	Rh.	103.
CHLORIN	Cl.	35.4	Rubidium	Rb.	85.4
Chromium	Cr.	52.1	Ruthenium	Ru.	101.7
Cobalt	Co.	59.	Samarium	Sm.	150.
Columbium	Cb.	94.	Scandium	Sc.	44.1
Copper	Cu.	63.6	SELENIUM	Se.	79.2
Erbium	Er.	166.	SILICON	Si.	28.4
FLUORIN	F.	19.	Silver	Ag.	107.9
Gadolinium	Gd.	156.	Sodium	Na.	23.
Gallium	Ga.	70.	Strontium	Sr.	87.6
Germanium	Ge.	72.5	SULFUR	S.	32.
Glucinum	Gl.	9.1	Tantalum	Ta.	183.
Gold	Au.	197.2	TELLURIUM	Te.	127.6
HELIUM	He.	4.	Terbium	Tb.	160.
HYDROGEN	H.	1.0075	Thallium	Tl.	204.1
Indium	In.	114.	Thorium	Th.	232.5
IODIN	I.	126.8	Thulium	Tu.	171.
Iridium	Ir.	193.	Tin	Sn.	119.
Iron	Fe.	55.9	Titanium	Ti.	48.1
KRYPTON	Kr.	81.8	Tungsten	W.	184.
Lanthanum	La.	138.9	Uranium	U.	238.5
Lead	Pb.	206.9	Vanadium	V.	51.2
Lithium	Li.	7.	XENON	Xe.	128.
Magnesium	Mg.	24.3	Ytterbium	Yb.	173.
Manganese	Mn.	55.	Yttrium	Yt.	89.
Mercury	Hg.	200.	Zinc	Zn.	65.4
Molybdenum	Mo.	96.	Zirconium	Zr.	90.4

APPENDIX B

Names and Formulas of Reagents and Solutions used in this Work

In the formulas given below, the water of crystallization has been omitted.

Acetic Acid	$H(C_2H_3O_2)$ or $H\overline{Ac}$
Acid Sodium Phosphate	Na_2HPO_4
Acid Sodium Tartrate	$NaH(C_4H_4O_6)$
Alcohol	C_2H_5OH
Aluminum Sulfate	$Al_2(SO_4)_3$
Ammonium Acetate	$NH_4(C_2H_3O_2)$
Ammonium Carbonate	$(NH_4)_2CO_3$
Ammonium Chlorid	NH_4Cl
Ammonium Hydroxid	NH_4OH
Ammonium Molybdate	$(NH_4)_2MoO_4$
Ammonium Oxalate	$(NH_4)_2C_2O_4$ or $(NH_4)_2\,\overline{Ox}$
Ammonium Sodium Hydrogen Phosphate	NH_4NaHPO_4
Ammonium Sulfid	$(NH_4)_2S$
Ammonium Sulfid (yellow)	$(NH_4)_2S_x$
Ammonium Tartrate	$(NH_4)_2(C_4H_4O_6)$
Antimony Chlorid	$SbCl_3$
Aqua Regia	$[3\,HCl + HNO_3]$
Arsenious Oxid	As_2O_3 or As_4O_6
Barium Carbonate	$BaCO_3$
Barium Chlorid	$BaCl_2$
Barium Hydroxid	$Ba(OH)_2$
Baryta Water	$[Ba(OH)_2 + (H_2O)_x]$
Bismuth Nitrate	$Bi(NO_3)_3$
Borax	$Na_2B_4O_7$
Bromin Water	$[Br + (H_2O)_x]$
Cadmium Nitrate	$Cd(NO_3)_2$
Calcium Chlorid	$CaCl_2$
Calcium Hydroxid	$Ca(OH)_2$
Carbon Disulfid	CS_2

Chlorin Water	$[Cl + (H_2O)_x]$
Chromium Sulfate	$Cr_2(SO_4)_3$
Cobalt Nitrate	$Co(NO_3)_2$
Copper Sulfate	$CuSO_4$
Ether	$(C_2H_5)_2O$
Ferric Chlorid	$FeCl_3$
Ferrous Chlorid	$FeCl_2$
Ferrous Sulfate	$FeSO_4$
Hydrochloric Acid	HCl
Hydrofluosilicic Acid	H_2SiF_6
Hydrogen Sulfid	H_2S
Lead Acetate	$Pb(C_2H_3O_2)_2$ or $Pb\overline{Ac}_2$
Lead Nitrate	$Pb(NO_3)_2$
Lime Water	$[Ca(OH)_2 + (H_2O)_x]$
Magnesium Sulfate	$MgSO_4$
Manganese Dioxid	MnO_2
Manganese Sulfate	$MnSO_4$
Mercuric Chlorid	$HgCl_2$
Mercuric Nitrate	$Hg(NO_3)_2$
Mercurous Nitrate	$HgNO_3$
Microcosmic Salt	NH_4NaHPO_4
Nessler's Reagent	$[HgI_2(KI)_2 + (KOH)_x]$
Nickel Nitrate	$Ni(NO_3)_2$
Nitric Acid	HNO_3
Oxalic Acid	$H_2C_2O_4$ or $H_2\overline{Ox}$
Platinum Chlorid	$PtCl_4$
Potassium Arsenate	K_3AsO_4
Potassium Arsenite	K_3AsO_3
Potassium Bichromate	$K_2Cr_2O_7$
Potassium Bromid	KBr
Potassium Chlorate	$KClO_3$
Potassium Chromate	K_2CrO_4
Potassium Cyanid	KCN
Potassium Ferricyanid	$K_3Fe(CN)_6$
Potassium Ferrocyanid	$K_4Fe(CN)_6$
Potassium Fluorid	KF
Potassium Iodid	KI

Potassium Nitrate (Saltpeter)	KNO_3
Potassium Nitrite	KNO_2
Potassium Pyroantimonate (Acid)	$K_2H_2Sb_2O_7$
Potassium Sulfocyanate	$KSCN$
Potassium Thiocyanate	$KSCN$
Rochelle Salt	$NaK(C_4H_4O_6)$
Saltpeter	KNO_3
Silver Nitrate	$AgNO_3$
Sodium Acetate	$Na(C_2H_3O_2)$ or $Na\overline{Ac}$
Sodium Arsenate	Na_3AsO_4
Sodium Carbonate	Na_2CO_3
Sodium Hydroxid	$NaOH$
Sodium Hypochlorite	$NaClO$
Sodium Metasilicate	Na_2SiO_3
Sodium Phosphate (Acid)	Na_2HPO_4
Sodium Pyroborate (Borax)	$Na_2B_4O_7$
Sodium Silicate	Na_4SiO_3
Sodium Sulfate	Na_2SO_4
Sodium Sulfite	Na_2SO_3
Sodium Tartrate (Acid)	$NaH(C_4H_4O_6)$ or $NaH\,\overline{Tr}$
Sodium Thiosulfate	$Na_2S_2O_3$
Stannic Chlorid	$SnCl_4$
Stannous Chlorid	$SnCl_2$
Strontium Chlorid	$SrCl_2$
Sulfuric Acid	H_2SO_4
Sulfurous Acid	H_2SO_3
Tartaric Acid	$H_2(C_4H_4O_6)$ or $H_2\overline{Tr}$
Zinc Sulfate	$ZnSO_4$

APPENDIX C

Preparation of Reagents and Solutions for Analysis

The strength of the solution, both of the reagent and the substance for analysis, is quite an important factor in the analysis. If the solutions are too strong, the bulk of the precipitate is often so great as to make the mass almost solid. This makes the precipitate difficult to handle and adds unnecessarily to the expenses of the laboratory. On the other hand, if the solutions are too dilute, some ingredient may fail of precipitation and so be missed in the analysis. Furthermore, solutions made up in a haphazard way will cause much annoyance in precipitation, especially in the more advanced portions of the work; it will be found to be much more convenient if the solutions are chemically equivalent, or of such relative strength that chemically equivalent amounts may be used. All solutions and dilutions are made with water, unless otherwise stated.

The normal solution of volumetric analysis is the best standard of strength. A normal solution is a solution so prepared that one liter shall contain the hydrogen equivalent of the active reagent, weighed in grams. In the case of substances in which the active reagent is univalent, the hydrogen equivalent is the same as the molecular weight. When the active reagent is bivalent or trivalent, the hydrogen equivalent is one half or one third of the molecular weight respectively. Thus the hydrogen equivalent of $NaOH$ is the molecular weight of $NaOH$, or 40, and one liter of water, containing 40 grams of $NaOH$, is therefore a normal solution. Again, the hydrogen equivalent of H_2SO_4 is one half of its molecular weight, since it contains two replaceable hydrogen atoms. The molecular weight of H_2SO_4 is 98, and one half of this number, or 49 grams, of H_2SO_4 in a liter makes a normal solution. In a normal solution of a salt the water of crystallization must also be taken into account. Thus the compound called microcosmic salt is $NH_4NaHPO_4 + 4\ H_2O$, and its molecular weight is 209, which is three times its hydrogen equivalent, phosphoric acid being tribasic, so that 69.6 grams of this salt in a liter makes a normal solution. In preparing these solutions it is not necessary to more than closely approximate these weights.

Normal solutions are marked N, half-normal solutions $\frac{N}{2}$, and double-normal solutions 2 N. For most operations one half normal, or even one fourth normal, solutions will be of sufficient strength. Some reagents may be used more dilute than this. Thus $AgNO_3$ may be used one fifth or one tenth normal for most reactions.

The concentrated acids have approximately the following strength, viz.: H_2SO_4, specific gravity 1.84, about 36 N; HNO_3, specific gravity 1.42, about 16 N; HCl, specific gravity 1.20, about 12 N; acetic acid, 30 per cent, about 5 N. Concentrated ammonia, specific gravity 0.90, has a strength of about 20 N.

These acids, and ammonia, are often used for other purposes than precipitation. It will be better, therefore, to make these somewhat stronger than the other reagents. About four times normal (4 N) will be found a convenient strength. H_2SO_4 diluted 1:8 is about 4 N; HNO_3 diluted 1:3 is about 4 N; HCl diluted 1:2 is about 4 N; ammonia diluted 1:4 is about 4 N. It will also be found convenient to have solutions of other reagents about 4 N in strength.

A few reagents are so difficultly soluble in water that only very dilute solutions can be obtained. A saturated solution of bromin in water is about $\frac{N}{2}$; chlorin water is about N; barium hydroxid (baryta water) about $\frac{N}{5}$; calcium hydroxid (lime-water) about $\frac{N}{20}$; calcium sulfate about $\frac{N}{30}$.

The strength of other solutions may be varied according to the purpose for which they are employed.

INDEX

ANNOUNCEMENTS

TEXT-BOOKS ON SCIENCE

FOR HIGHER SCHOOLS AND COLLEGES

	List price	*Mailing price*
Bergen and Davis's Principles of Botany	$1.50	$1.65
Bergen's Elements of Botany. (Revised Edition)	1.30	1.45
Bergen's Foundations of Botany	1.50	1.70
Blaisdell's Life and Health	.90	1.00
Blaisdell's Practical Physiology	1.10	1.20
Brown's Physiology for the Laboratory	.75	.85
Byrd's Laboratory Manual in Astronomy	1.25	1.35
Davis's Elementary Meteorology	2.50	2.70
Davis's Elementary Physical Geography	1.25	1.40
Davis's Physical Geography	1.25	1.40
Gage's Elements of Physics. (Revised Edition)	1.12	1.20
Hastings and Beach's General Physics	2.75	2.95
Higgins's Lessons in Physics	.90	1.00
Hough and Sedgwick's Human Mechanism	2.50	2.65
Linville and Kelly's Zoölogy	1.50	1.70
Meier's Herbarium and Plant Description. With directions for collecting, pressing, and mounting specimens	.60	.70
McPherson and Henderson's Elementary Study of Chemistry	1.25	1.40
Millikan and Gale's First Course in Physics	1.25	1.40
Moore's Laboratory Directions for Beginners in Bacteriology	1.00	1.05
Nichols, Smith, and Turton's Manual of Experimental Physics	.90	1.00
Norton's Elements of Geology	1.40	1.55
Pratt's Invertebrate Zoölogy	1.25	1.35
Sabine's Laboratory Course in Physical Measurements. (Revised Edition)	1.25	1.30
Seller's Elementary Treatise on Qualitative Chemical Analysis	.75	.80
Stone's Experimental Physics	1.00	1.10
Ward's Practical Exercises in Elementary Meteorology	1.12	1.25
Wentworth and Hill's Text-Book of Physics	1.15	1.25
Wentworth and Hill's Laboratory Exercises in Elementary Physics. (Revised Edition)	.25	.30
Williams's Elements of Chemistry	1.10	1.20
Young's Elements of Astronomy	1.60	1.75
Young's General Astronomy	2.75	3.00
Young's Lessons in Astronomy. (Revised Edition)	1.25	1.40
Young's Manual of Astronomy	2.25	2.45

GINN & COMPANY PUBLISHERS

PRINCIPLES OF BOTANY

By JOSEPH Y. BERGEN, recently Instructor in Biology in the English High School, Boston, and BRADLEY M. DAVIS, recently Assistant Professor of Plant Morphology in the University of Chicago.

12mo. Cloth. vii + 555 pages. Illustrated. List price, $1.50; mailing price, $1.65

A LABORATORY AND FIELD MANUAL OF BOTANY

By JOSEPH Y. BERGEN and BRADLEY M. DAVIS

PRINCIPLES OF BOTANY is a work especially suited for college and normal-school classes and for those high schools that are equipped to give more than an average course in this subject. It claims superior merit in the material which it offers for a consecutive series of studies of representative spore plants, so treated as to outline the evolutionary history of the plant world.

Some of the characteristics which make this volume superior to others of its kind are:

I. That it presents more adequately than any other on the market the subject-matter demanded by the College Entrance Examination Board and the state universities of the middle and far West.

II. That no other botany of its scope leads up to the more difficult portions of the subject in so easy and untechnical a manner.

III. That it is the first book of its class to present ecology as a connected subject and not as a series of snap-shot studies.

IV. That it is the only botany which gives a clear idea of the distribution of vegetation in the United States, with the reasons for it.

V. That it is better and more fully illustrated than any other book for beginners in botany.

With mature students a half year's course may be framed from the book.

GINN & COMPANY Publishers

AN ELEMENTARY STUDY OF CHEMISTRY

By WILLIAM McPHERSON, Professor of Chemistry in Ohio State University, and WILLIAM E. HENDERSON, Associate Professor of Chemistry in Ohio State University.

12mo. Cloth. 434 pages. Illustrated. List price, $1.25; mailing price, $1.40

THIS book is the outgrowth of many years of experience in the teaching of elementary chemistry. In its preparation the authors have steadfastly kept in mind the limitations of the student to whom chemistry is a new science. They have endeavored to present the subject in a clear, well-graded way, passing in a natural and logical manner from principles which are readily understood to those which are more difficult to grasp. The language is simple and as free as possible from unusual and technical phrases. Those which are unavoidable are carefully defined. The outline is made very plain, and the paragraphing is designed to be of real assistance to the student in his reading.

The book is in no way radical, either in the subject-matter selected or in the method of treatment. At the same time it is in thorough harmony with the most recent developments in chemistry, both in respect to theory and discovery. Great care has been taken in the theoretical portions to make the treatment simple and well within the reach of the ability of an elementary student. The most recent discoveries have been touched upon where they come within the scope of an elementary text. Especial attention has been given to the practical applications of chemistry, and to the description of the manufacturing processes in use at the present time.

EXERCISES IN CHEMISTRY. By William McPherson and William E. Henderson. *(In press.)*

GINN & COMPANY Publishers

THE HUMAN MECHANISM

ITS PHYSIOLOGY AND HYGIENE AND THE SANITATION OF ITS SURROUNDINGS

By THEODORE HOUGH, Associate Professor of Biology in Simmons College, Boston, and WILLIAM THOMPSON SEDGWICK, Professor of Biology in the Massachusetts Institute of Technology

IN ONE VOLUME. 12mo. Cloth. 564 pages. Illustrated, partly in color. List price, $2.00; mailing price, $2.15.

IN TWO VOLUMES. Volume I. Elements of Physiology. 12mo. Cloth. 321 pages. Illustrated. List price, ; mailing price, . Volume II. Hygiene and Sanitation. 12mo. Cloth. 271 pages. Illustrated. List price, ; mailing price, .

THE recent advances in our knowledge of personal and public hygiene and of sanitation have made indispensable for the use of progressive educators a practical and authoritative text-book of what may be called "the new physiology and hygiene." The present work has been prepared in recognition of this need. Professor Hough has been engaged in the study and teaching of physiology and personal hygiene for over ten years. Professor Sedgwick has had a large share in the advancement of the study of public health and sanitation in America. They have made the keynote of this work the right conduct of the physical life, and to this end everything else is subordinated. Anatomy and histology are only briefly outlined, while special chapters are devoted to practical matters of hygiene and sanitation.

The authors believe that the matter and method of this new text-book will go far toward rescuing physiology and hygiene from the neglected and too often despised place which they now occupy in schools, and promoting them to one of practical usefulness and corresponding esteem.

The book is intended for high and normal schools, and for short courses in colleges.

GINN & COMPANY PUBLISHERS

A TEXT-BOOK IN GENERAL ZOÖLOGY

By HENRY R. LINVILLE, Head of the Department of Biology, De Witt Clinton High School, New York City, and HENRY A. KELLY, Director of the Department of Biology and Nature Study, Ethical Culture School, New York City

462 pages. Illustrated. List price, $1.50; mailing price, $1.70

AN exposition of the science of zoölogy, presented without the interpolation of a laboratory guide.

Four years spent in careful examination of the original sources have resulted in a book filled with valuable material. The authors, through their extended service as teachers of biology in secondary schools, are well equipped for the task of writing a text-book designed, as this one is, chiefly for high-school use, although intended also to be available for elementary college classes.

The structure, the physiology, and the natural history of selected types of animals are described with accuracy and in language easily understood by young students.

The treatment of the subject is broad, and the inductive method is employed so far as each class and phylum of invertebrate animals is concerned. The definition of a group is not given until the student's conception of the group characters has grown to the point where the definition forms the fitting end to the logical process involved in the exposition.

The Insecta are discussed in the first chapters, and after the remainder of the Arthropoda are described, the other invertebrate phyla follow in a descending series, ending with the Protozoa. Then, beginning with the fishes, the order ascends to the mammals and closes with man.

A large portion of the book is devoted to the insects and vertebrates, because young students are more familiar with these groups and so take greater interest in them. The less known, however, are treated with care, the different features of morphology, physiology, and relation to environment being maintained in good measure throughout.

The book includes two hundred and thirty-three illustrations.

GINN & COMPANY PUBLISHERS

A FIRST COURSE IN PHYSICS

By ROBERT A. MILLIKAN, Assistant Professor of Physics in the University of Chicago, and HENRY G. GALE, Instructor in Physics in the University of Chicago

12mo. Cloth. 488 pages. Illustrated. List price, $1.25; mailing price, $1.40

A LIST OF LABORATORY EXPERIMENTS IN PHYSICS

FOR SECONDARY SCHOOLS

By ROBERT A. MILLIKAN and HENRY G. GALE

List price, 40 cents; mailing price, 45 cents

THIS one-year course in physics has grown out of the experience of the authors in developing the work in physics at the School of Education of the University of Chicago, and in dealing with the physics instruction in affiliated high schools and academies.

The book is a simple, objective presentation of the subject as opposed to a formal and mathematical one. It is intended for the third-year high-school pupils and is therefore adapted in style and method of treatment to the needs of students between the ages of fifteen and eighteen. It especially emphasizes the historical and practical aspects of the subject and connects the study very intimately with facts of daily observation and experience.

The authors have made a careful distinction between the class of experiments which are essentially laboratory problems and those which belong more properly to the class room and the lecture table. The former are grouped into a Laboratory Manual which is designed for use in connection with the text. The two books are not, however, organically connected, each being complete in itself.

All the experiments included in the work have been carefully chosen with reference to their usefulness as effective class-room demonstrations.

GINN & COMPANY PUBLISHERS