QUALITATIV
CHEMICAL ANALYSIS

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A. A. NOYES
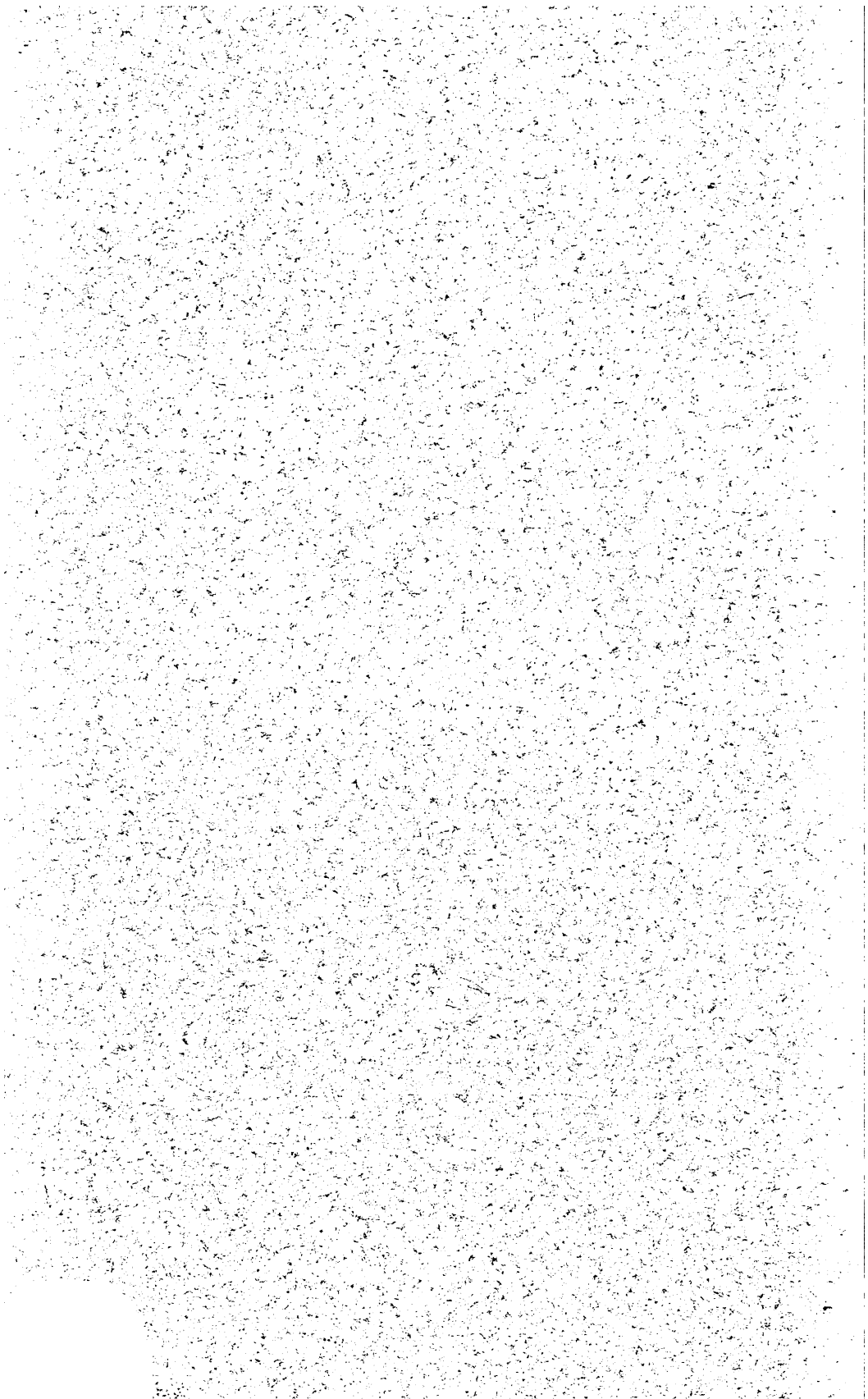
A COURSE OF INSTRUCTION

AND

SYSTEM OF PROCEDURE

IN

QUALITATIV

CHEMICAL ANALYSIS

BY

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PREFACE.

This text-book is an attempt, on the experimental side, to train the student of qualitativ. analysis in careful manipulation and exact methods of procedure, such as are commonly employed in quantitativ analysis. It is an attempt, on the theoretical side, to make clear to the student the reason for each operation and result, and to accustom him to apply to them the laws of chemical equilibrium and the principles relating to the ionization and complex formation of substances in solution. It is believed that in both these ways the educational value of the subject is greatly increased.

The book is divided into two main Parts, entitled The Course of Instruction and The System of Analysis. In presenting the system of analysis the plan adopted in the earlier editions of this book has been followed, namely, that of separating sharply the description of the operations from the discussion and explanation of them. The operations are described with as great definitness as possible in short paragraphs entitled "Procedures"; and each of these is followed by "Notes" in which are given the reasons for the operations, the precautions necessary and difficulties encountered in special cases, the chemical behavior of the different elements, the indications afforded of their presence, and the application of the theoretical principles to the reactions involved. The system of procedure has been thoroly revised as a result of the extended investigations made in the laboratory of this Institute during the past six years and described in volumes 29, 30, 31, and 34 of the Journal of the American Chemical Society. As a result of these investigations, in which the author has had the able cooperation of Professor W. C. Bray and Professor E. B. Spear, the process of analysis has been made much more reliable, so that now it is possible with careful manipulation to detect one milligram of any constituent in the presence of 500 milligrams of any other (except in a few combinations where the limit of detectability is two milligrams). At the same time the process has on the whole been considerably simplified. The larger size of the present edition is due, not to greater complexity of the process, but to the inclusion in the Procedures of the more explicit directions necessary to secure accuracy in the separations and reactions, to the insertion of confirmatory tests for most of the elements, to the development of a more systematic process for the detection of the acidic constituents, and to the elaboration of the notes and especially the inclusion in them of the theoretical explanations made possible by the recent development of our knowledge of solutions.

The Part entitled The Course of Instruction includes the directions for the laboratory work and a series of questions to be answered in connection with the laboratory exercises. The laboratory work from beginning to end is closely correlated with the systematic scheme of analysis. For experience has convinced the author that the plan followed in many text-books of requiring the student to study the separate reactions characteristic of the various elements before undertaking their systematic separation is highly unsatisfactory. However valuable the knowledge of the additional reactions may be, it is found in practis that the performance of such a large number of independent, disconnected experiments makes little impression on the student's mind and fails to awaken his interest in the subject. Qualitativ analysis affords an effectiv means of teaching a part of inorganic chemistry chiefly because it unites into a connected whole a great variety of isolated facts, and because the student sees a practical use of the information presented to him; but these advantages evidently do not apply to facts not directly related to the process of analysis.

The Questions on the Experiments are intended to aid in making sure that the student understands the work that he is doing in the laboratory and that he derives from the subject the mental training which it ought to afford. The questions are for the most part of such a character that, in order to answer them properly, the student not only must study the Notes on the Procedures, but must also giv to the questions some independent thought; the questions being in general of the nature of simple problems.

The best plan of conducting the course, when circumstances permit, is in the author's opinion as follows. The class, if large, is divided into sections of from 15 to 25 students. At the beginning of each laboratory exercise, which should be at least three hours long, or at the beginning of every second laboratory exercise, the instructor holds an informal conference with each section, at which the experiments to be next made are discussed in outline, and those made at the previous exercises are reviewed in detail. The conferences are carried on mainly by questioning the individual students and by encouraging them to ask questions as to matters which they do not understand. As preparation for each conference the student is expected to study the general plan of the analytical separations to be taken up as presented in the Tables preceding the description of the analysis of each group, and also to study the Notes on the Procedures which he has previously worked through and to answer the printed questions upon those Procedures. The best plan, when the laboratory time permits, is to require the student to read the notes at the time an experiment is being performed, and to write out in the laboratory the answers to the questions on that experiment before beginning the next one. The class is kept nearly together in the laboratory work by giving to the faster working students additional unknown solutions on each group, and by allowing those who are falling behind to omit some of the less important procedures.

Even when the time available for the subject of qualitativ analysis does not permit of so complete a course as that here presented, the student gets, in the

author's opinion, a better training by working through selected parts of an exact scheme of analysis carefully and thoroly than he does by covering the whole of an elementary scheme superficially. Portions of the system of analysis that may be well omitted in briefer courses are Procedures 63, 65, and 67–70, relating to the removal of phosphate and the separate detection of cobalt and nickel, and Procedures 4–8 and 119 relating to the treatment of substances insoluble in acids. In addition, the work on the acidic constituents may be limited to that referred to in the first two paragraphs of Procedure 100.

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PART I.

THE COURSE OF INSTRUCTION.

LABORATORY EXPERIMENTS.

DETECTION OF THE BASIC CONSTITUENTS.

Experiment 1.—*Separation of the Basic Constituents into Groups.*—In connection with this experiment refer to Table II (page 37). Measure out with the aid of a 10 cc. graduate 5 cc. portions of the test-solutions of $AgNO_3$, $Cu(NO_3)_2$, $Al(NO_3)_3$, $Zn(NO_3)_2$, $Ca(NO_3)_2$, and KNO_3. Mix the portions in a conical flask, add 5 cc. HNO_3 and 10 cc. NH_4Cl solution, and filter. Dilute the filtrate with water to a volume of 100 cc. Place it in a 200 cc. conical flask; insert a two-hole rubber stopper through which passes a tube leading to the bottom; and pass in a slow current of H_2S, until, upon shutting off the gas and shaking thoroly, the liquid smells strongly of it. Filter. Boil the filtrate till the H_2S is expelled, add to it 10 cc. NH_4OH, and note the result. Then add 3-5 cc. $(NH_4)_2S$. Shake the mixture and filter. Evaporate the filtrate to a volume of about 10 cc., filter, and to the cold solution add 30 cc. $(NH_4)_2CO_3$ reagent and 30 cc. alcohol, shake, and filter. Evaporate the filtrate to dryness in a small casserole, and ignite the residue by moving the disk to and fro in a gas flame till no more white fumes come off.

In this experiment and all subsequent ones observe carefully everything that happens, and record it clearly and neatly in the note-book, together with the equations expressing all the chemical changes that take place. Study carefully the Table and the Notes referred to in the directions; and then, before beginning the next experiment, write out in a small note-book devoted to the purpose answers to the "Questions" printed at the end of the "Laboratory Experiments". At the close of each exercise hand in both note-books to the instructor.

Notes.—1. The solutions of constituents to be tested for, here called the test-solutions, are all so made up as to contain 10 mg. (10 milligrams) of the constituent per cubic centimeter of solution. The mixture used in this experiment will, therefore, contain 50 mg. of each of the elements silver, copper, aluminum, zinc, calcium, and potassium. The student should acquire the habit of working with definit quantities of the constituents and of noting the

size of the precipitates which they yield. For a good qualitativ analysis should not only show the presence or absence of the various constituents, but should also furnish an estimate of the proportions in which they are present.

Test-solutions should not be used in place of reagents, nor reagents in place of test-solutions, since the concentrations are as a rule quite different. In regard to the concentrations of reagents, see Note 3, page 38, and Note 1, page 40.

2. In the note-book the operations should be indicated very briefly; but everything that happens should be recorded fully, tho concisely. Thus the report of the first experiment may be made in the following form:

Expt. 1.—Added HNO_3: no change observed.

Added NH_4Cl: white curdy ppt.
$$Ag^+NO_3^- + NH_4^+Cl^- = \underline{AgCl} + NH_4^+NO_3^-.$$
Passed in H_2S: large black flocculent ppt.
$$Cu^{++}(NO_3^-)_2 = \underline{CuS} + 2H^+NO_3^-.$$
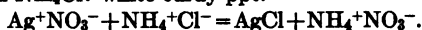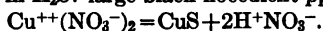
Solid substances involved in chemical reactions should be indicated by underlining their formulas. Largely ionized dissolved substances should be written with + and — signs attached to the formulas in such a way as to show the ions into which they dissociate. Slightly ionized dissolved substances should be distinguished by not attaching these signs to the formulas.

Experiment 2.—*Analysis of the Silver-Group.*—Mix a 15 cc. portion of the test-solution of $Pb(NO_3)_2$ with 5 cc. portions of the test-solutions of $AgNO_3$ and $Hg_2(NO_3)_2$, and with 5 cc. HNO_3, and treat the mixture by P. 11–15 (*i.e.*, by Procedures 11–15 of the System of Analysis described in Part II. See pages 38–40). Study Table III (page 38) before carrying out this experiment. At the time that the operations described in it are being executed read the Notes on P. 11–15.

Experiment 3.—*Precipitation by Hydrogen Sulfide.* To 10 cc. of the test-solution of $Hg(NO_3)_2$ add 5 cc. HNO_3, 10 cc. NH_4Cl solution, and 75 cc. water. Treat this solution by the first paragraph of P. 21. In passing the H_2S in this experiment shut off the gas after only a few bubbles have passed through, shake the mixture, and note the color of the precipitate. Then pass in more H_2S till the solution becomes saturated. Keep the precipitate in a moist condition for use in Expt. 6.—Read Notes 1, 3, and 4, P. 21.

To 10 cc. of the test-solution of $Bi(NO_3)_3$ add 5 cc. HNO_3, 10 cc. NH_4 Cl solution, and 75 cc. water; and, without filtering the mixture, pass H_2S into it till it becomes saturated.

To 10 cc. of the test-solution of H_3AsO_4 add 5 cc. HNO_3, 10 cc. NH_4Cl solution, and 75 cc. water. Treat this solution by the whole of P. 21.—Read Notes 2 and 5, P. 21.

Experiment 4.—*Effect of Acid on the Precipitation by Hydrogen Sulfide.*—Introduce into each of three test-tubes by means of a dropper

(see Note 2, P. 11) 2 drops of the test-solution of $Cd(NO_3)_2$. Add to the first tube 1 cc. HCl, to the second 3 cc. HCl, and to the third 9 cc. HCl. Then add to each solution enough water to make the volume about 20 cc., and pass a slow current of H_2S into it for about a minute.—Repeat the last test (with 9 cc. HCl), substituting $Cu(NO_3)_2$ for the $Cd(NO_3)_2$.—Read Note 6, P. 21.

Experiment 5.—*Effect of Oxidizing Substances on Hydrogen Sulfide.* —To 20 cc. of the test-solution of $Fe(NO_3)_3$ add 10 cc. NH_4Cl solution, 5 cc. HNO_3, and 65 cc. water, and pass in H_2S till the solution is saturated.—Read Notes 7 and 8, P. 21.

Experiment 6.—*Analysis of the Copper-Group: Behavior of Mercury.*—Treat the precipitate of HgS obtained in Expt. 3 by P. 31 and 32.—Read Notes 1–5. P. 31, and Notes 1–2, P. 32.

Experiment 7.—*Analysis of the Copper-Group: Behavior of Lead˙ and Copper.*—Mix 10 cc. portions of the test-solutions of $Pb(NO_3)_2$ and $Cu(NO_3)_2$, add 5 cc. HNO_3, and 75 cc. water, treat the mixtur e by P. 21, and treat the precipitate so obtained by P. 31, 33–35, 37, and 38.—Refer to Table IV (page 48), and read Note 1, P. 33; the Notes on P. 34, 35, and 37; and Notes 1–2, P. 38.

Experiment 8.—*Analysis of the Copper-Group: Behavior of Bismuth and Cadmium.*—Mix together 10 cc. portions of the test-solutions of $Bi(NO_3)_3$ and $Cd(NO_3)_2$. Add 5 cc. HNO_3, and treat the mixture by P. 31–38.—Refer to Table IV, and read Note 2, P. 33 and the Notes on P. 36 and 38.

Experiment 9.—*Analysis of an Unknown Solution for Elements of the Copper-Group.*—Ask the instructor for an unknown solution containing elements of the copper-group ("unknown *A*"), and analyze 10 cc. of it by P. 21 and P. 31–38, first adding 5 cc. HNO_3.

> *Note.*—Record the results of the analyses of unknown solutions in the same way as those of other experiments, except that the chemical equations need not be written. Sum up at the end, in the case of such analyses, the elements that are found to be present, giving also a rough estimate of the quantity of each per 10 cc. of solution. (Quantities less than 5 mg. may be reported as " small"; those from 5 to 50 mg., as "medium"; and those greater than 50 mg., as "large".)
>
> Keep all final tests in properly labelled test-tubes or flasks until the analysis has been completed and has been approved by the instructor.

Experiment 10.—*Separation of the Copper and Tin Groups.*—To a mixture of 10 cc. portions of the test-solutions of $Bi(NO_3)_3$ and of $SbCl_3$ add 5 cc. HNO_3 and 75 cc. water, and treat the mixture by P. 21, 22 and 23. In P. 22 use ammonium monosulfide and only one 10 cc. portion of it; and in P. 23 omit the filtration and washing of

the precipitate.—Refer to Table II (page 37); and read Note 1, P. 22 and Note 2, P. 23.

Experiment 11.—*Behaviors of Ammonium Monosulfide and Polysulfide on Acidification.*—Treat 5 cc. of ammonium monosulfide by P. 23 (omitting the filtration and washing of the precipitate).

Repeat the experiment with 5 cc. of ammonium polysulfide.

Repeat the experiment with a solution prepared by adding 4–5 drops of the test-solution of $Cu(NO_3)_2$ to 5 cc. of ammonium polysulfide, shaking, and filtering out the precipitate.

Read Notes 2–4, P. 22, and Notes 3–4, P. 23.

Experiment 12.—*Behavior of Ammonium Monosulfide and Ammonium Polysulfide towards Stannous Sulfide.*—To 10 cc. of the test-solution of $SnCl_2$ add 5 cc. HNO_3, 10 cc. NH_4Cl solution, and 75 cc. water; and treat the mixture by P. 21, 22, and 23, using in P. 22 10 cc. of ammonium monosulfide. Warm the residue undissolved by the ammonium monosulfide with 10 cc. of ammonium polysulfide, filter, and treat the filtrate by P. 41. Compare the two precipitates so obtained.—Read Notes 5–8, P. 22.

Experiment 13.—*Analysis of the Tin-Group.*—Mix together 10 cc. portions of the test-solutions of $AsCl_3$, $SbCl_3$, and $SnCl_4$; add 70 cc. water; and treat the mixture by P. 21. Filter with the aid of suction (see Note 1, P. 23), and suck the precipitate as dry as possible. Treat the precipitated sulfides by P. 41–46.—Refer to Table V (page 54), and read the Notes on P. 41–46.

Experiment 14.—*Analysis of an Unknown Solution for Elements of the Tin-Group.*—Ask for an unknown solution containing elements of the tin-group ("unknown *B*"), and analyze 10 cc. of it by P. 21 and P. 41–46.—In regard to recording the results, see the Note on Expt. 9.

Experiment 15.—*Analysis of an Unknown Solution for Elements of the Silver, Copper, and Tin Groups.*—Ask for an unknown solution containing elements of these groups ("unknown *C*"), and analyze 10 cc. of it by P. 11–46.

Experiment 16.—*Precipitation and Separation of the Aluminum and Iron Groups.*—Treat a mixture of 10 cc. portions of the test-solutions of $Al(NO_3)_3$ and of $Fe(NO_3)_3$ by P. 51–53.—Refer to Table II (page 37), and read Note 1, P. 51, and Notes 1–2, P. 52.

Experiment 17.—*Behavior of Elements of the Aluminum and Iron Groups towards Ammonium Hydroxide and Sulfide.*—To 5 cc. portions of the test-solutions of $Al(NO_3)_3$, $Cr(NO_3)_3$, $Fe(NO_3)_3$, $FeSO_4$, $Zn(NO_3)_2$, $Mn(NO_3)_2$, $Ni(NO_3)_2$, and $Co(NO_3)_2$ in separate test-tubes add 8–10

drops of NH$_4$OH, and note the result. Then add 2–3 cc. more NH$_4$OH. Filter out the Cr(OH)$_3$, precipitate and heat the filtrate to boiling. To the other tubes in which there is still a precipitate add 5 cc. NH$_4$Cl solution. Finally add 1–2 cc. (NH$_4$)$_2$S to each tube. Filter out the NiS precipitate, and boil the filtrate. Record the results of all these tests in a single table, so as to show at a glance how each element behaves upon the addition of each reagent.—Read Notes 2–5 and 8–10, P. 51.

Experiment 18.—*Behavior of Elements of the Aluminum and Iron Groups towards Sodium Hydroxide and Peroxide.*—To separate 5 cc. portions of the test-solutions named in Expt. 17, add 8–10 drops of NaOH, and note the result. Then add 2–3 cc. more, and again note the result. Finally to each of the mixtures add gradually 0.4–0.5 g. solid Na$_2$O$_2$, and heat it to boiling. Record all the results in a single table as in Expt. 17.—Read Notes 3–7, P. 52.

> *Note.*—Instead of weighing out solid substances, it is more convenient and usually sufficiently accurate to measure them in little horn-spoons which, when heaping full, hold 0.4–0.5 g. of the finely powdered solid compounds of sodium, potassium, and calcium that are used as reagents or as test substances in these experiments.

Experiment 19.—*Precipitation of Alkaline-Earth Elements by Ammonium Hydroxide in the Presence of Phosphate.*—Heat about 0.3 g. solid Ca$_3$(PO$_4$)$_2$ with 10 cc. water; then add 5 cc. HNO$_3$. To one-half of the solution add NH$_4$OH till the mixture after shaking smells of it and then 2–3 cc. more; filter out the precipitate; and add 1–2 cc. (NH$_4$)$_2$CO$_3$ reagent to the filtrate. To the other half add 5 cc. of the test-solution of Fe(NO$_3$)$_3$; then add NH$_4$OH, filter, and add (NH$_4$)$_2$CO$_3$, as before.—Read Notes 6–7, P. 51.

Experiment 20.—*Analysis of the Aluminum-Group.*—Treat a mixture of 10 cc. of the test-solutions of Al(NO$_3$)$_3$, Cr(NO$_3$)$_3$, and Zn(NO$_3$)$_2$ by the second paragraph of P. 52 and by P. 53–57. Treat one-half of the AlO$_3$H$_3$ precipitate obtained in P. 53 by the first paragraph of P. 54, and the other half by the second paragraph of P. 54.—Refer to Table VI (page 64), and read the Notes on P. 53–57.

Experiment 21.—*Analysis of the Iron-Group: Behavior of Manganese and Iron.*—Treat a mixture of 10 cc. portions of the test-solutions of Mn(NO$_3$)$_2$, Fe(NO$_3$)$_3$, Zn(NO$_3$)$_2$, Co(NO$_3$)$_2$, and Ni(NO$_3$) by the second paragraph of P. 52; and treat the precipitate thereby obtained by P. 61, 62, and 64. Reserve the ammoniacal filtrate obtained in P. 64 for use in Expt. 23.—Refer to the first part of Table VII (page 68), and read the Notes on P. 61, 62 and 64.

Experiment 22.—*Analysis of the Iron-Group: Behavior of Zinc, Nickel, and Cobalt.*—Treat the ammoniacal filtrate obtained in Expt. 21 by P. 66–70.—Refer to the last part of Table VII, and read the Notes on P. 66–70.

Experiment 23.—*Modification of the Analysis of the Iron-Group in the Presence of Phosphate for the Purpose of Detecting Alkaline-Earth Elements.*—Mix together 10 cc. portions of the test-solutions of $Fe(NO_3)_3$, of $Co(NO_3)_2$, and of $Ca_3(PO_4)_2$ in HNO_3. Treat one-tenth of this solution by P. 63, and treat the remainder of it by P. 65 and 66. To the filtrate obtained in P. 66 add 2–3 cc. $(NH_4)_2CO_3$ reagent. —Read the Notes on P. 65.

Experiment 24.—*Analysis of Unknown Solutions for Elements of the Aluminum and Iron Groups.*—Ask the instructor for two unknown solutions for this purpose ("unknowns D and E"), and treat 10 cc. of each solution by P. 51–70.

Experiment 25.—*Precipitation of the Alkaline-Earth Group.*—To 2 cc. of the test-solution of $Mg(NO_3)_2$ add 10 cc. water and 1–2 cc. $(NH_4)_2CO_3$ reagent and shake the mixture for about a minute. Then add (in accordance with P. 81) 15 cc. $(NH_4)_2CO_3$ reagent and 15 cc. 95 per cent alcohol, and shake for a minute more.

To 2 cc. of the test-solution of $Ca(NO_3)_2$ add 10 cc. water and 1–2 cc. $(NH_4)_2CO_3$ reagent, shake, and after 2–3 minutes filter out the precipitate. To the filtrate add 15 cc. $(NH_4)_2CO_3$ reagent and 15 cc. 95 per cent alcohol.—Read the Notes on P. 81.

Experiment 26.—*Analysis of the Alkaline-Earth Group.*—Mix together in a small flask 3 cc. portions of the test-solutions of $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$. Add to the mixture 30 cc. $(NH_4)_2CO_3$ reagent and 30 cc. 95 per cent alcohol, and shake it for about 5 minutes. Filter out the precipitate and treat it by P. 82–88. —Refer to Table VIII (page 75), and read the Notes on P. 82–88.

Experiment 27.—*Analysis of an Unknown Solution for Elements of the Alkaline-Earth Group.*—Ask the instructor for an unknown solution for this purpose ("unknown F"), and analyze 10 cc. of it by P. 81–88.

Experiment 28.—*Analysis of the Alkali-Group.*—Mix together 10 cc. portions of the test-solutions of KNO_3 and $NaNO_3$, add 10 cc. NH_4Cl solution and 10 cc. $(NH_4)_2CO_3$ reagent, and treat the mixture by P. 91–93.—Refer to Table IX (page 80), and read the Notes on P. 91–93.

Detection of Ammonium.—Treat 0.2–0.3 g. solid NH_4Cl by P. 96.— Read the Notes on P. 96.

Experiment 29.—*Determination of the State of Oxidation in which Iron is Present.*—To separate 5 cc. portions of the test-solution of $Fe(NO_3)_3$ add 1–2 cc. of solutions of KSCN, of $K_4Fe(CN)_6$, and of $K_3Fe(CN)_6$.

To 15 cc. of the test-solution of $FeSO_4$ in a test-tube add 1–2 cc. of H_2SO_4 and 0.5 g. iron filings, in order to reduce any ferric salt that may be present. After 5–10 minutes decant the solution from the iron, and add to separate 3–4 cc. portions of it 1–2 cc. of solutions of KSCN, $K_4Fe(CN)_6$, and $K_3Fe(CN)_6$.—Read P. 97 and the Notes on it.

Experiment 30.—*Analysis of Unknown Solutions for All the Basic Constituents.*—Ask the instructor for two unknown solutions for this purpose ("unknowns *G* and *H*"), and analyze 10 cc. of each of them by P. 11–93.

> *Note.*—In complete analyses of this kind where a number of different precipitates and filtrates are successivly obtained, any of these that are set aside, even temporarily, should be distinctly labelled, in order to avoid mistakes. A convenient method of doing this is to mark on the label simply the Procedure by which the precipitate or filtrate is next to be treated; thus the H_2S precipitate would be marked P. 22, and the filtrate from it P. 51. The final tests for any element may be marked Test for Pb, Test for Al, etc.

DETECTION OF THE ACIDIC CONSTITUENTS.

Experiment 31.—*Detection of the Constituents Yielding Readily Volatil Products.*—Try the tests described in the first paragraph of P. 100, substituting for "0.3 g. of the finely powdered substance" in successiv experiments 3 drops of the test-solutions of Na_2CO_3, of Na_2S, of Na_2SO_3, and of KNO_2, using with these four substances respectivly suspended drops of the solutions of $Ba(OH)_2$, $PbAc_2$, $Hg_2(NO_3)_2$, and KI and starch, respectivly.

Experiment 32.—*Distillation with Phosphoric Acid and Detection of Sulfate.*—Mix 3 cc. portions of the test-solutions of Na_2CO_3, Na_2SO_3, KCl, and K_2SO_4, and treat this mixture (in place of "2 g. of the finely powdered substance") by P. 101. Cork the flask containing the first distillate (after acidifying it with HAc), and keep it for use in Expt. 33. Add to the second distillate $AgNO_3$ solution. Treat the third distillate by P. 112.—Refer to Table X (page 87), and read the Notes on P. 101 and 112.

Experiment 33.—*Detection of Carbonate and Sulfite or Thiosulfate.*—Treat the whole of the first distillate obtained in Expt. 32 by the first paragraph of P. 102.—In the case of each one of Expts. 33–36 refer to the part of Table XI (page 90) that relates to that experiment, and read the Notes on the Procedure involved in it.

Experiment 34.—*Detection of Iodin-Liberating Constituents.*—Treat 10 cc. of the test-solution of NaOCl (which contains also an equivalent quantity of NaCl) by the first paragraph of P. 101. Treat the whole distillate so obtained by the first, second, and fourth paragraphs of P. 103. Test the aqueous layer finally obtained by adding to it 2–3 cc. HNO_3 and 2–3 cc. $AgNO_3$ solution (instead of by P. 110).

Treat 3 cc. of the test-solution of KNO_2 by the first two paragraphs of P. 103.

Experiment 35.—*Confirmatory Test for Nitrite.*—Treat 1 cc. of the test-solution of KNO_2 by P. 104.

Experiment 36.—*Detection of Sulfide.*—To 3 cc. of the test-solution of Na_2S add 3 cc. HAc and 2–3 cc. $Cd(NO_3)_2$ solution.

Experiment 37.—*Detection of Cyanide.*—Treat 3 cc. of the test, solution of KCN by P. 106.—Refer to Table XI, and read Notes 1–3- P. 106.

Experiment 38.—*Analysis of an Unknown Solution for Acidic Constituents Passing into the First Distillate.*—Ask the instructor for an unknown solution for this purpose ("unknown *I*"), and treat 10 cc. of it by the first paragraph of P. 101. Treat the distillate thereby obtained by P. 102–106.

Experiment 39.—*Constituents Precipitable by Silver Nitrate.*— Treat in separate test-tubes 3 cc. of the test-solutions of KCN, KI, and Na_2S by the first paragraph of P. 107.—Read the Notes on P. 107.

Experiment 40.—*Detection of Thiocyanate.*—To 3 cc. of the test-solution of KSCN add 2–3 drops of $FeCl_3$ solution and 2–3 drops HCl.—Read the Notes on P. 108.

Experiment 41.—*Detection of Free Halogen and of the Halides.*— Mix together 3 cc. portions of the test-solutions of KCl, KBr, KI, and I_2. Treat the mixture by P. 109 and 110, omitting the treatment of the chloroform-extract referred to in the last paragraph of P. 109. —Refer to the middle part of Table XII (page 96), and read the Notes on P. 109 and 110.

Experiment 42.—*Detection of Nitrate.*—Treat 3 cc. of the test-solution of KNO_3 by P. 111.—Read the Notes on P. 111.

Experiment 43.—*Analysis of an Unknown Solution for Acidic Constituents Passing into the Second and Third Distillates.*—Ask the instructor for an unknown solution for this purpose ("unknown *J*"), and treat 10 cc. of it by P. 101. Treat the second and third distillates by P. 107–112.—Refer to Table XII (page 96).

Experiment 44.—*Detection of Borate.*—Treat 0.2–0.3 g. of solid borax ($Na_2B_4O_7.10H_2O$) by P. 113.—In connection with each one of Expts. 44–49 refer to Table XIII (page 101), and read the Notes on the Procedure involved in the experiment.

Experiment 45.—*Detection of Fluoride.*—Treat 0.2–0.3 g. of solid CaF_2 by P. 114.

Experiment 46.—*Detection of Phosphate.*—Treat 0.2–0.3 g. of solid $Ca_3(PO_4)_2$ by P. 115.

Experiment 47.—*Detection of Hypochlorite.*—Treat 3 cc. of the test-solution of NaOCl by P. 116.

Experiment 48.—*Detection of Chlorate.*—Mix together 3 cc. portions of the test-solutions of KCl and $KClO_3$, add 50 cc. water and 10 cc. HNO_3, and treat the mixture by the last half of P. 117, beginning at "Add $AgNO_3$. . . ."

Experiment 49.—*Detection of Sulfite and Thiosulfate.*—Mix together 3 cc. portions of the test-solutions of Na_2SO_3 and $Na_2S_2O_3$, and treat the mixture (instead of "0.5 g. of the finely powdered original substance") by P. 118.

PREPARATION OF THE SOLUTION AND COMPLETE ANALYSES IN THE CASE OF UNKNOWN SOLID SUBSTANCES.

Experiment 50.—*Substances Soluble in Water or Dilute Acid.*—Ask the instructor for two such unknown substances ("unknowns 1 and 2"), and treat portions of each of them by P. 1, by P. 2 followed by P. 11–93, by P. 96, and by P. 101–118.—Read the Notes on P. 1 and 2.—Record and report the results in the note-book as directed in the Note on Expts. 9 and 30. In the case of a solid substance report not only the constituents and the proportions of them present, but state the compound or compounds of which the substance seems to be mainly composed.

> *Note.*—In analyzing unknown solids the quantity taken for the analysis should be weighed (within 0.1 g.) on a rough balance, not guessed at nor estimated in the way suggested in the Note to Expt. 18.

Experiment 51.—*Non-Metallic Substances Requiring Treatment with Concentrated Acids.*—Ask the instructor for three such substances ("unknowns 3, 4, and 5"), and treat portions of each of them by P. 1, by P. 2–3 (or 2–4, if necessary,) followed by P. 11–93 (or 21–93), and by P. 101–118. If there is any undissolved residue (of silica or silicate) at the end of P. 4, disregard it in these analyses.—Refer to Table I (page 25), and read Notes 1–4, P. 3, and Notes 1–2, P. 4.

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Experiment 52.—*Alloys Dissolved by Concentrated Acids.*—Ask the instructor for two such alloys ("unknowns 6 and 7"), and treat 0.5 g. of each by P. 3–4 and P. 11–70 (or P. 21–70).—Read Notes 5–9, P. 3, and Note 3, P. 4.

Experiment 53.—*Mineral Substances or Metallurgical Products Not Completely Dissolved by Concentrated Nitric and Hydrochloric Acids.*— Ask the instructor for such a substance ("unknown 8"). Treat 1 g. of it by P. 2–4. Treat the solution obtained in P. 4 by P. 21–93, and the residue obtained in P. 4 by P. 7, followed by P. 21–88. Reserve, as directed, one-half of the aqueous extract of the fused mass obtained in P. 7, and test it for acidic constituents as described in the last four paragraphs of P. 119.—Read the Notes on P. 7 and P. 119. Treat another 1 g. portion of the substance by P. 101, and test the distillates for carbonate, sulfide, chloride, and sulfate.

Ask the instructor for two more such substances ("unknowns 9 and 10"). Treat 1 g. of each of them by P. 2–6, followed by P. 11–93. —Refer to Table I (page 23), and read the Notes on P. 5 and 16.—Treat another 1 g. portion of each of the substances by P. 101, and test the distillates for carbonate, sulfide, chloride, and sulfate. Treat a third 1 g. portion of each of them by P. 119.

Experiment 54.—*Substances Containing Organic Matter.*—Ask the instructor for such a substance ("unknown 11"), and treat portions of it by P. 1, by P. 8 followed by P. 11–93, and by P. 101 followed by P. 102–118.—Read the Notes on P. 8.

QUESTIONS ON THE EXPERIMENTS.

Experiment 1.—1. In precipitating the silver-group in an actual analysis could the NH_4Cl be replaced by NaCl? by HCl? (*In the case of all questions which can be answered by "yes" or "no," giv the reasons for the answer.*)

2. If the NH_4Cl were not added, what would happen to the silver in the subsequent parts of the experiment? (*When the answer to a question is not known and it can be learned by a simple experiment, the student should try the experiment.*)

3. Of the six basic constituents present in the mixture why is silver the only one that is precipitated by NH_4Cl?

4. If enough H_2S were not used to precipitate all the copper, how would it behave on the subsequent addition of NH_4OH? of $(NH_4)_2S$?

5. What is the first reaction that takes place when NH_4OH is added to the filtrate from the H_2S precipitate?

6. If the H_2S had not been expelled from the solution before adding the NH_4OH, would there be any difference in the precipitate produced by the NH_4OH?

7. What would happen to the $(NH_4)_2S$ if it were added directly to the filtrate from the H_2S precipitate, without first adding NH_4OH?

8. What happens to the $(NH_4)_2S$ when the filtrate from the $(NH_4)_2S$ precipitate is evaporated? to the $(NH_4)_2CO_3$ when the filtrate containing it is evaporated?

9. What are the thick white fumes which come off when the dry residue is ignited?

10. If all the basic constituents had been present in the original mixture used for this experiment, what ones would have been precipitated by (*a*) NH_4Cl, (*b*) H_2S, (*c*) NH_4OH and $(NH_4)_2S$, (*d*) $(NH_4)_2CO_3$? (*e*) What ones would have been left with the potassium in the filtrate from the $(NH_4)_2CO_3$ precipitate?

Experiment 2.—1. What would be meant by the statement that a certain quantity of lead nitrate is equivalent to a certain other quantity of ammonium chloride?

2. In making up a 1-normal solution of NH_4Cl, how many grams of the salt should be weighed out, and how much water should be added to it? (For the atomic-weight values needed in answering this and other questions see the table near the end of the book.)

3. In making up a 6-normal solution of H_2SO_4 how many cubic centimeters of 96% sulfuric acid (s. g., 1.84) should be used, and how much water should be added to it?

4. Approximately how many cubic centimeters of the NH_4Cl solution would be required to precipitate 500 mg. of silver? (Calculate first the number of equivalents corresponding to 500 mg. Ag.—Since 1 g. of the unknown substance is ordinarily taken for the analysis for basic constituents, 500 mg. is as large a quantity of any element as is likely to be present.)

5. Why is a considerable excess of NH_4Cl added? (The word *excess* signifies the quantity added beyond the equivalent quantity theoretically required to produce the reaction in question.)

6. The solubility of $PbCl_2$ at 20 in water is 9.8 g. per liter and in 0.2-normal NH_4Cl solution is 2.6 g. per liter. Explain by the solubility-product principle why the NH_4Cl diminishes the solubility. (This question may be answered by shortening the complete explanation given in Note 8, P. 11, as follows: "In any dilute sol'n satur. with $PbCl_2$, $(Pb^{++}) \times (Cl^-)^2 = const.$ NH_4Cl added to such a sol'n causes, owing to its ionization into NH_4^+ and Cl^-, an increase in (Cl^-), and therefore raises $(Pb^{++}) \times (Cl^-)^2$ above the saturation value, so that $PbCl_2$ must ppt." (*All*

other questions as to the effect of one substance on the solubility of another substance should be answered in a similar way. Always consider the effect which the added substance may have on the concentration of each of the ions of the salt with which the solution is saturated, and state the reason for any such effect.)

7. From the preceding data calculate how many milligrams of lead would have to be present in 40 cc. water at 20°, in order that any precipitation of $PbCl_2$ may result on adding to it 10 cc. NH_4Cl solution.

8. The solubility of $PbCl_2$ in boiling water is 32 g. per liter. Calculate how much boiling water would be required to dissolve 500 mg. of lead in the form of $PbCl_2$.

9. The solubility of AgCl at 100° is 0.022 g. per liter. Calculate how many milligrams of silver might be lost if the chloride precipitate were washed with 100 cc. boiling water.

10. In testing for lead in P. 13, explain why the addition of H_2SO_4 to the solution and to the wash-water diminishes the solubility of the precipitate, and thus increases the delicacy of the test.

11. What other elements besides lead might be precipitated by adding H_2SO_4 to a solution in which they were present?

12. Since these other elements are precipitable by H_2SO_4, why does the formation of a precipitate in P. 13 show the presence of lead?

13. Would the validity of the conclusion that it is present be affected if the group-precipitate produced by HCl was not washed?

14. Explain by the solubility-product principle why the fact that $PbAc_2$ is a slightly ionized substance should cause $PbSO_4$ to dissolve much more readily in NH_4Ac solution than in water. (Answer in accordance with the Note on Question 6.)

15. Would you expect $PbCrO_4$ also to be more soluble in NH_4Ac solution than in water? Why or why not? if so, why does $PbCrO_4$ precipitate from the same NH_4Ac solution that dissolves $PbSO_4$?

16. Arrange all the compounds of lead thus far met with in the order in which their solubility in water decreases.

17. Explain by the solubility-product principle why the formation of the complex salt $Ag(NH_3)_2^+Cl^-$ causes AgCl to be much more soluble in NH_4OH solution than in water.

18. Formulate the mass-action expression for the equilibrium between the complex cation $Ag(NH_3)_2^+$ and its constituents. Show by reference to this expression and the solubility-product principle why the addition of HNO_3 causes AgCl to be precipitated out of its solution in NH_4OH.

Experiments 3 and 4.*—1. In precipitating with H_2S in P. 21 what is the reason for adding 5 cc. HNO_3 and diluting the solution to 100 cc.? Why not use less acid and thus avoid all risk of failing to precipitate the elements of the copper and tin groups?

2. In passing in H_2S, at what stage in the process does the solution after shaking begin to smell of the gas?

3. What principle determins how the quantity of H_2S dissolved by a given quantity of water varies with the pressure? How does it vary with the temperature?

4. Why would a larger quantity of an element have to be present in order to giv a precipitate if in P. 21 the solution were treated with H_2S in an open beaker, instead of in the closed flask?

5. Giv two reasons why a larger quantity of an element would have to be present to giv a precipitate if the solution were saturated with H_2S at 80°, instead of at 20°.

*Questions on two or more experiments should be answered after the last of the experiments is completed.

6†. Assuming that the solubility (in formula-weights per liter) of CdS in water is ten times as great as that of CuS, calculate by the principles discussed in Note 6, P. 21, the ratio of the hydrogen-ion concentrations at which the precipitation of the copper and cadmium will barely take place when the concentration of each of them has any definit value (for example, 0.0001 formula-weights per liter).

7. By what reaction is the HNO_3 destroyed when the arsenic solution to which HCl has been added is evaporated to dryness? Could HCl be destroyed in the same way by evaporating a solution of chloride with HNO_3?

8. If the HNO_3 were not so destroyed, what reaction would take place between it and the H_2S when the latter is passed into the hot, strongly acid solution? Write the equation expressing it.

Experiment 5.—1. What substances besides ferric salts might be present which would cause precipitation of sulfur in P. 21?

Experiment 6.—1. Describe a qualitativ experiment by which one could determin whether HgS dissolves to an appreciable extent when treated with hot dilute HNO_3 in the way directed in P. 31.

2. Explain by the solubility-product principle the fact that CuS, which is only slightly soluble in hot dilute HCl, dissolves readily in hot dilute HNO_3 of the same concentration.

3. Explain the fact that HgS, unlike CuS, does not dissolve even in hot dilute HNO_3.

4. Why is a black residue left undissolved by HNO_3 not sufficient evidence of the presence of mercury?

5. Suggest a reason why in the confirmatory test for mercury the addition of HCl with the $SnCl_2$ tends to prevent the immediate reduction of the Hg_2Cl_2 to Hg.

Experiment 7.—1. Why does the evaporation with H_2SO_4 convert the salts present into sulfates? Could sulfates be converted into nitrates by evaporating with a large excess of HNO_3?

2. Explain with reference to the solubility-product principle why $PbSO_4$ is much more soluble in dilute HNO_3 than in water. (H_2SO_4 in dilute solution is dissociated almost completely into H^+ and HSO_4^-; but the latter ion is only to a moderate extent dissociated into H^+ and SO_4^-).

3. What effect, as compared with that of HNO_3, would HCl have on the solubility of $PbSO_4$? What effect would KNO_3 have? Giv reasons. (K_2SO_4 in dilute solution, like other unibivalent salts, but unlike H_2SO_4, is almost completely dissociated into the simple ions, K^+ and SO_4^-, with formation of only a small proportion of the intermediate ion, KSO_4^-.)

4. Describe a qualitativ experiment which would determin whether PbS is more or less soluble in water than $PbSO_4$.

5. To what substance is the deep blue color of the ammoniacal copper solution due?

6†. Explain with the aid of the mass-action expressions involved why $Cu(OH)_2$, a substance very slightly soluble in water, is not precipitated by the NH_4OH. Show that the presence of the $(NH_4)_2SO_4$ in the solution must diminish the tendency of it to precipitate.

† The answer to any question to which a dagger is attached may be studied outside of the Laboratory, and written in the note book at the next exercise.

7. If the lead were not removed by the addition of H_2SO_4, would it be precipitated as $Pb(OH)_2$ on the addition of NH_4OH? What knowledge in regard to lead compounds would enable one to predict whether or not this precipitation would take place?

8. If $K_4Fe(CN)_6$ be added in P. 37 to the ammoniacal solution (without neutralizing it with HAc), no precipitate is produced unless a fairly large quantity of copper is present. Explain this fact.

9. What external evidence is there that the complex copper-ammonia ion is completely decomposed when KCN is added to the solution?

10. Explain why Cu_2S, a very slightly soluble sulfide, does not precipitate when H_2S is passed into the cyanide solution.

Experiment 8.—1. Explain by the solubility-product principle why HNO_3 increases the solubility of BiOCl, and why HCl increases it still more.

2. If in an actual analysis a precipitate of BiOCl formed on diluting the solution before passing in H_2S in P. 21 and that precipitate were filtered off, would a test for bismuth be obtained in P. 35 and 36? if it were not filtered off, would any change occur in it on passing in H_2S?

3. If lead were present and had not been completely precipitated by H_2SO_4 in P. 33, how would it behave in P. 35 and 36?

4. Write the equations expressing the formation of Na_2SnO_2 from $SnCl_2$ and NaOH; also that expressing the spontaneous decomposition of Na_2SnO_2 into tin and Na_2SnO_3.

5. Lead hydroxide, like $Sn(OH)_2$, is an amphoteric substance. What is meant by this statement? What experiments might be made to determin whether it is true?

6. Show from the solubility-product expressions that, if $Cd_2Fe(CN)_6$ is much more soluble than $Cu_2Fe(CN)_6$, the former can not be precipitated till enough $K_4Fe(CN)_6$ has been added to precipitate practically all the copper.

7. As shown in Expt. 4, CdS is a much more soluble sulfide than CuS. Why is CdS precipitated by H_2S from the KCN solution, while Cu_2S is not?

8. Silver forms a complex cyanide $K^+Ag(CN)_2^-$ analogous to $K^+Cu(CN)_2^-$, and Ag_2S is not precipitated from its solution by H_2S. Zinc and nickel form complex cyanides, $K^+_2Zn(CN)_4^-$ and $K^+_2Ni(CN)_4^-$, analogous to $K_2Cd(CN)_4$, and H_2S produces a precipitate in their solutions. What general conclusion would seem to be justified by these facts as to the stability of complex cyanides?

9. Describe in the form of a Procedure which might be substituted for P. 38 another method of separating cadmium and copper based on the results of Expt. 4.

10. What experiments would it be best to try in order to determin whether the new procedure described in the answer to Question 9 works satisfactorily?

Experiments 10–12.—1. Write chemical equations expressing the two stages of the hydrolysis of $(NH_4)_2S$. Explain by the ionic theory and the mass-action law why this hydrolysis takes place, taking into account the fact that water is ionized to a slight extent into H^+ and OH^-.

2. Why does not Bi_2S_3 dissolve in $(NH_4)_2S$, just as Sb_2S_3 does?

3. Why does not SnS dissolve in ammonium monosulfide as well as in ammonium polysulfide?

4. Make a table showing the solubility of each of the sulfides of the copper and tin groups in both ammonium monosulfide and ammonium polysulfide. Indicate in each case whether the sulfide is readily soluble, slightly soluble, or practically insoluble.

5. Why not use in all cases ammonium polysulfide, since this readily dissolves all the tin-group sulfides? Why is the precipitate first treated with a small quantity of it, even tho this makes necessary a second treatment?

6. Why does the addition of HCl to a solution of $(NH_4)_2SnS_3$ cause the precipitation of SnS_2?

7. Why does not the tendency of copper to form the complex copper-ammonia ion cause CuS to dissolve in NH_4OH?

Experiment 13.—1. In treating the sulfides with concentrated HCl why would much more of the As_2S_5 dissolve if the solution were boiled than if it were heated to 100° without boiling?

2. Why does the addition of $KClO_3$ cause the As_2S_5 to dissolve even in the more dilute HCl?

3. What does the fact that H_3AsO_4 does not combine with HCl forming $AsCl_5$ show in regard to the ionization of H_3AsO_4? Is it an amphoteric substance?

4. What is the expression for the solubility-product in the case of $MgNH_4AsO_4$? Why does the hydrolysis of this salt increase its solubility? Why is that hydrolysis decreased by an excess of NH_4OH? How is the hydrolysis affected by the presence of NH_4Cl? Would NH_4Cl affect the solubility in any other way?

5. What is a saturated solution? a supersaturated one? By what treatments can a precipitate be made to separate from a supersaturated solution?

6. Why does $MgNH_4AsO_4$ dissolve readily in HCl?

7. What difference in the ionization causes the behavior of arsenic acid towards H_2S to be so different from that of other elements of the copper and tin groups?

8. What determins whether one metal will be precipitated from its solution by another? Could one predict by this principle that zinc would precipitate antimony from the knowledge that zinc precipitates tin and tin precipitates antimony?

9. Explain why antimony precipitates on the platinum rather than on the tin.

10. How would the result be different if the tin did not touch the platinum?

11. Why does the tin dissolve in HCl more readily when it is in contact with the platinum?

12. In the confirmatory test for tin, why is lead used instead of zinc?

13. If zinc were used, how would the procedure have to be modified?

14. In the confirmatory test for tin how does the precipitation of a mercury compound show the presence of tin?

Experiment 16.—1. In an actual analysis how many cubic centimeters of NH_4OH would be required to neutralize the 5 cc. HNO_3 that are added before precipitating with H_2S?

2. How much more NH_4OH would be needed to neutralize the solution if 500 mg. Cu had been present in the form of $Cu(NO_3)_2$ in the solution precipitated by H_2S?

3. How does testing the vapors above the solution with $PbAc_2$-paper show that an excess of $(NH_4)_2S$, a non-volatil salt, has been added?

4. If in an actual analysis the mixture containing NH_4OH and $(NH_4)_2S$ were allowed to absorb CO_2 from the air before filtering, what difference would it make?

5. Why is the $(NH_4)_2S$ precipitate treated first with cold HCl? Why is HNO_3 subsequently added?

Experiments 17 and 18.—1. Which elements are soluble, *a*, in excess of NH_4OH (in the presence of NH_4Cl), but not in excess of NaOH; *b*, in excess of NaOH, but

not of NH_4OH (in presence of NH_4Cl); *c*, in excess both of NH_4OH and of $NaOH$; *d*, neither in excess of $NaOH$ nor of NH_4OH (in presence of NH_4Cl)?

2†. What are the explanations of the four typical cases *a*, *b*, *c*, *d*, referred to in the preceding question?

3. Could the hydroxide of an element which does not form a complex ammonia cation be soluble in NH_4OH and not in $NaOH$? Could an amphoteric hydroxide be readily soluble in $NaOH$ and entirely insoluble in NH_4OH?

4†. Show by formulating and combining the two mass-action equations involved that the quantity of aluminum dissolved (as AlO_2^-) in the presence of a base is proportional to the OH^- concentration in the solution.

5. Name all the elements that form ammonia complexes in all the groups thus far considered. What can be said as to the position of these elements in the periodic system? (Refer to a text-book of Inorganic Chemistry.)

6. If in an actual analysis no precipitate is obtained on the addition of NH_4OH, what conclusion may be drawn?

7. Which of the hydroxides precipitated by $NaOH$ undergo change on the addition of Na_2O_2, and into what compound is each of these hydroxides converted?

8. What substances are produced by the action of Na_2O_2 on water?

Experiment 19.—1. What does Expt. 19 show in regard to the behavior of the alkaline-earth elements in an actual analysis?

2. What must be the explanation of the fact that the phosphate combines with the iron rather than the calcium when both these elements are present?

3. If phosphate is known to be present, is it necessary to test for alkaline-earth elements in the filtrate from the $(NH_4)_2S$ precipitate?

4. If the original substance were soluble in water, would it be necessary to test for these elements in the $(NH_4)_2S$ precipitate?

5. If $CaCO_3$ were substituted for $Ca_3(PO_4)_2$ in the first part of Expt. 19, would the result have been the same? Would it have been the same if the original substance in an actual analysis had been $CaCO_3$ and the solution had been previously treated by P. 21?

6. If a solution of $Ca_3(PO_4)_2$ in HCl were treated by the second paragraph of P. 52, what would happen on the addition of each reagent? What would happen, if a large proportion of $FeCl_3$ were also present in the phosphate solution. (See Notes 7 and 8, P. 52.)

Experiment 20.—1. Since $AlCl_3$ is readily soluble in water, what precautions must be observed in order that the confirmatory test for aluminum may be delicate?

2. Giv two or three reasons why the dropping of H_2SO_4 into commercial HCl causes HCl gas to be evolved.

3. By what reagent other than $BaCl_2$ could the chromate be precipitated? What disadvantage would there be in the use of this reagent?

4. How can sulfate be present in the solution to which $BaCl_2$ is added?

5. If, without adding $BaCl_2$, H_2S were passed into the HAc solution, what chemical change would the chromate undergo? Write the equation expressing it.

6. What happens to nitrates, such as $Zn(NO_3)_2$ or $Co(NO_3)_2$, when they are ignited, as in the confirmatory test for zinc?

Experiment 21.—1. What are the oxides of manganese corresponding to its three stages of oxidation occurring in P. 61 and 62? What is the valence of manganese in each of these oxides? How do they differ with respect to the formation of salts with acids and with bases?

2. Write the equation expressing the reaction in HNO_3 solution between MnO_2 and bismuth peroxide, assuming the latter to be BiO_2.

3. If a permanganate were present in the original substance, what reaction would take place between it and H_2S in P. 21? Write the equation expressing it. What change in color would take place?

4. Why is a considerable excess of NH_4OH added in P. 64?

5. If FeS were treated by P. 31–38, how would it behave with each of the reagents?

Experiment 22.—1. Why is it necessary to test for zinc in the analysis of the iron-group?

2. Does the fact that the precipitated NiS and CoS do not dissolve in dilute HCl seem inconsistent with the behavior of nickel and cobalt in any earlier stage of the analysis? Suggest an explanation of the anomaly.

3. Why may zinc be precipitated by NaOH and Na_2O_2 in the first treatment in P. 52, and yet not be precipitated by them in the second treatment in P. 67?

4. When the original Na_2O_2 precipitate is so small that it need not be tested for zinc, how may P. 66–68 be simplified?

5. When the H_2S precipitate obtained in P. 66 is small, how may P. 67–68 be simplified?

6. Giv the steps in the chemical process by which the precipitate of potassium cobaltinitrite may be considered to be formed.

7. Does the NO_2^- as well as the K^+ coming from the excess of KNO_2 diminish the solubility of the precipitate? What else, from a mass-action standpoint, might it be expected to do?

8. Giv the steps in the chemical process by which in P. 70 potassium cobalti-cyanide may be considered to be formed.

9. What effect does the NaOBr have on this compound?

10. Describe the changes that are involved in the precipitation of $Ni(OH)_3$ in P. 70.

11. What general difference in the properties of the two elements causes the different behavior of nickel and cobalt in P. 69 and 70?

12. In the preparation of the NaOBr reagent, what is the chemical equation involved? What chemical reaction takes place in the NaOBr reagent on standing?

13. What reactions take place between NaOBr, KI, and starch, which serve to show when an excess of NaOBr is present?

14. If NiS were treated by P. 23–30, how would it behave with each of the reagents?

Experiment 23.—1. Why must the HNO_3 be removed before testing for iron with KSCN?

2. Why does the NH_4Ac solution become red only when the quantity of iron is more than equivalent to the quantity of phosphate present?

3. What is meant by a basic salt? What are two possible simple formulas for basic ferric acetate?

Experiment 25.—1. What does this experiment show as to the precipitation by $(NH_4)_2CO_3$ of magnesium and of the other alkaline-earth elements (which all behave nearly as calcium does)?

2. Why would a reagent which contained NH_3 and CO_2 in the molal ratio 1 : 1 not be suitable for the precipitation?

3. Why is there any advantage in adding more NH_3 than corresponds to the neutral salt $(NH_4)_2CO_3$?

4. If it were desired to work out a procedure for separating calcium, barium, and strontium from magnesium by means of $(NH_4)_2CO_3$, what experiments would one naturally make?

Experiment 26.—1. In order to make a separation of 1 mg. barium from 500 mg. strontium, what must be the concentration of CrO_4^-, stated with reference to the solubility-products of $BaCrO_4$ and $SrCrO_4$?

2. What must be true of the relativ values of these two solubility-products in order that this separation may be possible?

3. Write the chemical equations for the conversion of chromate-iron into hydro-chromate-ion, and for the conversion of the latter into bichromate-ion. Write also the mass-action expressions for the equilibrium of these reactions. Show by them what determins the proportion of CrO_4^- and of $HCrO_4^-$ in any solution, and what determins the concentration of $Cr_2O_7^-$ in any solution.

4. In practis what three substances must be added in proper proportions in order to secure the right CrO_4^- concentration in the solution?

5. Why is the second K_2CrO_4 precipitate obtained in the confirmatory test for barium more conclusiv evidence of its presence than the first K_2CrO_4 precipitate?

6. On addition of NH_4OH in P. 84 what chemical change causes the change in color from orange to yellow? Why from a mass-action standpoint does the addition of NH_4OH cause this change to take place? Why does this change cause strontium to precipitate?

7. Explain fully with reference to the value of the solubility-products why the carbonate-chromate mixture used in P. 85 does not affect $BaCrO_4$, and why it converts $SrCrO_4$ into $SrCO_3$.

8. Why does CaC_2O_4 dissolve in dilute H_2SO_4, but not in HAc?

9. How does P. 87 distinguish calcium from barium and strontium, which form much less soluble sulfates? How does it distinguish calcium from magnesium?

10. Could magnesium be precipitated by any other reagent in the form of a compound closely analogous to magnesium ammonium phosphate?

11. If a flocculent precipitate obtained in P. 88 contained calcium, how might it be treated so as to remove the calcium from it and enable the usual magnesium test to be again applied?

12. If a precipitate obtained in P. 88 contained $FePO_4$ (or $AlPO_4$, which behaves like it), how could the latter be separated from any $MgNH_4PO_4$ that might also be present?

Experiment 28.—1. If the ammonium salt were not completely removed by the ignition, how would it behave in the subsequent test for potassium?

2. How might a solution of $Na_3Co(NO_2)_6$ be prepared, judging from previous experience with an analogous compound?

Experiment 29.—1. Describe in detail a method by which it can be shown that the magnetic oxide of iron (Fe_3O_4) contains both ferrous and ferric iron.

2. If a solution of an iron salt in HNO_3 becomes decolorized and givs a precipitate of sulfur on passing in H_2S, does this show that the iron was in the ferric state in the original substance?

3. If a solution of an iron salt in HCl after treatment with H_2S and expulsion of the H_2S from the solution by boiling givs on adding NH_4OH a white precipitate of $Fe(OH)_2$ and not a brown one of $Fe(OH)_3$, does this show that the iron was in the ferrous state in the original substance?

4. Describe a method by which it can be shown that a solution made by dissolving mercury in HNO_3 contains both mercurous and mercuric salts.

5. What indications of the state of oxidation of tin would be afforded by the treatment with H_2S in P. 21 and with $(NH_4)_2S$ in P. 22 of a solution of $SnCl_2$? of a solution of $SnCl_4$?

6. What other constituents besides iron, mercury, and tin exist in two stages of oxidation in the form of salts? Giv the symbols of compounds illustrating these two states of oxidation.

7. Mention any phenomena that might be observed during the course of analysis which would distinguish from each other the two stages of oxidation of each of the constituents named in the answer to Question 6.

Experiment 32.—1. What two things determin whether or not an acid passes over into the first distillate?

2. Show by reference to the mass-action expressions for the ionization of the two acids what determins the extent to which an acid is displaced from its salt by another acid, taking K^+CN^- and $H^+H_2PO_4^-$ as an example.

3. Explain by reference to the mass-action expressions involved why $BaCO_3$ dissolves on adding HAc, and why $BaSO_3$ does not.

4. Show how phosphoric, pryophosphoric, and metaphosphoric acids are related to one another in composition.

5. If a compound of an element forming an insoluble phosphate (for example, $CaCO_3$) were distilled with H_3PO_4, would the insoluble phosphate separate in the distilling flask? Explain why or why not.

6. If H_2SO_3 is found in the first distillate, which of the other substances that may be in that distillate is it unnecessary to test for? Write the equation for the reaction which would take place between H_2SO_3 and each of these substances.

7. In a substance soluble in water which has been found to contain barium, which of the following constituents would it be unnecessary to test for: nitrate, phosphate, sulfide, sulfite, chloride, sulfate, carbonate?

8. Why would sulfite not be present in a mineral substance found in nature?

Experiment 33.—1. What different constituents of the original substance may giv rise to sulfur in the distillate? what ones to sulfurous acid?

2. Why is $BaSO_3$ readily dissolved by HCl, but scarcely at all dissolved by the HAc previously added to the first distillate?

3. Show that H_3PO_4 which had been thrown over mechanically into the first distillate would not interfere with the tests for sulfite and carbonate in P. 102.

Experiment 34.—1. What different constituents in the original substance may giv rise to chlorin in the first distillate? Write chemical equations illustrating its production from each of these constituents.

2. What different substances that might be present in the distillate would cause iodin to be set free on the addition of KI?

3. What conclusions could be drawn from the tests of the first two paragraphs of P. 103 as to the presence or absence of each of the three halogens in a distillate containing the following halogens: a, I_2, Br_2, and Cl_2; b, Br_2; c, Cl_2; d, no halogen?

4. Explain why the aqueous solution must be made strongly acid with HNO_3 to enable the Cl_2 to be extracted nearly completely from it by the chloroform.

5. Write chemical equations illustrating the process by which a small quantity of HNO_2 liberates a large quantity of iodin from KI.

Experiment 37.—1. In the test for cyanide what is the purpose of adding both $FeSO_4$ and $FeCl_3$?

2. Into what compounds is $K_4Fe(CN)_6$ decomposed when it is distilled with H_3PO_4?

3. Referring to the results of Expt. 29 with ferrous and ferric salts, suggest how a ferrocyanide could be distinguished from a ferricyanide by tests applied to a solution of the original substance.

Experiment 39.—1. To what extent is the analysis of the second distillate simplified when $AgNO_3$ gives no precipitate?

2. Some H_3PO_4 may pass over into the second distillate. Would Ag_3PO_4, which is only slightly soluble in water, precipitate in the $AgNO_3$ test, and thus obscure the test for the other constituents?

3. When is it necessary to test the second distillate for sulfide?

4. Explain by the mass-action principles why a sulfide may giv off an appreciable quantity of H_2S only in the second part of the distillation.

5. Show that Ag_2S must be much more soluble in dilute HNO_3 than in water. Explain then why it is so slightly soluble in dilute HNO_3?

6. When $2KCN$ are added to $1 AgNO_3$ the compound $K^+Ag(CN)_2^-$ forms almost quantitativly. How does this show that in the saturated solution of $AgCN$ the salt must be present mainly as Ag^+ and $Ag(CN)_2^-$?

Experiment 41.—1. What constituents in the substance are likely to giv rise to chlorin in the second distillate? to iodin?

2. Explain the fact that iodin is extracted more slowly from an aqueous solution when it contains iodide. State the law that determins the quantity extracted.

3. State the principles involved in the process used for the detection of the three halides in the presence of each other.

4. Does the fact that only a very small quantity of bromin is liberated in the first step of the process mean that the reaction between the bromide and $KMnO_4$ is in equilibrium under the conditions prevailing in the solution?

5. What is meant by the statement that a reaction is in equilibrium? How would one proceed to determin whether a given reaction is in equilibrium?

6. If the mixture of KBr, NaAc, HAc, and $KMnO_4$ were allowed to stand a day or a week, what would happen?

7. If the iodin set free in the first part of the process were not completely extracted by the chloroform, how would it interfere with the test for bromide?

8. Why is H_2SO_3 added in the last part of the process? Write the equation for the reaction which it causes.

9. Why is HNO_3 added with the $AgNO_3$ at the end of the process?

Experiment 42.—1. If the original substance contains both nitrite and nitrate, how would each of them be detected in this system of analysis?

2. If free chlorin (coming from a chlorate) were present in the second distillate, what would happen to it when treated by P. 111?

3. Iodin is not completely reduced to HI by $FeSO_4$, the four substances I_2, HI, ferrous salt, and ferric salt all being present in considerable quantity at equilibrium. If a solution containing I_2 or HI were submitted to P. 111, what would be the result?

Experiment 44.—1. Why not test for boric acid in the distillates obtained in the H_3PO_4 distillation?

2. What is the advantage in P. 113 of distilling the borate with H_2SO_4 and CH_3OH, rather than with H_2SO_4 with water?

Experiment 45.—1. Why must all the substances used in the test for fluoride be thoroly dry?

2. What happens to $KHSO_4$ when it is heated?

3. What are the main constituents of glass? What is the action of HF on it?

4. Since H_2SiO_3 is non-volatil, how can the deposit be driven up the tube by heating?

5. Of what does the white deposit left after washing the tube with water consist?

6. Show why it is appropriate to call the compound H_2SiF_6 "fluo-silicic" acid.

7. Why is it not satisfactory to test for fluoride in the distillates obtained in the H_3PO_4 distillation?

Experiment 47.—1. What different substances are present in the solution produced by acidifying the NaOCl solution with HAc?

2. What advantage would there be in making the hypochlorite test in alkaline solution, rather than in HAc solution? What disadvantage?

3. Assuming that the oxidation of the $PbAc_2$ to PbO_2 is caused by HOCl, but not by Cl_2, explain why the oxidation does not take place in a solution strongly acidified with HNO_3.

Experiment 48.—1. How may a chlorate giv off chlorin in the first part of the H_3PO_4 distillation? How in the second part?

2. Write the equation expressing the reaction that would take place between NaOCl and Na_3AsO_3.

3. If the hypochlorite were not reduced, AgCl and $AgClO_3$ would be formed in the HNO_3 solution by the action of the Cl_2 on the $AgNO_3$. Write the equation expressing this reaction.

Experiment 49.—1. If thiosulfate were present in the original substance, what indications of it would be obtained in the first distillate? Would these distinguish it from sulfite?

2. In what case would it be essential to employ P. 118 in order to establish the presence or absence both of sulfite and thiosulfate?

3. Explain with reference to the expressions for the two solubility-products how $BaSO_3$ can be converted into $BaCO_3$ by treatment with Na_2CO_3 solution.

4. Since $BaSO_3$ is less soluble than $SrSO_3$, why not use $Ba(NO_3)_2$ instead of $Sr(NO_3)_2$ for the separation of sulfite and thiosulfate?

5. Where could the $BaSO_4$ referred to in the second paragraph of P. 118 come from?

6. Assuming that the final thiosulfate test involves the equilibrium of the reaction $S_2O_3^- = S + SO_3^-$, show why a large H^+ concentration should promote the separation of sulfur from the thiosulfate. (Both hydrogens of the acid $H_2S_2O_3$, unlike those of the acid H_2SO_3, are to a large extent dissociated.)

Experiment 50.—1. Of what elements is organic matter mainly composed, and what causes it to blacken on heating?

2. Describe a method by which a substance might be tested for organic matter by converting the carbon into carbon dioxide.

3. Could a sirup be tested for aluminum by diluting it with water and analyzing the solution in the usual way? Could it be so tested for iron?

4. Name the different forms in which water may be present in a substance.

5. If a substance were ignited at a red heat (for example, to destroy organic matter) before submitting it to analysis, what basic constituents would be lost?

6. State how each of the following substances would behave in the closed-tube test: a, Na_3AsO_4; b, $MgNH_4PO_4$; c, FeS_2; d, $Pb(NO_3)_2$; e, $NaC_2H_3O_2$.

7. What acidic constituents will be detected, when present in considerable quantity, upon treating the substance with dilute HNO_3?

8. What is the behavior towards litmus of an aqueous solution of each of the following substances: Na_2SO_4; Na_2CO_3; $NaHCO_3$; $NaHSO_4$; $Ca(NO_3)_2$; $Fe(NO_3)_3$?

9. Name the basic constituents whose salts are nearly all readily soluble in water.

10. Name the acidic constituents whose salts are all or nearly all readily soluble in water.

11. Name the acidic constituents whose salts (except those of the alkali elements) are nearly all very slightly soluble in water.

12. Of the groups of salts named in the answer to Question 11, which are readily soluble in cold dilute HNO_3 or HCl? Why?

13. After the basic constituents present in "unknown 1" were determined, what conclusions could be drawn from the solubility of the substance as to the absence of any of the acidic constituents?

14. Answer the same question for "unknown 2."

Experiments 51 and 52.—1. What group of salts not dissolved by cold dilute HNO_3 are decomposed by hot concentrated HNO_3, because of its oxidizing action? what group because of its action as a strong acid?

2. State what happens (that is, what chemical changes occur and what phenomena are observed) at each step of the process when $PbSiO_3$ (which is decomposed by strong acids) is treated by P. 3.

3. State what happens at each step, namely, on heating with strong HNO_3, on evaporating to dryness and adding cold dilute HNO_3, and on heating the residue with strong HCl, when each of the following substances is treated by P. 3 and 4: *a*, Sb_2S_3; *b*, MnO_2; *c*, $PbSO_4$.

4. What metallic elements are scarcely ever found in alloys? How may the process of analysis therefore be shortened?

5. If there is no residue after treating an alloy by P. 3, what does it show as to the absence of certain elements?

Experiment 53.—1. State what happens to each of the substances whose symbols are given under *b* in Table I on fusing it with alkaline fluxes, on treating the fused mass with water, and on treating the residue with dilute HNO_3, as described in P. 7.

2. Name all the basic constituents for which it is useless to test after fusing the substance with alkaline fluxes in a porcelain crucible.

3. What are the only acidic constituents that it is ordinarily necessary to test for in minerals?

4. State what happens to each of the substances whose symbols are given under *b* in Table I when it is treated, as in P. 5: *a*, with concentrated H_2SO_4; *b*, then with HF; *c*, then, after evaporating to fuming, with water.

5. State what happens to feldspar (potassium aluminum silicate, an example of a silicate not much decomposed by acids other than HF) when it is treated by P. 5.

6. Explain with reference to the solubilities of the substances involved why $PbSO_4$ is completely converted into $PbCO_3$ by boiling with Na_2CO_3 solution in P. 6; and why $BaSO_4$, when much of it is present, is only partly converted into $BaCO_3$ by the same treatment.

PART II.

THE SYSTEM OF ANALYSIS.

PREPARATION OF THE SOLUTION.

PRELIMINARY EXAMINATION.

Procedure 1.—*Preliminary Examination.*—If the substance is a non-metallic solid, note its color, odor, and texture; examin it with a lens to determin whether it is heterogeneous, and, if so, note the appearance of its constituents. To determin whether organic matter or water is present and to get other indications, heat gently at first, then strongly, about 0.1 g. (0.1 gram) of the finely powdered substance in a hard glass tube (of about 0.6 cm. bore and 8 cm. length) closed at one end. Note whether the substance blackens, whether a tarry, aqueous, or other deposit forms on the cold part of the tube, and whether any odor is emitted. If organic matter is thus proved to be absent, pass to P. 2 (Procedure 2); if proved to be present, to P. 8.

If the substance is an alloy, treat it by P. 3.

If the substance is a solution, evaporate a measured volume of it to dryness in a small weighed dish, dry the residue thoroly at 120–130° in a hot closet or by keeping the dish in motion over a small flame, and weigh the dish again. Heat a portion of this residue in a closed tube as described above. Treat another portion by P. 2 if organic matter is absent, or by P. 8 if organic matter is present.

> *Notes.*—1. When a complete analysis in the wet way is to be made, it is usually not worth while to make a more extended preliminary examination in the dry way. The closed-tube test is, however, essential, in order to show whether organic matter is present; for certain kinds of organic matter, especially sugars and hydroxy-acids, such as tartaric, citric, and lactic acids, prevent the precipitation of the hydroxides of aluminum and chromium in the subsequent analysis, and must therefore be detected and removed. Moreover, a large quantity of organic matter of any kind interferes with the execution of the analysis; for example, with the operations of solution, filtration, and evaporation. Alloys do not contain organic matter or water; and therefore the closed-tube test need not be applied to them.

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2. Blackening accompanied by a burnt odor or by the formation of a tarry deposit shows organic matter. Blackening alone does not show it; for copper, cobalt, and nickel salts may turn black on heating, owing to the formation of the black oxides.

3. It is usually desirable to determin whether water is a constituent of the substance, and, if so, whether it is present in large or small proportion. This can be done with a fair degree of delicacy by the closed-tube test, provided care be taken to keep the upper part of the tube cool during the first of the heating. Water may be present as so-called water of constitution, as in FeO_3H_3 or Na_2HPO_4; as water of crystallization, as in $MgSO_4.7H_2O$; as enclosed water, as in some hydrated silicates like the zeolites or as mother-liquor within crystals; and as hygroscopic moisture on the surface. Water of constitution may be expelled only at a fairly high temperature, while in the other forms it is seldom retained above $200°$.

4. The closed-tube test may also furnish evidence of the presence of certain basic and acidic constituents when they are present in considerable quantity. Thus all ammonium salts and mercury compounds are volatilized much below a red heat. Ammonium salts and the chlorides of mercury giv a white sublimate. Most other mercury compounds giv a gray one, consisting of minute globules of mercury, made visible by a lens or by rubbing with a wire. Metallic As, As_2O_3, and As_2S_3 are also readily volatilized, forming black, white, and yellow sublimates, respectivly. Of the acid-forming elements or groups, free sulfur or a persulfide is shown by a sublimate of reddish-brown drops, changing to a yellow solid on cooling, and accompanied by odor of SO_2; a moist sulfide, by the odor of H_2S; a nitrate or nitrite, by brown vapors of NO_2; free iodin or a decomposable iodide, by a black sublimate of I_2 and by its violet vapor; a sulfite, by the odor of SO_2; a peroxide, chlorate, or nitrate, by evolution of oxygen, recognized by its inflaming a glowing wood-splinter held in the tube; and a carbonate or oxalate, by the evolution of CO_2, recognized by its causing turbidity in a drop of $Ba(OH)_2$ solution.

5. If the substance to be analyzed is a liquid, it is desirable to determin by evaporation how much, if any, solid substance is present in it; for enough must be taken for analysis to enable small quantities of the basic constituents to be detected. Moreover, if it is dissolved in a volatil organic solvent the latter must be removed by evaporation.

PREPARATION OF THE SOLUTION.

TABLE I.—PREPARATION OF THE SOLUTION IN THE CASE OF NON–METALLIC SUBSTANCES.

Heat the substance with water and dilute HNO_3 (P. 2).

If it all dissolves, treat the solution by P. 11.	*If it does not all dissolve, add more HNO_3, evaporate, dry completely, add dilute HNO_3 (P. 3).*			
	Solution: *Treat by P. 11.*	Residue:* *a.* Sb_2O_5, SnO_2, MnO_2, PbO_2, HgS. *b.* C, Al_2O_3, Cr_2O_3, AgCl, CaF_2, $PbSO_4$, $BaSO_4$, $SrSO_4$, SiO_2, and many silicates. *Heat with HCl or HCl and HNO_3, evaporate, add dilute HCl (P. 4).*		
	Solution: substances under *a.* *Treat by P. 21.*	Residue: substances under *b.* *Heat with H_2SO_4 and HF, evaporate off the HF, add water, boil (P. 5).*		
		Gas: SiF_4.	Residue: Pb, Ba, Sr,(Cr), as sulfates. *Treat by P. 6.*	Solution: other elements as sulfates. *Treat by P. 11.*

* Only the more common substances that are likely to be present in the residue are here mentioned.

Procedure 2.—*Treatment of Non-Metallic Substances Free from Organic Matter.*—Add to 1 g. of the finely powdered substance (see Note 1) in a casserole 10–30 cc. water, heat to boiling if there is a residue, and test the solution with litmus paper. (If the solution is alkaline, add to it 6–normal HNO_3 drop by drop till it becomes barely acid.) Add, without filtering out any residue, just 5 cc. 6–normal HNO_3; and, if there is still a residue, heat the mixture to boiling. Note whether there is an odor or effervescence.

If the substance has dissolved completely, treat the solution by P. 11.

If the substance has not dissolved completely, treat the mixture, without filtering out the residue, by P. 3.

Notes.—1. In order that difficultly soluble substances may be dissolved, the substance must be reduced to a very fine powder. This is usually best accomplished by grinding the substance, a small quantity at a time, in a por-

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celain or agate mortar. With hard substances, and in general with minerals, an agate mortar should be used. As such a mortar is likely to be broken by a blow, the substance should be ground, not pounded, in it.

2. The quantity of the substance taken for analysis should always be approximately known; for a good qualitativ analysis should not only show the presence or absence of the various elements in the substance, but should enable their relative quantities to be estimated. Since 1 or 2 mg. of almost any element can be detected by this system of analysis, the presence of 0.1–0.2% of an element will be detected when one gram of substance is taken, and this degree of delicacy is ordinarily sufficient. If much more than this quantity is taken, the precipitates may be so large that much time is consumed in filtering and washing them.

3. When the substance dissolves only partly in water, it is not worth while to filter off the residue and analyze it and the solution separately, unless special information in regard to the soluble constituents is desired. It is, therefore, directed to treat at once with HNO_3.

4. Just 5 cc. HNO_3 must be added in order that the acid concentration may be properly adjusted in the subsequent H_2S precipitation. For the same reason, when the solution is alkaline, it must be first made nearly neutral before adding the 5 cc. of HNO_3.

5. If the aqueous solution has an alkaline reaction, the addition of an acid may cause precipitation of any substance held in solution by an alkaline solvent; for example, sulfur or sulfides of the tin group from an alkaline sulfide solution; silver chloride or cyanide from a potassium cyanide solution; silicic acid from sodium silicate solution; or basic hydroxides from solutions in alkalies. These last substances redissolve when the excess of HNO_3 is added.

6. An acid reaction of the aqueous solution towards litmus is due to hydrogen-ion, which may arise from free acid, from an acid salt of a strong acid, or (by hydrolysis) from a neutral salt of a strong acid and a weak base. An alkaline reaction is due to hydroxide-ion, which may arise from a soluble hydroxide, or (by hydrolysis) from a carbonate, sulfide, phosphate, borate, cyanide, or a salt of some other weak acid.

7. When an acid is added to a nonmetallic substance or its aqueous solution, the evolution of any gas and its odor should be noted, since this indicates the nature of the acidic constituent present. Thus carbonates evolve CO_2; sulfides, H_2S; sulfites and thiosulfates, SO_2; and cyanides, HCN.

8. When the substance dissolves completely in dilute HCl, this acid may be substituted for HNO_3. It is advantageous to do this in the case of a few substances, such as MnO_2, Sb_2O_5, and hydrated SnO_2, which dissolve in HCl, but not in HNO_3. With these substances it is best to add the HCl first, to warm till solution has taken place, and then to dilute with water and treat with H_2S by P. 21. Just 5 cc. 6–normal HCl must be added, and care must be taken to avoid loss by evaporation, as in the case of HNO_3.—As to the reasons for recommending the use of HNO_3, rather than of HCl, as the usual procedure, see Note 4, P. 3.

9. The following general statements may be made in regard to the solubility of substances in water and dilute acids:

All the ordinary salts of sodium, potassium, and ammonium are readily soluble in water.

The salts of bismuth, antimony, and tin are hydrolyzed by water with precipitation of basic salts, which dissolve readily in dilute HNO_3 or HCl.

The nitrates, chlorates, and acetates of all the elements are readily soluble in water (except certain basic nitrates and acetates).

The hydroxides, carbonates, phosphates, borates, arsenates, and arsenites of all the elements except the alkalies are only slightly soluble in water, but dissolve readily in dilute HNO_3 or HCl. ($Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ are, however, fairly soluble in water.)

The chlorides, bromides, iodides, and thiocyanates of all the elements except lead, silver, and mercury, and the sulfates of all the elements except calcium, strontium, barium, lead, and silver are readily soluble in water. (In regard to the solubility of these and other salts of the alkaline earths and of silver and lead, see the Table of Solubilities of Slightly Soluble Substances at the end of the book.

Procedure 3.—*Treatment of Non-Metallic Substances not dissolved by Dilute Nitric Acid and of Alloys.*—If the substance is non-metallic and has not dissolved in dilute HNO_3, to the mixture obtained in P. 2 add 5–10 cc. HNO_3 (s.g., 1.42), and evaporate just to dryness.

If the substance is an alloy, convert it into a form offering a large surface and treat 0.5 g. of it in a casserole with 10 cc. 6–normal HNO_3. Cover the dish with a watch-glass, heat the mixture nearly to boiling as long as any action continues, adding a little HNO_3 (s.g., 1.42) if action is renewed thereby, or a little water if crystalline salts have separated, and then evaporate just to dryness.

Heat the residue obtained in either case at 100–130° until it is perfectly dry, by keeping the casserole in motion over a small flame. Loosen the residue from the dish and rub it to a fine powder with a pestle; add to it just 5 cc. 6–normal HNO_3, cover the dish, and warm the mixture, taking care that none of the acid evaporates. Dilute with 20 cc. water, heat to boiling, filter, and wash the residue. (Residue, P. 4; solution, P. 11.)

> *Notes.*—1. On heating the HNO_3 solution, the presence of sulfides is indicated by the separation of sulfur as a spongy or pasty mass, which floats on the surface and may be removed by means of a spatula or rod; and the presence of iodides is shown by the liberation of free iodin, which may separate as a black precipitate, which imparts a brown color to the solution, and which gives rise to violet vapors above it.
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> 2. When a silicate is decomposed by acid, silicic acid may separate as a gelatinous precipitate, but even then a part of it always remains in solution, mainly as a colloid. When thoroly dried at 100–130°, it is partially dehydrated and becomes entirely insoluble. The HNO_3 acid solution is therefore evaporated to dryness and the residue is heated at 100–130°, in order to remove the silica at this point; for, if it were not removed, it would appear as a gelatinous precipitate at some later stage of the analysis; thus, if it did not separate earlier, it would be precipitated by NH_4OH together with the iron group and might then be mistaken for aluminum hydroxide. In the case of nonmetallic substances which cannot contain silica, the heating may be omitted.

3. If the substance is nonmetallic, the residue insoluble in HNO_3 probably consists of one or more of the following substances: the partially dehydrated hydroxides of tin, antimony, and silicon; the nativ or ignited oxides of the same elements, of aluminum, and of chromium; anhydrous chromic salts; the peroxides of manganese and lead; the sulfates of barium, strontium, and lead; the sulfides of mercury and molybdenum; silica; the silicates and fluo-silicates of many elements; fluoride of calcium; the halides of silver and lead; phosphate of tin; ferrocyanide of iron; sulfur; carbon; silicon carbide.

4. In dissolving nonmetallic substances HCl may be used in place of HNO_3. Each of these acids has advantages and disadvantages of its own, as follows: HNO_3 dissolves, owing to its oxidizing power, many sulfides not attacked by HCl, but fails to dissolve certain oxides, especially MnO_2, Sb_2O_5, and hydrated SnO_2, which dissolve in HCl. HCl may cause the precipitation of chlorides of the silver group; while strong HNO_3 on heating oxidizes sulfides partially to sulfates, and may cause the precipitation of lead, barium, strontium, and calcium sulfates; thus in either case making it sometimes impossible to determin whether complete decomposition has resulted. HNO_3 oxidizes mercurous, arsenous, antimonous, stannous, and ferrous compounds to the higher state of oxidation; consequently almost all the antimony and tin will usually be found in the residue insoluble in dilute HNO_3 after evaporation, all the mercury will be in the H_2S precipitate, and sulfur will always be precipitated by H_2S when iron is present. When HCl is used as a solvent, mercury and arsenic in the arsenous form would be wholly or partly lost, owing to the volatility of their chlorides, in the subsequent evaporation, which is necessary in order to remove silica. For this last reason, and for the reason that the procedure is a more general one in that it provides for the solution of alloys and of a larger proportion of nonmetallic substances and for the isolation of the silver group, the use of HNO_3 is here recommended.

5. Alloys can not ordinarily be powdered by grinding in a porcelain or agate mortar. They may usually be converted into a form that offers a large surface by hammering in a steel mortar, filing with fine steel file, shaving with a knife, or converting into turnings with a lathe. Only 0.5 g. of an alloy is taken for analysis; for, owing to the absence of acidic constituents, the same quantity of basic elements is contained in a smaller amount of substance.

6. By the treatment of alloys with strong HNO_3, all the more common elements are dissolved by strong HNO_3 except antimony, tin, and silicon. These are oxidized to antimonic acid ($Sb_2O_5.nH_2O$), metastannic acid (nH_2SnO_3), and silicic acid (H_2SiO_3), which separate at once as white amorphous precipitates when considerable amounts of these elements are present. Certain nitrates, especially that of lead, may separate in crystalline form from the strong HNO_3, but these dissolve upon adding water and heating to boiling.

7. In the case of an alloy the evaporation to dryness and heating at 120-130° serve to partially dehydrate the hydroxides of silicon, tin, and antimony, whereby they are rendered nearly insoluble in HNO_3. This makes possible a conclusion in regard to their presence or absence. Thus, if after having thoroly dried the mixture at this temperature there is no residue insoluble in the HNO_3, it shows the absence of silicon and tin in quantity as large as 1 mg., and that of antimony in quantity as large as 2 or 3 mg. The fact must not be overlooked, however, that in the dehydrated form even a very small

residue or slight turbidity may correspond to an appreciable quantity of one of these elements. Therefore, if no residue can be seen, rub the sides of the dish gently with the rubber-covered end of a glass rod, pour into a small flask, allow the liquid to stand 2 or 3 minutes, and note whether there is any residue whatever. The knowledge that tin is absent enables the subsequent procedures for the detection of this element to be omitted. The subsequent procedures for antimony may, in the absence of a residue, also be omitted, provided quantities as small as 3 mg. are not to be tested for. In addition to the hydroxides named above, the residue may also contain a considerable quantity of stannic phosphate or arsenate when tin and phosphorus or arsenic are simultaneously present, or of bismuth hydroxide when both antimony and bismuth are present; also small quantities of various other elements enclosed in a residue consisting of the substances already mentioned.

8. The hydroxides of antimony, tin, and silicon usually separate also in the treatment of nonmetallic substances with HNO_3 when the corresponding elements are present; but the nonexistence of a residue must not, except in the case of silicon, be regarded as conclusiv evidence of their absence in such substances. For the presence of certain acidic constituents, such as chloride or sulfate, may cause a considerable quantity of tin or antimony to dissolve.

9. A black or metallic residue insoluble in HNO_3, obtained in the case of an alloy, may contain carbon or carbides, certain alloys of iron, such as ferrochrome or ferrosilicon, gold, or any of the platinum metals. If there is no such residue, it shows the absence of gold and platinum.

Procedure 4.—*Treatment of the Residue Insoluble in Nitric Acid.*— To the residue insoluble in HNO_3 (P. 3) in a casserole add gradually 5–10 cc. 12–normal HCl, and heat as long as action continues, adding more acid if necessary. If the substance does not dissolve completely in HCl, add to the mixture without filtering one-third its volume of HNO_3 (s.g., 1.42), and heat gently as long as action continues, adding more of the acids if necessary.

Evaporate this solution in HCl alone, or in HCl and HNO_3, without filtering off any residue. Heat the residue till it is perfectly dry by keeping the dish in motion over a small flame. Moisten the residue with 12–normal HCl, and heat again till the residue becomes perfectly dry. Add to the residue 5 cc. 6–normal HCl, measured in a small graduate, and about 20 cc. water; boil gently for a few minutes if there is a residue; filter, and wash the residue thoroly with boiling water. Pour the filtrate into a graduate, and add enough water to make its volume 100 cc. (Residue, P. 5, filtrate, P. 21.)

Notes.—1. Of the substances that may be present in the residue undissolved by HNO_3 (see P. 3, Note 3), the peroxides of manganese and lead are reduced and dissolved by concentrated HCl; antimonic acid, stannic phosphate, and much metastannic acid are also dissolved by it. Upon the addition of HNO_3, whereby the strongly oxidizing mixture known as *aqua regia* is produced, gold, platinum, and mercuric sulfide are entirely dissolved; and silver

compounds, such as $AgBr$, AgI, and $AgCN$, are converted into $AgCl$. The chloride of silver and the sulfates of strontium and lead dissolve in large quantity in the concentrated acids, but only in much smaller quantity in the small amount of dilute HCl added after the evaporation. Some of the other substances that may be in the residue, especially the oxides and certain silicates, are slowly attacked by the strong acids, but the solvent action is not rapid enough to make this a practicable method of getting them into solution.

2. The solution is evaporated to render insoluble silicic acid which may have come from the decomposition of silicates, and to remove the large quantity of acid which would otherwise interfere with the H_2S precipitation. A measured quantity of HCl is added and the solution is diluted to a definit volume, in order to produce the acid concentration required for the H_2S precipitation.

3. If the original substance was an alloy, a residue after the treatment with HCl and HNO_3 is likely to consist of metastannic or silicic acid or of carbon, a platinum metal, or an alloy of iron with chromium, silicon, etc. It is best treated with H_2SO_4 and HF by P. 5, in order to test for and remove silica and to dissolve metastannic acid and iron-alloys. If a black or metallic residue still remains, it may be tested for graphite by rubbing a dried portion on the fingers or on paper; and to bring it into solution the remainder may then be fused with Na_2O_2 in a nickel crucible, the mass treated with water and HCl, and the solution analyzed as usual, except that nickel cannot be tested for.

4. If the original substance was an alloy and a large, nonmetallic residue remains after treatment with HNO_3 (P. 3), it is sometimes advantageous, instead of treating it by P. 4, to analyze the residue separately by the following procedure, by which a large quantity of metastannic acid is more readily dissolved: Add to the residue in a casserole 3–4 cc. H_2SO_4 (s.g., 1.84), and heat under the hood until the acid has evaporated to a volume of about 2 cc. Cool, add an equal volume of water, cool again, add 5 cc. HCl to dissolve antimonic oxide, and heat to boiling. Cool completely, filter if there is a residue (which may consist of silicic acid), and add the acid solution drop by drop, with constant shaking, to a mixture of 10 cc. ammonium monosulfide, 1 cc. ammonium polysulfide, and 10 cc. NH_4OH (s.g., 0.90) in a flask. Cover the flask and digest for a few minutes on a steam bath. Filter out the precipitate, which may consist of small quantities of sulfides of the copper and iron groups. Dilute the filtrate, and make it slightly acid with HCl. Shake to coagulate the precipitate, filter, and wash with hot water. Analyze the precipitate for the tin group by P. 41; reject the filtrate or test it for phosphate by P. 115.

Procedure 5.—*Fluoride Treatment of the Residue Insoluble in the Common Acids.*—Transfer to a platinum crucible the residue after treatment with acids (P. 4), add 2 cc. H_2SO_4 (s.g., 1.84) from a graduate, heat with a moving flame until white fumes are given off, and cool completely.

To test for silicate, add carefully (see Note 1) from the loop of a platinum wire pure 48% HF drop by drop until 5–6 drops have been

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* If the use of a platinum crucible or of hydrofluoric acid is impracticable, the less dangerous, but less satisfactory, alternativ method described in P. 7 may be employed (see Note 6, P. 5).

added, and warm the mixture over a steam bath. (Formation of gas bubbles, presence of SILICA or SILICATE.)

Then add 2–5 cc. more pure 48% HF, cover the crucible with a platinum cover, digest on a steam bath for about 15 minutes unless the residue dissolves more quickly; remove the cover and evaporate under a hood until white fumes of H_2SO_4 are given off, carefully heating the sides of the crucible with a moving flame, or, better, with a ring-burner to avoid spattering. [Unless it is known from the presence of solid substance at this point or from other indications that the residue treated with H_2SO_4 and HF contained other constituents than silica, determin this by evaporating off the H_2SO_4 under a hood, taking care not to ignite the dry residue. If a significant residue remains, add from a graduate 1.5 cc. H_2SO_4 (s.g., 1.84), and heat until the residue is redissolved, not allowing the acid to evaporate.] Cool, pour the contents of the crucible into 10 cc. water, and rinse out the contents with a little water. Boil to dissolve slowly dissolving sulfates; cool, shake, filter, and wash the residue, first with 6–normal H_2SO_4 and then with a little water. (Residue, P. 6; filtrate, P. 11.)

Notes.—1. *A student using this procedure for the first time should work under the direct supervision of an instructor. Great care must be taken not to breathe the fumes of HF nor to get it on the hands; for it is extremely irritating and produces dangerous burns.*

2. The test for silica or silicate depends on the formation of SiF_4 gas, which is insoluble in strong H_2SO_4, but dissolves in water in the presence of HF with formation of fluosilicic acid, H_2SiF_6. With free silica the evolution of gas takes place in the cold; but with slowly decomposing silicates, such as feldspar, the test is obtained only upon warming. A few silicates are not acted upon by HF and H_2SO_4, and, of course, do not show the test for silica at this point. The test is delicate enough to enable 1 mg. of silica, whether free or in a decomposable silicate, to be detected. Moreover, after the substance has been treated with acids as in P. 4 and warmed with H_2SO_4, an evolution of gas with HF is not produced with the compounds of any element other than silicon. It should be borne in mind that a small quantity of silica will be introduced if ordinary filters (which have not been washed with HF) have been employed and have been destroyed by acids or by ignition, or if a strongly alkaline solution has been boiled in glass vessels, or if a substance has been fused with sodium carbonate in a porcelain crucible.

3. Since glass and porcelain consist of silicates which are readily attacked by HF, this acid must not be allowed to come into contact with these materials. In handling cold HF solutions, vessels and funnels of celluloid or paraffin or of glass coated with paraffin may be used; but platinum vessels must be employed when the solutions are to be heated. Care must be taken not to introduce into a platinum vessel any solution containing chlorin or bromin or any acid mixture containing nitrates and chlorides by which chlorin would be

evolved. Platinum is so slowly attacked by hot concentrated H_2SO_4 that even when 2–3 cc. of the acid are rapidly evaporated in a crucible less than 0.5 mg. passes into solution.

4. The digestion with HF decomposes most silicates and dissolves silica. The subsequent evaporation with H_2SO_4 expels the excess of HF and decomposes the fluorides produced, as well as some other substances that may have been left undissolved by the HNO_3 and HCl. The H_2SO_4 solution is diluted with a small quantity of water so as to cause the complete precipitation of $BaSO_4$, $SrSO_4$, and $PbSO_4$. These sulfates are moderately soluble in strong H_2SO_4 and may not appear till after dilution. The addition of much water is avoided, since $SrSO_4$ and $PbSO_4$ are somewhat soluble in water; and the residue is washed with dilute H_2SO_4 for the same reason. The solution is boiled so as to dissolve anhydrous sulfates, such as those of aluminum and iron.

5. The residue insoluble in dilute H_2SO_4 contains as sulfates all the barium, strontium, and lead, and all of the calcium in excess of 5–10 mg., left undissolved by HNO_3 and HCl; more or less of the chromium (according as the H_2SO_4 has been more or less strongly heated) as a pink anhydrous sulfate; and part of the bismuth as basic sulfate and antimony as antimonic hydroxide, when much of these elements was left undissolved by the previous treatments with acids. The residue may also contain still undecomposed substances, especially the following: silver chloride; corundum, Al_2O_3; chromite, $FeCr_2O_4$; cassiterite, SnO_2; some anhydrous silicates and fluosilicates, such as cyanite or andalusite (Al_2SiO_5) and tourmalin; graphite and carbides; and certain compounds of the rarer elements.

6. If the use of a platinum crucible or of hydrofluoric acid is impracticable, the residue insoluble in HCl and HNO_3 may be fused in a porcelain crucible with a mixture of Na_2CO_3 and K_2CO_3, as described in P. 7, instead of being treated by P. 5–6. This is, however, a far less satisfactory method of analysis for the following reasons. Compounds of the alkali elements are used as a flux, and aluminum, calcium, and silica are introduced from the porcelain crucible, so that these elements can not be tested for in the subsequent analysis. Moreover, the treatment with HF and H_2SO_4 is almost always a shorter process, since when the residue consists only of silica, as is often the case with minerals, no further treatment is necessary, and since in other cases there is often no residue to be boiled with Na_2CO_3 solution (P. 6). A fusion in a platinum crucible with alkali-metal carbonate would be less objectionable; but this is not possible, unless reducible metals are known to be absent in the residue (see Note 5, P. 7).

Procedure 6.—*Treatment of the Residue from the Fluoride Treatment.*—Transfer the residue insoluble in dilute H_2SO_4 (P. 5) to a casserole, add about 25 cc. saturated Na_2CO_3 solution, cover the casserole, and boil gently for 10 minutes. Filter and wash the residue thoroly. (Filtrate, reject.) Heat the residue with just 5 cc. HNO_3 and 10–20 cc. water. Filter out any undissolved residue, and treat the solution by P. 11, subsequently testing it only for lead, bismuth, chromium, barium, strontium, and calcium.

Notes.—1. The boiling with Na_2CO_3 converts into carbonates the sulfates of lead, calcium, strontium, and bismuth completely, and at least 80% of

the sulfate of barium, even when large quantities of them are present. A second treatment, which should be applied to the residue if there are indications that barium is present, completely decomposes $BaSO_4$. The carbonates dissolve readily in HNO_3. Anhydrous chromic sulfate, which is left undissolved by dilute H_2SO_4 (P. 5) as a fine pink or gray powder, is slowly changed by boiling with Na_2CO_3 to a greenish blue hydroxide which dissolves in the HNO_3, leaving behind the still undecomposed sulfate. Antimonic oxide dissolves only to a small extent (2–4 mg.) in the Na_2CO_3 solution or in the dilute HNO_3.

2. Any residue insoluble in HNO_3 can therefore consist only of barium or chromic sulfate, of antimonic oxide, or of some of the original substance still undecomposed, which is likely to consist of one of the nativ oxides or silicates mentioned in P. 5, Note 5. If such a residue is obtained, it can ordinarily be rendered soluble by fusion with Na_2CO_3, K_2CO_3, and KNO_3, as described in P. 7; but in this case a platinum crucible may be used for the fusion, provided the residue be first heated with HCl to extract any Sb_2O_5 that may be present and provided silver is not found present in the H_2SO_4 solution obtained in P. 5.

Procedure 7.—*Alternativ Treatment of the Residue Insoluble in the Common Acids.*—If the use of HF (P. 5) is impracticable, transfer the residue insoluble in acids (P. 4), with the filter if necessary, to a porcelain crucible, heat until the residue is dry or until the filter is destroyed, mix the residue, which must be very finely divided, with ten to twenty times its weight of a mixture of anhydrous Na_2CO_3 and K_2CO_3, cover the crucible, heat strongly over a powerful burner so that complete fusion takes place, and continue the heating for 10–20 minutes. If dark particles of undecomposed substance can still be seen, add gradually in small portions 0.1–0.5 g. of solid KNO_3, and heat strongly for several minutes. Cool, boil the crucible and its contents with water until the fused mass is disintegrated, filter, and wash the residue thoroly. Warm the residue with HNO_3 until action ceases, and filter out any still undecomposed substance.

Test one half of the carbonate solution for acidic constituents as described in the last four paragraphs of P. 119.

Mix a tenth of the HNO_3 solution with a tenth of the carbonate solution, making the mixture acid with HNO_3, if it is not already so. If no precipitate forms, mix the remainder of the acid solution with the remainder of the carbonate solution. Add 3–5 cc. HCl (or more if the solution is still alkaline), and filter. Test the precipitate for silver and lead by P. 12. Evaporate the solution, and heat the residue until it is thoroly dry at 120–130° by keeping it in motion over a small flame. Moisten the residue with HNO_3 (s.g., 1.42), and heat again till the residue becomes perfectly dry. Add from a

graduate just 5 cc. 6–normal HNO_3 and about 20 cc. water, and heat to boiling. Filter out any residue (see Note 2), dilute the filtrate to 100 cc., and treat it by P. 21.

If a precipitate forms on mixing the small portions of the HNO_3 solution and the carbonate solution, treat these solutions separately as described in the preceding paragraph, uniting the precipitates formed by the same group reagent in the subsequent analysis.

Notes.—1. Upon fusion with sodium carbonate most compounds undergo metathesis, the acidic constituent of the compound combining with the sodium, and the basic element with the carbonate. The carbonate formed is, however, sometimes decomposed by heat with production of the oxide or of the metal itself. Acid-forming oxides, such as SiO_2, As_2O_5, and less rapidly Al_2O_3, expel CO_2 from the carbonate and form sodium salts. Such reactions are illustrated by the following equations:

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$
$$Fe_2SiO_5 + Na_2CO_3 = Na_2SiO_3 + Fe_2O_3 + CO_2.$$
$$4AgCl + 2Na_2CO_3 = 4NaCl + 4Ag + 2CO_2 + O_2.$$
$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$
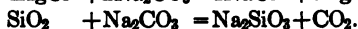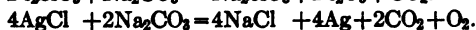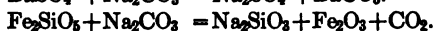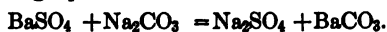
After the treatment with water, the acidic constituent of the substance is therefore found with the excess of carbonate in the aqueous extract, while the basic element remains undissolved by the water and passes into the acid solution. The first and third reactions are examples of cases where the aqueous and acid solutions must not be mixed, for upon mixing $BaSO_4$ or $AgCl$ would again be formed.

2. Of the basic elements that may be present, all or a part of the arsenic, antimony, tin, aluminum, chromium and manganese are contained in the carbonate solution; and this solution must therefore be analyzed for basic elements. Since this solution may also contain Na_2SiO_3, the solution after the addition of acid is evaporated to dryness, and the residue is heated at 120–130°, in order to dehydrate the silicic acid and render it insoluble. The residue insoluble in HNO_3 after this treatment usually consists only of silicic acid. To prove whether it consists wholly of this acid, it may be treated with H_2SO_4 and HF as described in P. 5.

3. Some substances which are not much acted upon by alkali carbonates alone are readily attacked when an oxidizing substance like KNO_3 is present. Thus, sulfides are converted into sulfates and chromium compounds (such as chromite, $FeOCr_2O_3$) into chromates. A few substances, however, such as the nativ or ignited oxides of tin and aluminum, may be only partially decomposed even by long-continued fusion with the mixed fluxes. Such an undecomposed residue may be fused with KOH in a nickel or silver crucible and the fusion treated first with water and then with HCl. The oxides of aluminum and stannic tin, if finely powdered, dissolve rapidly in fused KOH. The aqueous extract contains the aluminum as aluminate and most of the tin as stannate. The residue undissolved by water may consist of black nickel oxide from the crucible, stannic hydroxide, and of other hydroxides accompanying the aluminum or tin oxides; all of which dissolve in HCl.

4. Aluminum, calcium, and silica are taken up from the porcelain crucible

by the flux, so that these elements, as well as the alkali elements, cannot be tested for later in the analysis. The crucible is, moreover, so attacked by the flux that it cannot well be used for a second fusion.

5. Whenever it is permissible, it is therefore better to make the fusion in a platinum crucible, since then no foreign substances are introduced from the crucible. It is not permissible, however, to heat in platinum compounds of the elements of the silver, copper, and tin groups that may be reduced to the metal by heating with an alkaline flux. The same is true of sulfur, sulfides, and in the presence of organic matter of phosphates; for all these elements form easily fusible alloys with the platinum, and thus spoil the crucible. Moreover, alkaline hydroxides and strongly oxidizing fluxes (such as peroxides and nitrates) must not be fused in platinum, since they attack it fairly rapidly. Therefore, if the fusion is made in platinum, no more KNO_3 should be added than is necessary.

6. If platinum is not available, or if it is not known that reducible elements are absent, a pure nickel crucible can be used with advantage in place of the porcelain one. This enables aluminum, calcium, and silica to be tested for. Some nickel, but only a few milligrams, will then be found in the acid solution of the fusion. Reducible elements, if present, would alloy with the nickel, but the destruction of a crucible of this cheap material is not of much consequence. Ordinarily a nickel crucible can be used repeatedly.

Procedure 8.—*Destruction of Organic Matter.*—If the closed-tube test (P. 1) has shown the presence of organic matter, powder, or cut into small pieces, 1–5 g. of the substance (according to the quantity of organic matter present). Add to it in a casserole about 5 cc. H_2SO_4 (s.g., 1.84); warm gently until the substance is well charred; cool; add slowly, with constant stirring, under a hood, HNO_3 (s.g., 1.42), until violent reaction ceases; digest for a few minutes on a steam bath, and then heat over a flame, keeping the dish moving, until the substance is thoroly charred. Cool, again add HNO_3 (s.g., 1.42) as before, and heat until thick fumes of H_2SO_4 are evolved; cool somewhat, and add a little HNO_3. Repeat this process till the mixture becomes light-colored and remains so when heated strongly.

If the substance has dissolved completely (or even if it has not, if the use of HF is impracticable), evaporate off the H_2SO_4 under a hood till only 1.5 cc. remains, cool completely, add very carefully 10–20 cc. water, and boil. (If a precipitate separates, filter it off and treat it by P. 6.) Treat the solution by P. 11.

If the substance has not dissolved completely, transfer the mixture to a platinum crucible, evaporate off the H_2SO_4 till only 1.5 cc. remain, cool completely, and treat the mixture by the second and third paragraphs of P. 5.

Notes.—1. This method of destroying organic matter is of very general application, being effective even when such stable substances as paraffin and

cellulose are present. Organic matter can also be destroyed by ignition, but this has the disadvantages of volatilizing certain elements, especially mercury and arsenic, and of making some substances very difficultly soluble. When the organic matter consists only of oil, as is the case with an oil paint, it may be better to extract it with ether, especially when it is desired to determin the proximate constituents of the substance.

2. The residue contains: any substances originally present that have not been attacked by HNO_3 or H_2SO_4, especially silicates; all the lead, strontium, and barium that may have been present in any form, since the sulfates of these elements are insoluble in dilute H_2SO_4; all the silica, since silicic acid is dehydrated and made insoluble by heating with H_2SO_4; some of the calcium, bismuth, antimony, and tin, when these elements are present in considerable quantity, since their sulfates (or oxides) are not readily soluble in dilute H_2SO_4; and substantially all of the chromium, since its sulfate is converted into the insoluble anhydrous form.

3. After the organic matter is destroyed, the solution is evaporated to 1.5 cc., in order that the concentration of the acid may be properly adjusted in the subsequent H_2S precipitation.

DETECTION OF THE BASIC CONSTITUENTS.

TABLE II.—DIVISION OF THE BASIC ELEMENTS INTO GROUPS.

SOLUTION IN DILUTE NITRIC ACID CONTAINING ALL THE COMMON BASIC ELEMENTS. *Add NH₄Cl (P. 11).*

Precipitate: SILVER-GROUP (PB,* AG, HG*), as chlorides. See Table III.

Filtrate. *Saturate with H₂S gas (P. 21).*

- **Precipitate: COPPER-GROUP and TIN-GROUP** as sulfides. *Treat with (NH₄)₂S₂ (P. 22).*
  - **Residue: COPPER-GROUP** (HG, PB, BI, CU, CD), as sulfides. See Table IV.
  - **Solution: TIN-GROUP** (AS, SB, SN), *Add HCl (P. 23).*
    - **Precipitate:** As₂S₆, Sb₂S₆, SnS₂, as sulfo-salts. See Table V.

- **Filtrate:** *Add NH₄OH and (NH₄)₂S (P. 51).*
  - **Precipitate: ALUMINUM-GROUP and IRON-GROUP,** as hydroxides and sulfides. *Dissolve in acid, add NaOH and Na₂O₂ (P. 52).*
    - **Filtrate: ALUMINUM-GROUP** (AL, CR, ZN), as sodium salts. See Table VI.
    - **Precipitate: IRON-GROUP** (MN, FE, CO, NI), as hydroxides. See Table VII.
  - **Filtrate:** *Add (NH₄)₂CO₃ (P. 81).*
    - **Precipitate: ALKALINE-EARTH-GROUP** (BA, SR, CA, MG), as carbonates. See Table VIII.
    - **Filtrate: ALKALI-GROUP** (NH₄, K, NA), as nitrates, etc. See Table IX.

* Lead is precipitated with the silver-group only when a large quantity is present, and then only partially; mercury is precipitated only when it is in the mercurous state.

PRECIPITATION AND ANALYSIS OF THE SILVER-GROUP.

TABLE III.—ANALYSIS OF THE SILVER-GROUP.

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Precipitate: AgCl, Hg$_2$Cl$_2$, PbCl$_2$. *Treat with hot water (P. 12).*	

Solution: PbCl$_2$. Add H$_2$SO$_4$ (P. 13).	Residue: AgCl, Hg$_2$Cl$_2$. *Pour NH$_4$OH through the filter (P. 15).*

Precipitate: PbSO$_4$. *Dissolve in* NH$_4$Ac, *add* K$_2$CrO$_4$ (P. 14).	Black Residue: Hg and Hg$\diagdown\substack{Cl\\NH_2}$	Solution: Ag(NH$_3$)$_2$Cl. Add HNO$_3$ (P. 15).
Yellow precipitate: PbCrO$_4$.		White precipitate: AgCl.

Procedure 11.—*Precipitation of the Silver-Group.*—Place the cold solution of the substance (P. 2, 3, 5, 6, or 8), which should contain 5 cc. 6–normal HNO$_3$ (or H$_2$SO$_4$) and should have a volume not greater than 30 cc., in a conical flask, and add to it 10 cc. NH$_4$Cl solution. (White precipitate, presence of SILVER–GROUP.)   Filter, and wash the precipitate with a small quantity of cold 1–normal HCl, not allowing the washings to run into the filtrate. (Precipitate, P. 12; filtrate, P. 21.)

Notes.—1. It is recommended that in general hard-glass conical flasks (the so-called Erlenmeyer flasks of Jena or Bohemian glass), rather than beakers or test-tubes, be employed for holding solutions that are being subjected to the operations of precipitation and heating.

2. Even in cases where it is not essential to add a perfectly definit volume of a reagent, the analyst should make it a practis to measure out the quantity to be added, rather than to pour in an indefinit quantity from the reagent bottle. For this purpose a 10 cc. graduate should be constantly at hand. For adding smaller quantities than 1 cc. a dropper should be used. This may be made by drawing out one end of a short glass tube to a wide capillary and capping the other end with a rubber nipple.

3. Unless the concentration is specified, it is understood that all salt solutions used as reagents are 1–normal; that is, that they contain one equivalent of salt per liter of solution.

4. By one *equivalent* of any substance is meant that weight of it which reacts with one atomic weight (1.008 grams) of hydrogen in any of its compounds or with the weight of any other substance which itself reacts with one atomic weight of hydrogen. Thus, one equivalent is the quantity in grams corresponding to the following formulas: 1NaOH, ½Ba(OH)$_2$, 1HCl, ½H$_2$SO$_4$, ⅓H$_3$PO$_4$, 1NH$_4$Cl, ½Na$_2$SO$_4$, ½CaSO$_4$, ⅓FeCl$_3$. When a substance may take part either in a reaction of metathesis or in one of oxidation and reduction, its *metathetical equivalent* has to be distinguished from its *oxidation equivalent*. Thus the

metathetical equivalent of nitric acid is 1HNO₃; but its oxidation equivalent (when it is reduced to NO) is ⅓HNO₃. In this book the term equivalent will always be used to denote the metathetical equivalent.—Note that the number of equivalents of a substance is a certain quantity of it; but that the term *normal* denotes its *concentration*, that is, the quantity of it per unit-volume (more specifically, the number of equivalents of it per liter).

5. If NH₄Cl produces no precipitate, it proves the absence of silver and mercurous mercury, but not of lead, since PbCl₂ is fairly soluble in water. Its solubility is greatly decreased by the addition of NH₄Cl; but a considerable quantity of lead may remain in solution, and thus escape detection in this group.

6. A white precipitate of BiOCl or SbOCl may separate on the addition of NH₄Cl when a large quantity of bismuth or antimony is present in the solution; but either of these precipitates dissolves upon washing with the 1-normal HCl.

7. The NH₄Cl precipitate is washed with 1-normal HCl, rather than with water, since PbCl₂ and AgCl are much less soluble in this dilute acid than in pure water, and since any BiOCl or SbOCl that may be present is dissolved out of the precipitate by the acid. The washings are not allowed to run into the filtrate, since a definit quantity of acid (equal to that previously added) must be present in the subsequent precipitation with H₂S (in P. 21). Incidentally, it is an advantage to remove from the solution some of the bismuth or antimony when a large quantity of either of these elements is present. An acid much more concentrated than 1-normal should not be used, since the silver-group chlorides are much more soluble in it, owing to the formation of acids with complex anions, such as $H^+AgCl_2^-$.

8. The fact that the solubility of PbCl₂ is greatly decreased by the addition of NH₄Cl or HCl is explained by the solubility-product principle as follows: In any dilute solution saturated at a definit temperature with lead chloride, the ion-concentration product $(Pb^{++}) \times (Cl^-)^2$ must, according to the mass-action law, have a constant value.* This particular value which the ion-concentration product has when the solution is saturated is commonly called the *solubility-product;* but the principles involved are less likely to be misunderstood if it be called the *saturation-value of the ion-concentration product.* Any solution in which the ion-concentration product exceeds the saturation-value of that product is evidently supersaturated and tends to deposit the solid substance; and any solution in which the ion-concentration product is less than the saturation-value is evidently undersaturated and tends to dissolve more of the solid substance. Now, when NH₄Cl or HCl is added to a saturated solution of PbCl₂ in water, the immediate effect is to increase the value of (Cl^-), and therefore of the product $(Pb^{++}) \times (Cl^-)^2$; but the solution becomes thereby supersaturated, and PbCl₂ will precipitate out of it until the saturation-value of the product $(Pb^{++}) \times (Cl^-)^2$ is restored.

Procedure 12.—*Extraction of the Lead with Boiling Water.*—Pour repeatedly through the filter containing the NH₄Cl precipitate (P. 11) a portion of 10–20 cc. boiling water. Wash the residue thoroly with hot water. (Residue, P. 15; solution, P. 13.)

*In mass-action expressions of this kind, chemical formulas within parentheses denote the *concentrations* of the respective substances, that is, the molal quantities of them per liter of solution.

Procedure 13.—*Precipitation of Lead with Sulfuric Acid.*—Add to the aqueous extract from the NH_4Cl precipitate (P. 12) one-fifth its volume of H_2SO_4 (s.g., 1.84); cool, shake the mixture, and allow it to stand for 5 minutes. (White precipitate, presence of LEAD.) Filter, wash the precipitate with H_2SO_4 (see Note 1), and then with a little water. (Precipitate, P. 14; filtrate, reject.)

> *Notes.—1. When it is directed to add HCl, HNO₃, H₂SO₄, HAc, NH₄OH, or NaOH without specifying the specific gravity or concentration, the ordinary reagent consisting of the 6-normal acid or base should be employed.*
>
> 2. $PbSO_4$ is slightly soluble in water, but much less so in dilute H_2SO_4; hence H_2SO_4 is added in excess to the solution and 6-normal H_2SO_4 is used for washing the precipitate.

Procedure 14.—*Confirmatory Test for Lead.*—Pour repeatedly through the filter containing the H_2SO_4 precipitate (P. 13) a 5–20 cc. portion of NH_4Ac solution; add to the filtrate a few drops K_2CrO_4 solution. (Yellow precipitate, presence of LEAD.)

> *Notes.—1. When two quite different limiting quantities of the reagent are specified (for example, 5–20 cc. as in this procedure), the quantity added should be adjusted to the size of the precipitate.*
>
> *2. The symbol Ac is used throughout this book to denote the acetate-radical ($C_2H_3O_2$). Thus NH_4Ac denotes ammonium acetate; HAc, acetic acid.*
>
> 3. The solubility of $PbSO_4$ in NH_4Ac solution depends on the formation by metathesis of undissociated $PbAc_2$, this salt being much less ionized than most other salts of the same valence-type. On the addition of a chromate to this solution the much more difficultly soluble $PbCrO_4$ is precipitated.
>
> 4. This confirmatory test distinguishes $PbSO_4$ from the difficultly soluble sulfates of barium, strontium, and calcium, since the chromates of all of these are more soluble than the sulfates.

Procedure 15.—*Detection of Silver and Mercury.*—Pour repeatedly through the filter containing the residue insoluble in hot water (P. 12) a 10–20 cc. portion of NH_4OH. (Black residue on the filter, presence of MERCUROUS MERCURY.) Acidify the filtrate with HNO_3. (White precipitate, presence of SILVER.)

> *Notes.—1.* The black residue produced by the action of NH_4OH on Hg_2Cl_2 is a mixture of finely divided mercury with the white mercuric compound $HgClNH_2$. The reaction is expressed by the equation:
> $$Hg_2Cl_2 + 2NH_4OH = HgClNH_2 + Hg + NH_4Cl + 2H_2O.$$
> The compound $HgClNH_2$ may be considered to be a derivative of $HgCl_2$, formed by replacing an atom of chlorin by the univalent radical NH_2.
>
> 2. An NH_4OH solution contains a considerable proportion of (unhydrated) NH_3; and AgCl dissolves readily in it, owing to the formation of a soluble complex salt, $Ag(NH_3)_2Cl$, which in solution is largely ionized into $Ag(NH_3)_2^+$ and Cl^- ions. This complex cation has so slight a tendency to dissociate into Ag^+ and NH_3 that the ratio of its concentration to that of the simple Ag^+ ion is about 10^7 in a normal solution of NH_4OH.
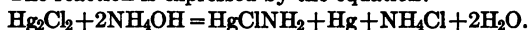
3. If the PbCl₂ was not completely extracted from the NH₄Cl precipitate by boiling water (in P. 12), it will be converted into a basic salt (Pb(OH)Cl) by the NH₄OH, and may pass through the filter, yielding a turbid filtrate. This basic salt will, however, dissolve on the addition of HNO₃.

PRECIPITATION AND SEPARATION OF THE COPPER AND TIN GROUPS.

See Table II, Page 37.

Procedure 21.—*Precipitation of the Copper and Tin Groups.*— Dilute to 100 cc. the filtrate from the NH₄Cl precipitate (P. 11) or the solution of the substance in HCl (P. 4), which should contain just 5 cc. of 6–normal HNO₃, H₂SO₄, or HCl. Place this solution in a conical flask provided with a two-hole rubber stopper in which is a tube leading to the bottom of the flask. Pass into it in the cold a slow current of H₂S, until, upon shutting off the gas and shaking thoroly, the liquid smells strongly of H₂S. Filter at once, wash the precipitate with hot water (see Note 1), and treat it by P. 22. Heat the filtrate nearly to boiling (to 70–90°), and pass H₂S into it at that temperature for 5–10 minutes.

If there is no further precipitate, treat the solution by P. 51.

If there is a further precipitate, boil the solution till it no longer smells of H₂S, filter out the precipitate, and evaporate the solution almost to dryness. Add 3–5 cc. 12–normal HCl and evaporate just to dryness (see Note 2), to destroy the HNO₃. Then add 10–15 cc. 6–normal HCl, saturate the cold solution with H₂S, heat it to 70–90°, and pass H₂S into it for 5–10 minutes. Filter out the precipitate, collecting it with that previously obtained from the hot solution; wash it, and test it for arsenic by P. 42. Treat the filtrate by P. 51.

Notes.—1. The washing of precipitates should in general be continued until the wash-water will no longer giv a test for any substance known to be present in the filtrate (for example, in this case for acid with blue litmus-paper or for chloride with AgNO₃). Precipitates which are practically insoluble in water (like all the sulfides and hydroxides that are met with in this System of Analysis) are best washed with nearly boiling water, as this runs through the filter more rapidly and extracts soluble substances more readily. Precipitates which are appreciably soluble should be washed with cold water and with only a small quantity of it. The wash-water should in general not be allowed to run into the filtrate, so as not to dilute it unnecessarily. When, however, a considerable proportion of the solution is likely to be retained in the filter and precipitate, it is well to add the first washings to the filtrate.

2. When it is directed, as in the last part of this procedure, to evaporate a solution just to dryness, this should be done on a steam-bath or by keeping the dish moving over a small flame in such a way as not to overheat the residue.

4

3. The formation of a white precipitate on diluting the solution to 100 cc. shows the presence of much bismuth or antimony. The precipitate, which consists of BiOCl or SbOCl, need not be filtered off. The formation, on passing in H₂S, of a white or yellowish precipitate which immediately turns black with more H₂S indicates mercury. (The white compound is HgCl₂.2HgS, and this is converted into black HgS by the excess of H₂S.) The formation of an orange precipitate shows antimony; of a yellow one, cadmium, arsenic, or stannic tin. All the other sulfides are black.

4. The acid concentration is made 0.3 normal (5 cc. of 6–normal acid being present in 100 cc.) and the solution is saturated with H₂S gas in the cold, since under these conditions even 1 mg. of cadmium, lead, or tin precipitates, and even 300 mg. of zinc remain in solution. This statement in regard to zinc is true, however, only when the solution contains also a considerable quantity of chloride-ion, such as was added in P. 11, and when it is not allowed to stand.

5. The solution is afterwards heated nearly to boiling and again saturated with H₂S, in order to ensure the detection of arsenic; for this element, when present in the higher state of oxidation (as arsenic acid) is only very slowly precipitated by H₂S in the cold. At 70–90° the precipitation is much more rapid, especially if the solution has been previously saturated with H₂S in the cold. Under these conditions even 1 mg. As gives a distinct precipitate in less than 5 minutes. Continuous treatment with H₂S at 70–90° in an open vessel does not, however, completely precipitate a large quantity of arsenic from such a weakly acid solution even within an hour. For this reason, when a considerable precipitate forms in the hot solution, it is directed to evaporate the filtrate, to add HCl to destroy the HNO₃ (which in the concentrated state would decompose the H₂S), to dissolve the residue in HCl, and to pass H₂S through the hot solution. From this concentrated acid solution the arsenic precipitates completely in 5–10 minutes. The reasons for this peculiar behavior of arsenic in the higher state of oxidation are presented in Note 2, P. 43.

6. The effect of acid on the precipitation of the sulfides is explained by the mass-action law and ionic theory as follows: When a dilute solution, whether aqueous or acid, is saturated at a definit temperature with H₂S gas under the atmospheric (or any definit) pressure the H₂S present as such always has the same concentration. This ionizes, however, to a slight extent into H⁺ and HS⁻, and to a still less extent into 2H⁺ and S⁻. It is only the latter form of ionization that needs to be considered here. Now between the H₂S and its ions must be maintained the equilibrium expressed by the equation $(H^+)^2 \times (S^-) = \text{const.} \times (H_2S)$; or, since in this case $(H_2S) = \text{const.}$, as just stated, it follows that also $(H^+)^2 \times (S^-) = \text{const.}$ From this it is evident that when (H^+) is increased by the addition of acid to the solution, (S^-) must be decreased in the proportion in which the square of (H^+) is increased; thus, if (H^+) is doubled, (S^-) will be reduced to one-fourth. But in order that a sulfide—for example, of the formula $M^{++}S^-$—may precipitate, the concentration-product $(M^{++}) \times (S^-)$ must attain a value equal to the solubility-product, which is the value of this concentration product which prevails in pure water in contact with the solid sulfide. The solubility-product varies, however, with the nature of the sulfide and with the temperature; and therefore the acid concentration that will barely permit of precipitation when (M^{++}) has a definit value (for example, 1 mg. in 100 cc.) will be different for different

sulfides and for the same sulfide at different temperatures. Thus if the elements are arranged in the order in which they are precipitated from cold HCl solutions as the acid-concentration is progressivly decreased, the series is approximately as follows: arsenic, mercury and copper, antimony, bismuth and stannic tin, cadmium, lead and stannous tin, zinc, iron, nickel and cobalt, manganese. The acid concentration which permits precipitation also varies with the ionization of the acid; thus zinc is precipitated from a fairly concentrated solution of acetic acid, since, owing to the slight ionization of this acid, the H^+ concentration is less than in a far more dilute solution of HCl. The three acids, HCl, HNO_3, and H_2SO_4, do not, however, differ greatly in this respect, since they are all largely ionized in dilute solution.

   7. A white, finely divided precipitate of free sulfur will be formed if the solution contains substances capable of oxidizing H_2S. The most important of these likely to be present are ferric salts, chromates, permanganates, and chlorates. The reduction by H_2S of ferric salts to ferrous is attended by a change in color from yellow to colorless; of chromates to chromic salts, from orange to green; and of permanganates to manganous salts, from purple to colorless. Nitric acid, if it were fairly concentrated, would also destroy the H_2S; but at the concentration in question (0.3 normal) it has scarcely any oxidizing action even in boiling solution.

Procedure 22.—*Separation of the Copper and Tin Groups by Ammonium Sulfide.*—Transfer the H_2S precipitate (P. 21) to a small casserole, add to it 10–25 cc. ammonium monosulfide (if the original substance was treated with strong HNO_3 in P. 3), or 5–10 cc. ammonium polysulfide (if it was dissolved in water or in dilute HNO_3 in P. 3), cover the dish, and warm the mixture slightly (to 40–60°) for about 10 minutes with frequent stirring. Add 10 cc. water, filter, and wash once with hot water. [If the residue is large and much has been extracted from it by this treatment, as indicated by its appearance or as determined in P. 23, warm it again with ammonium monosulfide or polysulfide, and filter, collecting the filtrate separate from the first one.] Wash the residue thoroly with hot water (or, in case the precipitate tends to pass through the filter, with hot water containing about 5% NH_4NO_3), not adding the washings to the filtrate. (Residue, P. 31; solutions, P. 23.)

    Notes.—1. *When a small precipitate is to be treated with a solvent, this may be done by pouring a portion of the solvent repeatedly through the filter. When a considerable precipitate is to be so treated, the filter is opened, the portions to which no precipitate adheres are torn off, and the remainder is laid along the side of a casserole; the solvent is then poured over it and is swashed to and fro, so as to wash the precipitate off the filter. If this succeeds, the filter is drawn out and thrown away; otherwise, it is allowed to disintegrate and filtered out together with any residue.*

    2. The chemical action of ammonium sulfide in dissolving the sulfides of the tin-group depends on the formation of soluble salts of sulfoacids with

complex anions. When the monosulfide is used, the reactions are as follows:

$$\left\{ \begin{array}{l} As_2S_3 \\ Sb_2S_3 \end{array} \right\} + 3(NH_4)_2S = 2 \left\{ \begin{array}{l} (NH_4^+)_3AsS_3^= \\ (NH_4^+)_3SbS_3^= \end{array} \right\}$$

$$\left\{ \begin{array}{l} As_2S_5 \\ Sb_2S_5 \end{array} \right\} + 3(NH_4)_2S = 2 \left\{ \begin{array}{l} (NH_4^+)_3AsS_4^= \\ (NH_4^+)_3SbS_4^= \end{array} \right\}$$

$$SnS_2 \quad + \quad (NH_4)_2S = \quad (NH_4^+)_2SnS_3^=.$$
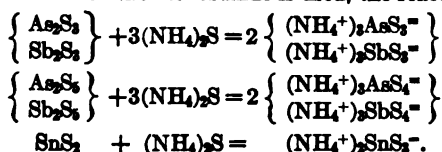
The excess of sulfur in the polysulfide oxidizes the lower sulfides (As_2S_3, Sb_2S_3, SnS) to the same sulfosalts as are obtained by dissolving the higher sulfides (As_2S_5, Sb_2S_5, SnS_2) in ammonium monosulfide. It will be seen that these sulfo-salts are analogous to the salts of the familiar oxygen acids of these elements, the difference being that sulfur has replaced oxygen; and they are so named as to indicate this relationship. Thus the five sulfo-salts whose formulas are given above are called ammonium sulfarsenite, sulfantimonite, sulfarsenate, sulfantimonate, and sulfostannate.

3. When the polysulfide has to be employed, a small volume (5–10 cc.) is used at first, so that upon acidifying it (in P. 23) only a small quantity of sulfur will separate, thus making it possible to determin the presence or absence of tin-group sulfides.

4. The ammonium monosulfide reagent is a solution of $(NH_4)_2S$ and of the products of its hydrolysis, NH_4SH, NH_4OH, and a little H_2S. The polysulfide contains in addition various polysulfides of the forms $(NH_4)_2S_{2-5}$ and $(NH_4)HS_{2-5}$ in unknown proportions. The monosulfide is prepared by saturating concentrated NH_4OH with H_2S gas (whereby NH_4SH is formed), adding an equal volume of NH_4OH, and diluting the solution. The polysulfide is prepared from this solution by dissolving sulfur in it. These reagents, especially the monosulfide, should be kept as far as possible out of contact with the air, which is conveniently done by storing them in small, completely filled, glass-stoppered bottles; for the oxygen of the air destroys the sulfide with liberation of sulfur, which at first combines with the still unchanged sulfide, but later precipitates when the oxidation becomes more complete.

5. In separating the copper-group from the tin-group (colorless) ammonium monosulfide is used rather than (yellow) polysulfide whenever the H_2S precipitate must contain any tin and most of any antimony present in the state of the higher sulfide (SnS_2 or Sb_2S_5). This is the case when hot concentrated nitric acid was used originally in dissolving the substance, but may not be so when water or dilute HNO_3 was used; hence the directions as to the choice between the two solvents. The polysulfide has the disadvantage that it dissolves a not inconsiderable quantity of CuS and HgS, thus making the tests for copper and mercury less delicate, and making it more difficult to determin from the color of the HCl precipitate obtained from the ammonium sulfide solution in P. 23 whether or not elements of the tin-group are present. The polysulfide must, nevertheless, be used if tin may be present as SnS, or much antimony as Sb_2S_3; for in the monosulfide SnS is only slightly soluble, and Sb_2S_3 only moderately soluble.

6. More specifically, the behavior of the various sulfides, when warmed with 10 cc. of these reagents, is as follows: Of the sulfides of the copper-group none dissolves to a significant extent in ammonium monosulfide. 5–10 mg. CuS and 0.5–1.0 mg. HgS may, however, dissolve in the polysulfide when the substance

contains a large quantity of these elements. Yet when only 2 mg. are present, either of these elements can be detected in the analysis of the copper-group, even when the polysulfide is used, provided only one treatment with it has been made. Of the sulfides of the tin-group, 500 mg. of As as As_2S_3 or As_2S_5, of Sb as Sb_2S_5, or of Sn as SnS_2 dissolves in either the monosulfide or polysulfide, and 500 mg. of Sn as SnS or of Sb as Sb_2S_3 dissolve in the polysulfide. Scarcely any SnS and only 50–100 mg. Sb as Sb_2S_3 dissolve in the monosulfide.

7. Even when a quantity of only 1 or 2 mg. of arsenic or antimony is present with a large quantity (even 500 mg.) of an element of the copper group, enough is extracted by either the monosulfide or polysulfide to be detected in the subsequent tests. With tin, however, the separation is imperfect; for, when a large quantity of elements of the copper-group and only 3–5 mg. of tin are present, the whole of this may remain undissolved; indeed, when much cadmium is present and the tin is in the stannous state, as much as 15 mg. of the latter may be wholly left in the residue, even when the polysulfide is used. On this account it is necessary to test for tin in the course of the analysis of the copper group.

8. Some sulfides, especially CdS, upon washing pass through the filter in the colloidal condition; the addition of a salt, such as NH_4NO_3, prevents this by coagulating the colloidal particles.

Procedure 23.—*Reprecipitation of the Tin-Group.*—Dilute in a small flask the first portion of the ammonium sulfide solution (P. 22) with about 20 cc. water, make it slightly acid with HCl, and shake the mixture vigorously for 2 or 3 minutes to coagulate the precipitate. (White or pale yellow precipitate, absence of TIN–GROUP; deep yellow or orange precipitate, presence of TIN–GROUP.) [Treat the second portion of the ammonium sulfide solution (P. 22) in the same way, and unite the precipitate, if considerable in amount, with the first one.] Filter out and wash the precipitate, using suction, finally sucking it as dry as possible. (Precipitate, P. 41; filtrates, reject.)

Notes.—*1. In cases where the filtration is slow, where the precipitate must be washed with very little water, or where (as in this case) it must be freed as far as possible from water, it is advisable to filter with the aid of suction. This operation is carried out by reinforcing the ordinary filter with a small hardened filter placed below it in the funnel, by inserting the funnel in a rubber stopper in the neck of a filter-bottle, and connecting the side arm of the filter-bottle to a suction-pump by means of a rubber tube carrying a screw-clamp. The suction should be applied very gradually so as to avoid breaking the filter. The filtrate should be poured out of the filter-bottle before beginning to wash the precipitate.*

2. Whenever it is directed to make a solution slightly acid or alkaline, this should be done carefully as follows: Add from a graduate somewhat less acid or alkali than will neutralize the alkali or acid known to be present in the solution. Then add from a dropper more of the acid or alkali, a drop or two at a time, till a glass rod dipped in the solution and touched to a piece of blue or red litmus paper placed on a watch-glass changes the color of the litmus.

3. When the HCl is added to the solution of the sulfosalts, the corresponding sulfoacids which are liberated decompose immediately into H_2S and the solid sulfides. These are now necessarily in the higher state of oxidation, since the lower sulfides, if originally present, have been oxidized by the polysulfide. The fact that the sulfoacids decompose while the sulfosalts are stable is a consequence of the mass-action-law. Thus, since the complex anions dissociate according to the equations,

$$SnS_3^- = SnS_2 + S^-, \quad 2AsS_4^- = As_2S_5 + 3S^-, \quad 2SbS_4^- = Sb_2S_5 + 3S^-,$$

this law evidently requires that the anion decompose to a greater extent into the unionized sulfides (SnS_2, etc.) the smaller the concentration of the S^- ion in the solution. Now in the solution of the largely ionized $(NH_4)_2S$ there is a fairly large concentration of S^- ion; but when the solution is made acid with HCl, the S^- ion is, for the most part, converted by the relativly large concentration of the H^+ ion into the slightly ionized substances HS^- and H_2S. Consequently the concentration of the unionized sulfides becomes great enough to supersaturate the solution, and the solid sulfide separates out.

4. Much time is ordinarily saved by determining at this point whether or not any element of the tin-group is present. When ammonium monosulfide has been used, there is never any difficulty in drawing a definit conclusion in regard to this from the size and appearance of the HCl precipitate; for in the absence of the tin-group only a very small, nearly white precipitate of finely divided sulfur separates. Even when ammonium polysulfide has been used, it is usually possible to decide as to the presence or absence of a small quantity of arsenic, antimony, or tin; for, altho considerable sulfur is then liberated, yet the precipitate is distinctly lighter colored and smaller in appearance when it consists only of sulfur than it is when even 1 mg. of arsenic, antimony, or tin is present with the sulfur. The difference is most marked when only a slight excess of HCl has been used in the acidification and when the acidified mixture has been shaken, but not heated.

5. When, however, the HCl precipitate from a polysulfide solution is fairly small and is dark brown (indicating copper) or dark gray or black (indicating mercury) or of unpronounced yellow or orange color, so as to make any conclusion as to the tin-group doubtful, the precipitate is best treated as follows: Heat it with 15–20 cc. NH_4OH almost to boiling for 5 minutes and filter; test the precipitate for copper by P. 31, 35, and 37 if it has not already been found present; add to the filtrate a few drops of ammonium monosulfide, filter out any precipitate, heat the filtrate to boiling, make it acid with HCl, shake, filter out the precipitate, and treat it by P. 41 as usual. The character of the HCl precipitate now obtained will clearly indicate the presence or absence of the tin-group; for by the treatment with NH_4OH the excess of sulfur originally present and any CuS is left undissolved, and by the $(NH_4)_2S$ added to the solution any mercury present is precipitated, so that the HCl precipitate can contain only sulfides of the tin-group and a very little sulfur. As_2S_5, Sb_2S_5, and SnS_2 all dissolve in NH_4OH (tho in the cases of Sb_2S_5 and SnS_2 less abundantly than in ammonium sulfide), owing to the formation of a mixture of salts of partially sulfurated acids, such as H_3AsO_2S and $H_3AsO_2S_2$. The addition of $(NH_4)_2S$ to the NH_4OH solution and the heating serve to convert these into the fully sulfurated acids, such as H_3AsS_4; from which $\overline{H}Cl$ will then precipitate the simple sulfides much more completely.—The inci-

dental removal of the small amounts of CuS and HgS by the NH_4OH treatment is not necessary so far as the analysis of the tin-group is concerned, since their presence does not interfere with the detection of even 1 mg. of arsenic, antimony, or tin; but it does enable 1 or 2 mg. of copper to be detected which might otherwise be lost.—In this connection it may be mentioned that a mixture of SnS_2 and Sb_2S_5 does not always have a color intermediate between the yellow and orange colors of the separate sulfides, but that it may be brown or dark gray.

ANALYSIS OF THE COPPER-GROUP.

TABLE IV.—ANALYSIS OF THE COPPER–GROUP.

RESIDUE FROM AMMONIUM SULFIDE TREATMENT: HgS, PbS, Bi₂S₃, CuS, CdS.

RESIDUE FROM AMMONIUM SULFIDE TREATMENT: HgS, PbS, Bi_2S_3, CuS, CdS.
Boil with HNO_3 (P. 31).

Residue: HgS. *Add Br_2 solution (P. 32).*	Solution: Pb, Bi, Cu, Cd as nitrates. *Add H_2SO_4, evaporate, add water (P. 33).*				
Residue: Sulfur.	Solution: HgBr₂. *Add $SnCl_2$.*	Precipitate: PbSO₄. *Dissolve in NH_4Ac, add K_2CrO_4 (P. 34).*	Filtrate. *Add NH_4OH (P. 35).*		
	White or gray precipitate: Hg_2Cl_2 or Hg.		Precipitate: Bi(OH)₃. *Dissolve in HCl, evaporate, add to water (P. 36).*	Filtrate: $Cu(NH_3)_4SO_4$, $Cd(NH_3)_4SO_4$.	
		Yellow precipitate: PbCrO₄.		*To a small part add HAc and $K_4Fe(CN)_6$ (P. 37).*	*To the remainder add KCN and H_2S (P. 38).*
			White precipitate: BiOCl. *Add Na_2SnO_2.*		
			Black residue: Bi.	Red precipitate: $Cu_2Fe(CN)_6$. White precipitate: $Cd_2Fe(CN)_6$.	Yellow precipitate: CdS.

Procedure 31.—*Treatment of the Sulfides with Nitric Acid.*—To the residue from the ammonium sulfide treatment (P. 22) in a casserole add 10–20 cc. 2–normal HNO_3 solution, heat to boiling, and boil gently for a minute or two. (Black residue, possible presence of MERCURY.) Filter and wash. (Residue, P. 32; solution, P. 33.)

Notes.—1. Boiling HNO_3 of this concentration dissolves the sulfides of lead, bismuth, copper, and cadmium almost immediately, and is therefore preferable to a more dilute acid, with which the reaction would require for its completion several minutes' boiling. Scarcely any HgS is dissolved by the above treatment, unless the boiling is long continued.

2. Moderately concentrated HNO_3 dissolves sulfides much more rapidly than HCl or H_2SO_4 of the same concentration; for with the latter acids the sulfide-ion is removed from the solution only by combination with the hydrogen-ion and by the volatilization of the H_2S formed thereby, while with HNO_3 the sulfide-ion (or the H_2S in equilibrium with it) may also be destroyed by oxidation to ordinary sulfur. The oxidizing effect of HNO_3 is, however, small, unless it is hot and moderately concentrated.

3. That HgS, unlike the other sulfides, does not dissolve in the dilute HNO_3 is doubtless due to the much smaller concentration of its ions in its saturated solution and to the fact that at this small concentration sulfide-ion (or the H_2S in equilibrium with it at a correspondingly small concentration) is oxidized only very slowly by the dilute HNO_3. HgS is, however, readily dissolved by more vigorous oxidizing agents, such as *aqua regia* or bromin solution, since they react rapidly with sulfide-ion (or with H_2S) even when its concentration is very small.

4. If more concentrated HNO_3 be used, or if the acid become concentrated by long boiling, the black HgS is dissolved in part, and the remainder is converted into a heavy, white, difficultly soluble compound $(Hg(NO_3)_2.2HgS)$.

5. When much lead, copper, or bismuth is present the sulfur formed will generally enclose enough of the undissolved sulfide to give it a black color. A black residue is therefore not necessarily HgS, but must be further tested for mercury as described in P. 32.

6. Some sulfur is always oxidized to H_2SO_4 by the boiling HNO_3; but, even in the presence of much lead, $PbSO_4$ is not precipitated, owing to its moderate solubility in HNO_3.

7. Any SnS or SnS_2 not extracted by the ammonium sulfide treatment will be converted by the HNO_3 into metastannic acid $(H_2SnO_3,)$ most of which remains undissolved. Therefore, even a light-colored residue must be carefully collected if tin is to be tested for in this group.

Procedure 32.—*Confirmatory Test for Mercury.*—Transfer the residue undissolved by HNO_3 (P. 31), with the filter if necessary, to a casserole, add 10–40 cc. saturated Br_2 solution, cover the dish, and warm slightly for 5–10 minutes, with frequent stirring. Boil the mixture until the bromin is expelled, and filter. (Residue, see Note 3.) Cool the solution, and add to it a few drops of HCl and one drop of $SnCl_2$ solution; then add 3–5 cc. $SnCl_2$ solution. (White precipitate turning gray, or gray precipitate, presence of MERCURY.) (Residue and solution, reject.)

Notes.—1. In the final test for mercury HCl is added to prevent the precipitation of a basic tin salt when the $SnCl_2$ reagent is diluted, and to cause the formation at first of white Hg_2Br_2 or Hg_2Cl_2. For the latter reason, also, a single drop of $SnCl_2$ solution is first added to the cold solution. By the excess of $SnCl_2$ the white precipitate is reduced to gray, finely divided mercury.

2. The presence of mercury at this point shows that it was originally in the mercuric state only when the substance was dissolved (in P. 2) without the use of hot or concentrated HNO_3.

3. If elements of the copper-group are present in large quantity (100–500 mg.), the residue from the Br_2 treatment should be tested for tin, in order to guard against overlooking the presence of a small quantity of this element in the substance. For, as stated in P. 22, Note 7, a quantity of tin as large as 5 mg. (or even larger when stannous tin and cadmium are both present) may remain entirely in the residue undissolved by ammonium sulfide when this residue is large. To recover the tin, proceed as follows: Digest the residue from the Br_2 treatment, if it is still dark-colored, with another portion of Br_2

solution (to extract the rest of the mercury), filter, reject the filtrate, and warm the residue slightly with 2–5 cc. ammonium monosulfide. Filter, and unite the solution with the main ammonium sulfide solution obtained in P. 22. By this procedure 2 mg. Sn can be detected.

4. Bromin solution dissolves HgS, but leaves in the residue any metastannic acid. In case tin need not be tested for at this point, the residue may be more quickly dissolved by warming it with HCl and adding gradually a little solid KClO₄. Metastannic acid, being soluble in HCl, then passes into solution with the mercuric salt, but it does not interfere with the test for mercury.

Procedure 33.—*Precipitation of Lead with Sulfuric Acid.*—To the HNO₃ solution (P. 31) add 2–3 cc. H₂SO₄ (s.g., 1.84), and evaporate in a casserole to a volume of 2–3 cc. until dense white fumes of H₂SO₄ begin to come off. Cool the mixture and pour it into 10–15 cc. cold water, rinsing out the casserole with the same solution. Cool again, shake, and allow the mixture to stand 5 minutes, but not much longer. (Finely divided white precipitate, presence of LEAD.) Filter and wash the precipitate with 6–normal H₂SO₄, and finally with a little water. (Precipitate, P. 34; filtrate, P. 35.)

Notes.—1. PbSO₄ is somewhat soluble both in water and in concentrated H₂SO₄, but much less so in moderately dilute H₂SO₄, its solubility being scarcely appreciable in mixtures containing one volume of H₂SO₄ (s.g., 1.84) and two to six volumes of water. That the solubility in dilute H₂SO₄ is less than that in water is due mainly to the common-ion effect. Concentrated H₂SO₄ is, of course, an entirely different solvent. PbSO₄ dissolves fairly readily in dilute HNO₃, owing to the tendency to form the intermediate HSO₄⁻ion; hence, to ensure complete precipitation of PbSO₄, the HNO₃ must be removed by evaporation.

2. When much bismuth is present it ordinarily dissolves at first when the water is added to the concentrated H₂SO₄, provided the mixture is kept cold; but from this solution a coarsely crystalline precipitate of an oxysulfate, such as (BiO)₂SO₄, separates slowly upon standing in the cold but almost immediately upon heating, and to such an extent that there may remain in solution not more than 50 mg. of bismuth. If the precipitate is of this character, free it from bismuth before applying the confirmatory test for lead by pouring repeatedly through the filter a 5–10 cc. portion of HCl and treating the solution so obtained by P. 33. The evaporation with H₂SO₄ is necessary in order to ensure reprecipitation of the PbSO₄ that has been dissolved by the HCl.

Procedure 34.—*Confirmatory Test for Lead.*—Pour repeatedly through the filter containing the H₂SO₄ precipitate (P. 33) a 10–20 cc. portion of NH₄Ac solution. To the filtrate add a few drops of K₂CrO₄ solution and 2–5 cc. HAc. (Yellow precipitate, presence of LEAD.)

Note.—This confirmatory test for lead should not be omitted; for the H₂SO₄ precipitate may consist not only of PbSO₄ but of (BiO)₂SO₄ or of BaSO₄, which last closely resembles PbSO₄ in appearance. (BiO)₂SO₄ dissolves in NH₄Ac

solution and gives a yellow precipitate on adding K_2CrO_4; but this precipitate, unlike $PbCrO_4$, dissolves readily in acetic acid. $BaSO_4$ is not dissolved by NH_4Ac solution, owing to its very slight solubility in water and the fact that barium acetate, unlike lead acetate, is a largely ionized salt.

Procedure 35.—*Precipitation of Bismuth with Ammonium Hydroxide.*—To the H_2SO_4 solution (P. 33) add NH_4OH slowly until a strong odor of it persists after shaking. (White precipitate, possible presence of BISMUTH; blue solution, presence of COPPER.) Shake to cause coagulation, filter, and wash the precipitate. (Precipitate, P. 36; filtrate, P. 37 and 38.)

> *Notes.*—1. The precipitate produced by NH_4OH may consist also of $Fe(OH)_3$, or of other hydroxides of the iron-group, if these elements were carried down in the H_2S precipitate or were not completely removed from it by washing. The formation of a small precipitate is, therefore, not a sufficient proof of the presence of bismuth, and the confirmatory tests of P. 28 must be applied.
>
> 2. $Cd(OH)_2$ or $Cu(OH)_2$, tho only very slightly soluble in water, dissolves in NH_4OH owing to the combination of the Cd^{++} or Cu^{++} ion present in the saturated solutions with NH_3, forming the complex cation $Cd(NH_3)_4^{++}$ or $Cu(NH_3)_4^{++}$. These complex cations have an extremely small ionization tendency; thus in a normal NH_4OH solution the ratio of the concentration of the complex cadmium ion to the simple cadmium ion is about 10^7. The solubility of these hydroxides in NH_4OH is greatly increased by the presence of ammonium salts, since these salts, owing to the common-ion effect, greatly reduce the ionization of the NH_4OH, and therefore the OH^- concentration in the solution, thus enabling the Cd^{++} or Cu^{++} concentration, and therefore also the corresponding complex ion concentration, to attain a much larger value than in the saturated solutions of $Cd(OH)_2$ or $Cu(OH)_2$ in NH_4OH alone. It will be noticed that four distinct equilibria are involved—that between solid $Cd(OH)_2$ or $Cu(OH)_2$ and its ions; that between Cd^{++} or Cu^{++}, NH_3 and $Cd(NH_3)_4^{++}$ or $Cu(NH_3)_4^{++}$; that between NH_4OH, NH_3, and H_2O; and that between NH_4OH, NH_4^+, and OH^-. It may be further mentioned that, since in any dilute solution the concentration of the water is substantially constant, the concentration of any hydrate (like NH_4OH) is proportional to that of the anhydrous substance (NH_3).

Procedure 36.—*Confirmatory Tests for Bismuth.*—Dissolve the NH_4OH precipitate (P. 35) by pouring a little HCl through the filter, evaporate off the acid almost completely, leaving the residue only barely moist with it, add 1–2 cc. water, pour the solution into a flask containing 100 cc. water heated to 50–70°, and allow the mixture to stand 2 or 3 minutes. (White precipitate, presence of BISMUTH.) Filter the liquid (even if it looks clear), wash the filter with a little water, and pour through it a freshly prepared solution of sodium stannite. (Black residue, presence of BISMUTH.)

> *Notes.*—1. The white precipitate of BiOCl formed in the first confirmatory test for bismuth is produced by the hydrolysis of $BiCl_3$. If HCl, the other

product of the hydrolysis, is present in the solution, the reaction will not be complete, and a greater or less quantity of bismuth will remain in solution. This quantity increases very rapidly with the acid concentration. For this reason, if 0.5 mg. of bismuth is to be detected, the HCl must be removed by evaporation so completely that not more than 0.2 cc. remain, and the solution must be added to a large volume of water. Warm water is used, because the precipitation of BiOCl takes place more rapidly at the higher temperature. Antimony under these conditions givs a similar precipitate, but it can not be present in the HNO_3 solution of the sulfides in quantity sufficient to giv a precipitate with NH_4OH.

2. The expression for the solubility-product of BiOCl is $(Bi^{+++}) \times (O^-)$ $\times (Cl^-) = $ const. Acids greatly increase its solubility because their H^+ ion combines with the O^- ion to form water, which is a very slightly ionized substance. Chlorides also increase its solubility; for the increase of (Cl^-) which they directly produce is more than compensated by the decrease of (Bi^{+++}) which arises from the formation of unionized $BiCl_3$ (and probably also of complex anions, such as $BiCl_4^-$).

3. The solution of sodium stannite (Na_2SnO_2) is prepared when needed by adding NaOH solution to $SnCl_2$ solution until the $Sn(OH)_2$ first formed is dissolved. The solution must be freshly prepared, because it decomposes spontaneously into sodium stannate (Na_2SnO_3) and metallic tin, and because it oxidizes in contact with air to sodium stannate. SnO_2H_2 is an example of a so-called amphoteric substance—one which acts either as a base or an acid as is shown by its solubility in both acids and alkalies.

4. The final test with sodium stannite depends on the reduction of BiOCl to black metallic bismuth. The test is an extremely delicate one, and by it may be detected a quantity of bismuth so small as to produce only a scarcely visible turbidity of BiOCl; for, when the precipitate in such a solution is collected on a filter and treated with stannite, the black color of the bismuth is very apparent. Antimony oxychloride, even if present, would not be blackened by the stannite. The NH_4OH precipitate itself might be directly tested with this reagent; for the other reducible substances, like $Fe(OH)_3$, $Pb(OH)_2$, or $Cu(OH)_2$, that might possibly be present in that precipitate are not reduced by short contact with stannite solution in the cold. It is, however, often desirable to get the double indication of the presence of bismuth, as furnished by the precipitation of the oxychloride by water and by its blackening with the sodium stannite.

Procedure 37.—*Confirmatory Test for Copper.*—Acidify one-fourth of the NH_4OH solution (P. 35) with HAc, add one drop $K_4Fe(CN)_6$ solution, and allow the mixture to stand for several minutes. (Red precipitate, presence of COPPER.) Then add 1–2 cc. more $K_4Fe(CN)_6$ solution. If it is uncertain whether there is a precipitate, pour the solution through a filter and wash with a little water. (Pink color on the filter, presence of COPPER.)

Notes.—1. The confirmatory test for copper is more delicate than the formation of a blue color with NH_4OH (P. 35). It should, therefore, be tried even when the NH_4OH solution is colorless. Cadmium is also precipitated

by $K_4Fe(CN)_6$; but the precipitate is white, and does not prevent the pink color of the copper compound from being detected, provided only a small quantity of $K_4Fe(CN)_6$ is added ; for the copper salt, owing to its smaller solubility, is first precipitated.

2. Nickel, like copper, givs a blue solution with excess of NH_4OH; but even if present it would giv a green, not a red, precipitate with $K_4Fe(CN)_6$.

Procedure 38.—*Detection of Cadmium.*—Treat the remainder of the NH_4OH solution (P. 35) with KCN solution (see Note 1), adding only a few drops if the solution is colorless, but enough to decolorize it if it is blue, and pass in H_2S gas for about half a minute. (Flocculent yellow precipitate, presence of CADMIUM.)

Notes.—1. In working with KCN bear in mind that it is extremely poisonous. Take care not to get it on the hands; also not to breathe its fumes, especially when a solution containing it is acidified.

2. By the addition of KCN the copper salt is reduced from the cupric to the cuprous state and then combines with the excess of KCN to form the complex salt $K^+Cu(CN)_2^-$ (potassium cuprocyanide). This result is due to the fact that cupric cyanide tends to decompose spontaneously into cuprous cyanide (CuCN) and cyanogen $(CN)_2$, and that this reaction takes place completely in KCN solution, owing to removal of the CuCN by combination with the excess of KCN. In the presence of NH_4OH the cyanogen is not evolved as a gas, but reacts with it, forming cyanate (NH_4CNO) and cyanide and other more complex products. The fact that neither CuS nor Cu_2S is precipitated from this solution by an alkaline sulfide shows that neither the Cu^{++} nor Cu^+ concentration is sufficient to cause the value of the product $(Cu^{++}) \times (S^-)$ or $(Cu^+)^2 \times (S^-)$ to attain that prevailing in solutions saturated with CuS or Cu_2S. The extremely small Cu^+ concentration is due to the very slight ionization tendency of the complex anion $Cu(CN)_2^-$; thus it has been estimated that in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple Cu^+ ion is about 10^{26}.

3. The cadmium ammonia salt is also converted by KCN into a complex cyanide, namely, $K^+_2Cd(CN)_4^-$ (potassium cadmicyanide), since its complex anion has a much smaller ionization tendency than the cation $Cd(NH_3)_4^{++}$; thus in a normal KCN solution the ratio of the concentration of the complex anion to that of the simple Cd^{++} ion is about 10^{17}. Yet this complex anion is sufficiently dissociated into Cd^{++} to cause the solution to become supersaturated with CdS when an alkaline sulfide is added.

4. A very small black precipitate (which may be due to HgS or PbS) may sometimes be produced in the final test for cadmium with H_2S ; but, provided the analysis has been properly conducted, not in sufficient quantity to prevent the yellow color of 1 or 2 mg. of CdS from being seen. In case a black precipitate is produced, and thus prevents a positiv conclusion as to the presence or absence of a little cadmium, the precipitate may be treated, in order to eliminate the black sulfide, as follows: Boil the precipitate gently for about 5 minutes in a covered casserole with about 15 cc. of a mixture of one volume of 6–normal H_2SO_4 with four volumes of water, filter, cool the filtrate, add to it three times its volume of water, and pass H_2S into it for 5–10 minutes. A yellow precipitate of CdS should then be obtained, if cadmium is present.

ANALYSIS OF THE TIN-GROUP.

TABLE V.—ANALYSIS OF THE TIN-GROUP.

PRECIPITATE FROM AMMONIUM SULFIDE SOLUTION: As_2S_5, Sb_2S_5, SnS_2.
Heat with 10 cc. 12–normal HCl (P. 41).

Solution: $SbCl_3$, $SnCl_4$. *Dilute to 50 cc., heat, and pass in H_2S (P. 44).*		Residue: As_2S_5. *Dissolve in HCl and $KClO_3$ (P. 42).*
Orange precipitate: Sb_2S_3. *Dissolve in HCl, add Sn and Pt (P. 45).*	Solution: $SnCl_4$. *Cool, dilute, pass in H_2S (P. 46).*	Solution: H_3AsO_4. *Add NH_4OH, NH_4Cl, and $MgCl_2$ (P. 42).*
Black deposit: Sb. *Treat with NaOCl.*	Yellow precipitate: SnS_2. *Evaporate without filtering, add Pb, boil (P. 46.)*	White precipitate: $MgNH_4AsO_4$. *Dissolve in HCl, add H_2S (P. 43).*
Black deposit: Sb.	Solution: $SnCl_2$. *Add $HgCl_2$ (P. 46).*	Yellow precipitate: As_2S_5, As_2S_3, and S.
	White precipitate: Hg_2Cl_2.	

Procedure 41.—*Treatment of the Sulfides with Strong Hydrochloric Acid.*—Transfer the precipitated sulfides dried by suction (P. 23) to a wide test-tube, add from a small graduate exactly 10 cc. 12-normal HCl, and heat nearly but not quite to boiling (preferably by immersing the test-tube in boiling water or in a steam bath) for about 10 minutes with frequent stirring. Add 5 cc. water from a graduate containing 40 cc. water, filter, wash once with about 5 cc. water from the graduate, collecting this wash-water with the filtrate; remove the filtrate, and add to it the water remaining in the graduate. Wash the residue with 6–normal HCl. (Residue, P. 42; filtrate, P. 44.)

Notes.—1. If a much weaker HCl solution than the acid of 12–normal concentration is used, or if the acid becomes diluted by an unnecessary quantity of water left in the precipitate, much Sb_2S_5 will be left undissolved. Even with the strong acid some Sb_2S_5 may remain undissolved, especially when a large quantity is present, in which case the residue if small in amount will have an orange color. This small quantity of Sb_2S_5 would be only very slowly removed by further treatments with HCl; it does not, however, interfere with the subsequent tests for arsenic. Moreover, when only a small quantity of Sb_2S_5 is

originally present, a large proportion of it is extracted, so that it will not escape detection. Sb_2S_5 dissolves with formation of $SbCl_3$ and liberation of sulfur; SnS_2, with formation of $SnCl_4$.

2. If the solution be kept just below the boiling-point during the treatment with HCl, the amount of As_2S_5 which dissolves in ten minutes is insignificant. But this is no longer true if the solution be allowed to boil; for the boiling rapidly expels from the solution the H_2S liberated from the other sulfides or by slight decomposition of the As_2S_5 itself, and thus enables the decomposition of the latter to proceed further.

3. As_2S_3 is more rapidly dissolved by HCl than is As_2S_5. If the former can be present in the precipitate (which can be the case only when ammonium monosulfide was used for separating the copper and tin groups), the procedure should be modified by saturating with H_2S gas the cold concentrated HCl with which the sulfides are treated, and by passing a slow current of H_2S gas through the mixture during the heating. Under these conditions scarcely any As_2S_3 dissolves.

4. About 5 cc. water are added to the HCl solution to enable it to be filtered. If more is added and the H_2S has not all been expelled from the solution, a precipitate of Sb_2S_3 may separate. If this happens after the filtration, it does, of course, no harm.

5. Care must be taken to follow closely the directions in regard to the quantities of HCl and water used; for the subsequent separation of antimony and tin (P. 45) depends upon a proper concentration of the acid.

6. The greater part of any CuS and HgS present will be dissolved by the HCl, and will be precipitated later with the Sb_2S_3 (P. 44). A little remains with the As_2S_5, but this does not interfere with the tests for arsenic.

Procedure 42.—*Detection of Arsenic.*—Warm the residue from the HCl treatment (P. 41) with 5–10 cc. 6–normal HCl, adding solid $KClO_3$ in small portions until the reaction is complete; filter off the sulfur, and evaporate the solution to about 2 cc. Add NH_4OH gradually until the solution after shaking smells of it; cool, filter off and reject any precipitate. Add to the filtrate in a test-tube about one-third its volume of NH_4OH (s.g., 0.90) and several drops of magnesium ammonium chloride reagent, and shake. If no precipitate appears, rub the walls of the test-tube gently with a glass rod for a minute or two. (White crystalline precipitate, presence of ARSENIC.) Collect the precipitate on a filter and wash it once with 6–normal NH_4OH. (Precipitate, P. 43; filtrate, reject.)

Notes.—1. The main reaction between $KClO_3$ and concentrated HCl is the formation of Cl_2; the yellow color results from the formation of a small proportion of chlorine dioxide, ClO_2.

2. As_2S_5, tho only very slowly dissolved by HCl alone, is dissolved rapidly by it in the presence of Cl_2, because of the destruction by oxidation of the sulfide-ion and of the H_2S formed from it. The same principles are involved as in the action of HNO_3 on sulfides (see P. 31, Note 2). It is dissolved with formation of H_3AsO_4; $AsCl_5$ has not been shown to exist. When, as here,

arsenic is present in the higher state of oxidation, solutions of it may be boiled without loss of an amount of arsenic significant in qualitativ analysis.

3. A white precipitate produced on adding NH_4OH may arise from the presence of mercury. The NH_4OH solution may contain not only arsenic, but also the small quantities of copper (if ammonium polysulfide was used), antimony, and stannic tin that were not dissolved out of the sulfide precipitate by HCl.
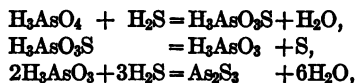
4. The test for arsenic depends on the formation of magnesium ammonium arsenate, $Mg(NH_4)AsO_4$. This salt is somewhat soluble even in cold water, and therefore the solution tested should be fairly concentrated. Owing to hydrolysis (into NH_4OH and $Mg^{++}HAsO_4^{-}$), the precipitate is much more soluble in water than in a strong NH_4OH solution; hence the addition of a large quantity of the latter. Like other crystalline precipitates, it tends to form a supersaturated solution. Precipitation is promoted by agitation, by rubbing the walls of the tube with a glass rod, and by increasing the degree of supersaturation, which is done by concentrating the solution and adding NH_4OH. Provided these precautions are taken and the total volume of the final solution does not exceed 5 cc., the presence of 0.5 mg. of arsenic can be detected. Care must be taken not to scratch the glass by violent rubbing, since the powdered glass may be mistaken for the $MgNH_4AsO_4$ precipitate.

5. The magnesium ammonium chloride reagent contains $MgCl_2$ and NH_4Cl. The presence of the latter salt, by reducing the OH^- concentration, prevents the precipitation of $Mg(OH)_2$ by NH_4OH.

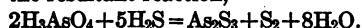**Procedure 43.**—*Confirmatory Test for Arsenic.*—Dissolve the $MgCl_2.NH_4Cl$ precipitate (P. 42) by pouring a little HCl through the filter, saturate the solution with H_2S, heat it nearly to boiling, and pass in H_2S for 5 minutes. (White precipitate turning yellow, presence of ARSENIC.) (Precipitate and solution, reject.)

Notes.—1. The slow formation of a pale yellow precipitate with H_2S is a characteristic test for H_3AsO_4. The precipitate is a mixture of As_2S_5, As_2S_3, and sulfur; but the proportion of As_2S_5 is comparativly small when the precipitation takes place from a hot solution.

2. A considerable amount of H_2S is absorbed by a cold H_3AsO_4 solution before any precipitate appears. This is due to the conversion of a part of the H_3AsO_4 into H_3AsO_3S, which then decomposes slowly, giving H_3AsO_3 and sulfur. This last decomposition is accelerated by increasing the H^+ concentration and by raising the temperature. The H_3AsO_3 formed reacts at once with H_2S, and As_2S_3 is precipitated. The reactions taking place are:

$$H_3AsO_4 + H_2S = H_3AsO_3S + H_2O,$$
$$H_3AsO_3S \qquad = H_3AsO_3 + S,$$
$$2H_3AsO_3 + 3H_2S = As_2S_3 \quad + 6H_2O,$$

which together giv the resultant reaction,

$$2H_3AsO_4 + 5H_2S = As_2S_3 + S_2 + 8H_2O.$$

The rate of this reaction depends upon the rate of the slowest of the separate reactions—the decomposition of the H_3AsO_3S—and on the quantity of this substance which has been produced by the first reaction. This quantity seems to be determined by the equilibrium-conditions of the first reaction rather

than by its rate; for it is larger when the solution is saturated in the cold with H_2S, doubtless owing to the greater solubility of the H_2S in the cold solution. This explains why it is advantageous to saturate the solution with H_2S first in the cold. Having formed in this way as large a proportion of H_3AsO_3S as possible, the solution is then heated in order to cause decomposition of this substance according to the second reaction.—As_2S_5 is produced by an independent reaction, taking place very slowly, as follows:

$$2H_3AsO_4 + 5H_2S = As_2S_5 + 4H_2O.$$
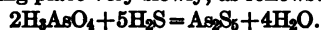
Procedure 44.—*Separation of Antimony and Tin.*—Heat the solution of the sulfides (P. 41), which should contain 10 cc. 12–normal HCl in a total volume of 50 cc., to about 90°, and pass in H_2S gas for about 5 minutes, keeping the solution at about 90°. If no precipitate appears, add about 5 cc. water, and again saturate with H_2S at the same temperature as before. (Orange-red precipitate, presence of ANTIMONY.) Filter while hot, add 5 cc. water, heat the filtrate nearly to boiling, again saturate it with H_2S to ensure complete precipitation of antimony, and if a further precipitate forms, collect it on a separate filter. Wash the precipitates with hot water. (Precipitate, P. 45; filtrate, P. 46.)

> *Notes.*—1. By following carefully the directions given in P. 41 and in this procedure, a good separation of antimony and tin may be obtained; thus, when only 1 mg. of antimony is present it is precipitated, while even 500 mg. of (stannic) tin giv no precipitate. If, however, the HCl solution be too concentrated, a small quantity of antimony will escape detection; hence the precaution of adding a little water to the solution and repeating the treatment with H_2S. If the HCl solution be too dilute, or if it be not kept hot, some SnS_2 may precipitate when a large amount of tin is present. When SnS_2 is mixed with a little Sb_2S_3 a brown precipitate results.
>
> 2. If mercury or copper be present in the substance and ammonium polysulfide has been used, HgS or CuS may be precipitated at this point as a gray or black precipitate.

Procedure 45.—*Confirmatory Test for Antimony.*—Dissolve the H_2S precipitate (P. 44) in a little 12–normal HCl in a small casserole, and evaporate the solution to about 1 cc. Introduce beneath the solution a piece of platinum foil and place upon it a piece of pure tin. After several minutes wash the platinum foil carefully with water and cover it with (alkaline) NaOCl solution. (Black deposit on the platinum undissolved by NaOCl, presence of ANTIMONY.) (Precipitate and solution, reject.)

> *Notes.*—1. Mercury and copper, if present, will also be precipitated in the metallic condition upon the platinum, but the antimony may be easily distinguished from them by its black color. Tin is used, rather than zinc, in precipitating the antimony, since zinc would also precipitate tin from the solution.

5

2. The treatment with NaOCl serves to prove that the black precipitate does not consist of arsenic ; for this element is readily dissolved by it, while antimony is not. Since, however, 5–10 mg. of arsenic must be present before the treatment with tin would giv a deposit on the platinum, an arsenic deposit will probably never be obtained in an actual analysis.

Procedure 46.—*Detection of Tin.*—Cool the filtrate from the H_2S precipitate (P. 44), dilute with 20 cc. water, and pass in H_2S for 10 minutes. (Yellow precipitate, presence of TIN.) If there is a precipitate, evaporate the mixture without filtering to about 3 cc., pour it into a small conical flask, add 10 cc. water and 10 g. of finely granulated lead, cover the flask with a small watch-glass, and boil slowly for 5 to 10 minutes. Pour the hot solution through a filter into 10 cc. 0.2 normal $HgCl_2$ solution. If there is a precipitate, heat the mixture to boiling. (White precipitate, presence of TIN.)

Notes.—1. The solution is precipitated with H_2S in the cold, because a small quantity of SnS_2 would not separate from a hot solution unless the acid were more diluted. The addition of much water is avoided, since it has to be evaporated off in the confirmatory test.

2. With respect to the confirmatory test the following points deserve mention. The precipitate of SnS_2 is not filtered off but is dissolved by concentrating the acid by evaporation, since it clogs the filter and tends to pass through it. Since $SnCl_2$ oxidizes rapidly in the air, the solution in HCl must be immediately added to the $HgCl_2$ solution. The mixture is finally heated to boiling to make sure that the precipitate is not $PbCl_2$.

PRECIPITATION AND SEPARATION OF THE ALUMINUM AND IRON GROUPS.

See Table II, page 37.

Procedure 51.—*Precipitation of the Aluminum and Iron Groups.*—
Boil the filtrate from the H_2S precipitate (P. 21) till the H_2S is ex-
pelled. Add to it 10 cc. NH_4OH, shake, and note whether there is
a precipitate. Add ammonium monosulfide slowly (or, in case nickel
seems to be present, pass in H_2S) until, after shaking, the vapors
in the flask blacken a piece of filter-paper moistened with $PbAc_2$
solution. To coagulate the precipitate shake the mixture or heat
it nearly to boiling. Filter, and wash the precipitate, first with
water containing about 1% of the $(NH_4)_2S$ reagent, and then with
a little pure water. If the filtration is slow, keep the funnel covered
with a watch-glass. To the filtrate add a few drops $(NH_4)_2S$, boil
the mixture for a few seconds (or, in case it is dark colored, until it
becomes colorless or light yellow); filter if there is a precipitate,
uniting it with the preceding one. (Precipitate, P. 52; filtrate, P. 81.)

Notes.—1. The H_2S is boiled out and the effect of the addition of NH_4OH
alone is noted because it often givs a useful indication as to what elements are
present. To save time the expulsion of the H_2S may be omitted when this
indication is considered unimportant. Only a slight excess of ammonium
monosulfide is used, in order to prevent as far as possible dissolving the NiS.
By passing H_2S into the ammoniacal solution, instead of adding $(NH_4)_2S$, the
dissolving of NiS is entirely prevented; therefore, tho the operation takes a
little longer, the use of H_2S is to be preferred when nickel is likely to be present.
The mixture is shaken in order to coagulate the precipitate and make it filter
more readily. Heating also promotes the coagulation of the precipitate; heat
is therefore applied when the precipitate does not coagulate and settle quickly
on shaking. The filtrate is boiled for a few moments to ensure the complete
precipitation of $Cr(OH)_3$, or longer to ensure that of NiS, whose presence is
indicated by a brown or nearly black color of the filtrate. Finally, it is directed
to wash with water containing a little $(NH_4)_2S$ and to keep the filter covered,
in order that some excess of $(NH_4)_2S$ may always be present; for, if the $(NH_4)_2S$
adhering to the precipitate is removed by oxidation or by volatilization (as
H_2S and NH_3), the sulfides are oxidized to soluble sulfates by the air.

2. Under the conditions of the procedure, which provides for a small excess
of NH_4OH in the presence of ammonium salt, aluminum, chromium, and iron
are completely precipitated. $Al(OH)_3$ is white; $Cr(OH)_3$, grayish green. The
color of the precipitated iron hydroxide varies with the state of oxidation of the
iron, pure ferrous salts yielding a white precipitate, and ferric salts a reddish
brown one, while mixtures of them yield green or black precipitates ; in the
alkaline mixture the precipitate is rapidly oxidized by the oxygen of the air and
undergoes corresponding changes in color. Manganous salts are also oxidized
rapidly, with the result that brown $Mn(OH)_3$ separates. Under the conditions
of the procedure zinc and nickel, when present alone, are completely dissolved;
the same is true of cobalt, except when it is present in large quantity; but zinc

is precipitated when chromium is also present. The ammoniacal solution of nickel is blue and that of cobalt of a reddish color. The latter darkens rapidly on exposure to the air, owing to oxidation. If a smaller excess of NH_4OH is used than is directed, some zinc hydroxide, as well as cobalt hydroxide, may remain undissolved when large amounts of these elements are present, but this has no effect on the subsequent analysis. If, on the other hand, a much larger excess of NH_4OH is employed, a few milligrams of aluminum and chromium may be dissolved, the latter giving a pink colored solution.

3. The presence of ammonium salts in the solution serves to prevent the precipitation of $Mg(OH)_2$, and also to lessen the amount of $Al(OH)_3$ dissolved by the NH_4OH.

4. The influence of an excess of the NH_4OH and of the presence of ammonium salt on the solubilities of the various hydroxides is explained by the mass-action law and ionic theory as follows: In order that any hydroxide, say of the type MO_2H_2, may be precipitated, it is necessary that the product $(M^{++}) \times (OH^-)^2$ of the concentrations of the ions M^{++} and OH^- in the solution in question attain the definit value which is known as the solubility-product. This value varies, of course, with the nature of the hydroxide, but for all the elements of the iron-group and for magnesium, it is so small that even in a solution containing in 50 cc. only 1 mg. of the element and a slight excess of NH_4OH, the product $(M^{++}) \times (OH^-)^2$ exceeds it, and precipitation results. When, however, much ammonium salt is also present, this greatly reduces, in virtue of the common-ion effect, the ionization of the NH_4OH and therefore the OH^- concentration in the solution, so that now for certain elements the product $(M^{++}) \times (OH^-)^2$ does not reach the value of the solubility-product, even when (M^{++}) is moderately large (say 500 mg. in 50 cc.). This is true of magnesium and manganese; but in the cases or aluminum, chromium, and ferric iron the solubility of the hydroxides in water is so slight that even in ammonium salt solution the solubility is not appreciable.

If these were the only effects involved, the greater the excess of NH_4OH added, the less would be the solubility of any hydroxide; but other influences come into play with certain of the elements. These influences are of two kinds. The first of these is shown by zinc, nickel, and cobalt. In the case of these elements, just as with silver and copper, the excess of ammonia combines with the simple cation M^{++}, forming complex cations of the types $M(NH_3)_2^{++}$ and $M(NH_3)_4^{++}$, thereby removing the simple cation from the solution and making it necessary for more of the hydroxide to dissolve in order to bring back the value of $(M^{++}) \times (OH^-)^2$ to that of the solubility-product. In such a case the presence of ammonium salt increases the solubility still further, since it greatly decreases the value of (OH^-), owing to the common-ion effect on the ionization of the NH_4OH. Chromium also forms similar ammonia complexes, but in much smaller proportion.

The second kind of effect is exhibited in the case of AlO_3H_3. This hydroxide is another example of an amphoteric substance; for it behaves both as a base and as an acid in consequence of its being appreciably ionized both into OH^- and Al^{+++} and into H^+ and $AlO_2H_2^-$ (or into H^+, AlO_2^-, and H_2O). With the H^+ arising from the latter form of ionization the OH^- coming from the excess of NH_4OH combines to form H_2O, so as to satisfy the mass-action expression for the ionization of water, $(H^+) \times (OH^-) = $ a constant (which

has the very small value 10^{-14} at 25°). This causes more AlO_3H_3 to dissolve until the value of $(AlO_2^-) \times (H^+)$ again attains that of the solubility-product. This shows that the quantity of aluminum dissolved increases with the OH^- concentration in the solution, and that therefore it would be much greater in a solution of a largely ionized base like NaOH than in that of a slightly ionized base like NH_4OH. It also shows that the presence of ammonium salts tends to neutralize the solvent action of an excess of NH_4OH, since they decrease the OH^- concentration in its solution.

5. It follows from the statements in the preceding notes that, if NH_4OH produces no precipitate, it proves the absence of as much as 1 mg. of aluminum and iron; also of chromium, if the mixture is heated to boiling after the addition of NH_4OH. Care must be taken not to overlook a small precipitate which might otherwise escape detection on account of its transparency. The mixture should therefore be well shaken and allowed to stand 2 or 3 minutes, in order that the precipitate may collect in flocks. This treatment also oxidizes the iron when present in small quantity, and thus enables it to be more readily detected; for its precipitation in the ferric state is more complete.

6. When phosphate is present, magnesium, calcium, strontium, barium, and manganese may be partially, or even completely, precipitated by NH_4OH. The reasons for this are as follows. The normal phosphates and the mono-hydrogen phosphates of these elements are difficultly soluble in water, but dissolve readily in acids, owing to the formation in solution of the much more soluble dihydrogen phosphates and of free phosphoric acid. Upon the addition of an excess of NH_4OH to such a solution these acid compounds are converted into the normal phosphates, and these are reprecipitated. It is therefore necessary, when phosphate is present, to provide for the detection of the alkaline-earth elements in the analysis of the NH_4OH precipitate. They are, however, not necessarily found in that precipitate; for, when other elements, like iron and aluminum, which form much less soluble phosphates are also present, they may combine with all the phosphate radical present, thus leaving the alkaline-earth elements in solution.

7. The presence of any other acidic constituent which forms with the alkaline-earth elements salts soluble in dilute acids but insoluble in ammonia may also cause their precipitation at this point. Fluoride is the only common inorganic constituent of this kind, and it will ordinarily have been removed in the evaporation with acids in the preparation of the solution.

8. $(NH_4)_2S$ precipitates ZnS, MnS, NiS, and CoS, and converts $Fe(OH)_2$ into FeS, and $Fe(OH)_3$ into Fe_2S_3. The hydroxides of aluminum and chromium are not affected by the $(NH_4)_2S$.

9. The sulfides of iron, nickel, and cobalt are black; ZnS is white; and MnS is flesh-colored, but turns brown on standing in the air, owing to oxidation to hydrated Mn_2O_3.

10. When nickel is present alone or when it forms a large proportion of the $(NH_4)_2S$ precipitate, several milligrams of it usually pass into the filtrate, giving it a brown or black color; and some NiS also passes through the filter with the wash-water. In this case it is useless to try to remove the NiS by filtering again, but it can be coagulated by boiling for several minutes. The brown solution is formed only in the presence of ammonium polysulfide. Its formation can, as stated above, be avoided altogether by passing H_2S into the

NH₄OH solution, instead of adding the ammonium monosulfide reagent, which after exposure to the air always contains some polysulfide. The nature of the brown solution is not known.

Procedure 52.—*Separation of the Aluminum-Group from the Iron-Group.*—Transfer the $(NH_4)_2S$ precipitate (P. 51), with the filter if necessary, to a casserole; add 5–20 cc. HCl, stir for a minute or two in the cold, and then boil the mixture for 2 or 3 minutes; if a black residue still remains, add a few drops HNO_3 (s.g., 1.42) and boil again. Dilute with a little water, filter off the sulfur residue, and evaporate the filtrate to a small volume to remove the excess of acid.

Dilute the solution to 10 or 20 cc., and make it alkaline with NaOH solution, avoiding a great excess, and adding 10–20 cc. more water if so large a precipitate separates that the mixture becomes thick with it. Place the casserole in a dish of cold water and add 0.5–3 g. solid Na_2O_2 in small portions with constant stirring. Then add 10 cc. Na_2CO_3 solution; boil for 2 or 3 minutes to decompose the excess of Na_2O_2, cool, dilute with an equal volume of water, filter with the help of suction, and wash with hot water. (Precipitate, P. 61; filtrate, P. 53.)

Notes.—1. All the hydroxides and all the sulfides, except NiS and CoS, usually dissolve readily in cold HCl. If, therefore, there is considerable black residue after adding the HCl, it shows the presence of nickel or cobalt; a very small black residue may, however, be due to FeS enclosed within sulfur. The fact that there is no such dark-colored residue does not, however, prove that nickel and cobalt are entirely absent; for a considerable quantity of them (even 5 mg.) may dissolve completely in the HCl when large quantities of other elements, especially iron, are also present.

2. The $(NH_4)_2S$ precipitate is first treated with HCl, partly in order to furnish the indication just referred to of the presence of nickel or cobalt, but also because much more free sulfur and sulfate would be formed by oxidation if HNO_3 or *aqua regia* were used at the start. (The presence of much sulfate in the solution interferes with the subsequent test for chromate.) If NiS or CoS is present in the residue, HNO_3 must, however, be subsequently added, to ensure the solution of these sulfides.

3. By NaOH, iron, manganese, nickel, and cobalt are completely precipitated and do not dissolve in moderate excess; while aluminum, chromium, and zinc remain in solution or dissolve when a sufficient excess is added. The solubility of the last three elements is due to the fact that their hydroxides are amphoteric substances which form with the NaOH soluble aluminate $(NaAlO_2)$, chromite $(NaCrO_2)$, and zincate (Na_2ZnO_2), respectivly. When zinc and chromium are simultaneously present they are precipitated in the form of a double compound $(ZnCr_2O_4)$. Chromium would also be completely precipitated, owing to hydrolysis of the chromite and the formation of a less soluble solid hydroxide, if the NaOH solution were boiled before adding Na_2O_2. $Mn(OH)_2$ is white, but rapidly turns brown, owing to oxidation to $Mn(OH)_3$;

$Ni(OH)_2$ is light green; $Co(OH)_2$ is pink, but from cold cobalt—salt solutions a blue basic salt is first precipitated. If a large excess of NaOH be added, a little $Co(OH)_2$ dissolves, yielding a blue solution, doubtless forming a salt such as Na_2CoO_2. This is to be avoided, since then the cobalt will not be completely oxidized and precipitated upon the subsequent addition of Na_2O_2.

4. By the addition of Na_2O_2, $Fe(OH)_2$ is changed to dark red $Fe(OH)_3$, $Mn(OH)_2$ to brown hydrated MnO_2, and $Co(OH)_2$ to black $Co(OH)_3$, all of which are insoluble in excess of NaOH. Chromium, which after the addition of cold NaOH is present as soluble sodium chromite, is converted by Na_2O_2 into chromate (Na_2CrO_4). This remains in solution together with the zinc, which is still present as zincate.

5. Even a cold solution of Na_2O_2 decomposes rapidly with evolution of oxygen, and this decomposition takes place with explosiv violence when the solution is hot. The peroxide is therefore added in small portions to the cold solution. A steady evolution of gas continuing after the mixture has been well stirred is an indication that sufficient peroxide has been added. The solution is diluted before filtering in order to avoid the disintegration of the filter-paper. It is also often advantageous to support the filter by folding it together with a small, hardened filter.

6. This separation with NaOH, Na_2O_2, and Na_2CO_3 is a very satisfactory one, except in the case of zinc. This element, when present in small quantities, is completely carried down in the precipitate when much iron, nickel, or cobalt, or especially manganese, is present. Provision for the detection of zinc in the precipitate must therefore be made.

7. The Na_2CO_3 is added to ensure the complete precipitation of magnesium, calcium, strontium, and barium, whose hydroxides, especially that of barium, are somewhat soluble even in the presence of NaOH. $ZnCO_3$, tho insoluble in a dilute solution of Na_2CO_3 alone, dissolves when much NaOH is present, owing to nearly complete conversion of the zinc-ion into zincate-ion (ZnO_2^{--}). The Na_2CO_3 also serves to decompose the chromates of the alkaline-earth elements; if it is not added, chromium may remain in the precipitate and escape detection. It is unnecessary to add the Na_2CO_3 when the alkaline-earth elements are known to be absent.

8. Phosphate, if present, divides itself in this procedure between the precipitate and solution in a proportion which depends on the nature and quantities of the basic elements present. (See P. 51, Note 6.) Its presence does not cause any of the elements to precipitate which would not otherwise do so, in spite of the slight solubility of aluminum and zinc phosphates. This is due to the fact that the cations of these elements (Al^{+++}, Zn^{++}) are present in the NaOH solution only at an extremely small concentration, owing to their conversion by the OH^- into anions (AlO_2^-, ZnO_2^-).

9. If Na_2O_2 is not available, sodium hypobromite, NaBrO (prepared by mixing NaOH and bromin, as described in P. 70, Note 3), may be used as the oxidizing agent; but it is not quite so satisfactory as Na_2O_2, for it does not oxidize $Cr(OH)_3$ so readily, and it is apt to oxidize some of the manganese to $NaMnO_4$ (especially if there is not a sufficient excess of NaOH present).

ANALYSIS OF THE ALUMINUM-GROUP.

TABLE VI.—ANALYSIS OF THE ALUMINUM-GROUP.

FILTRATE FROM THE SODIUM HYDROXIDE AND PEROXIDE TREATMENT: Na_2ZnO_2, $NaAlO_2$, Na_2CrO_4. *Acidify with HNO_3, add NH_4OH (P. 53).*		
Precipitate: $Al(OH)_3$. *Dissolve in HCl, add ether, pass in HCl gas (P. 54).*	**Filtrate.** *Add HAc and $BaCl_2$ (P. 55).*	
	Precipitate: $BaCrO_4$. *Dissolve in HCl and H_2SO_3, evaporate (P. 56).*	**Filtrate: Zinc salt.** *Pass in H_2S (P. 57).*
White precipitate: $AlCl_3.6H_2O$.		
	Green color: $CrCl_3$.	**White precipitate: ZnS.** *Dissolve in HNO_3, add $Co(NO_3)_2$ and Na_2CO_3, ignite (P. 57).*
		Green residue: $ZnO.xCoO$.

Procedure 53.—*Separation of Aluminum from Chromium and Zinc.*—Acidify the alkaline solution (P. 52) with HNO_3 (s.g., 1.42), avoiding a large excess; add NH_4OH until the mixture after shaking smells of it, and then add 2–3 cc. more. (White flocculent precipitate, presence of ALUMINUM.) Heat almost to boiling in order to coagulate the precipitate, filter, and wash thoroly with hot water. (Precipitate, P. 54; filtrate, P. 55.)

> *Notes.*—1. The alkaline solution is acidified with HNO_3, instead of with HCl, because the latter acid might reduce chromic acid, especially if a large quantity were added, or if the acid solution were heated. A moderate excess of NH_4OH must be added in order to keep the zinc in solution, which it does because of the production of the complex cation $Zn(NH_3)_4^{++}$; but a large excess is to be avoided, since it dissolves $Al(OH)_3$, owing to formation of $NH_4^+AlO_2^-$. The zinc is dissolved even when carbonate or phosphate is present.
>
> 2. Since aluminum and silica are very likely to be present in the NaOH and Na_2O_2 used as reagents, and since they may be taken up from the dishes, a blank test for these impurities should be made whenever new reagents are employed for the first time, by following P. 52 and P. 53 and comparing the NH_4OH precipitate with that obtained in the actual analysis. It is also well at the same time to test for zinc by acidifying the NH_4OH solution with acetic acid and following P. 57.

Procedure 54.—*Confirmatory Test for Aluminum.*—Dissolve the precipitate (P. 53) by pouring a hot 5–10 cc. portion of HCl repeatedly through the filter, using another portion of acid if necessary. Place the solution in a small flask. Add to it a volume of ether equal to one and one-half times that of the solution; and pass into it HCl gas until a single layer results and until fumes of HCl are copiously evolved, keeping the flask cool during the process. Cover the flask, and let the mixture stand 15 minutes. (White crystalline precipitate, presence of ALUMINUM.)

Alternativ Confirmatory Test for Aluminum.—Dissolve the precipitate (P. 53), or a small portion of it if it is large, in 5 cc. HNO_3. To the solution add from a dropper half as many drops of a $Co(NO_3)_2$ solution containing 1% Co as the number of milligrams of aluminum estimated to be present in the solution. Evaporate the solution almost to dryness in a casserole, add a drop or two of water, and soak up the solution in a small piece of filter paper. Make a small roll of the paper, wind a platinum wire around it in the form of a spiral, and incinerate the paper in a small flame, finally heating the residue strongly. (Blue residue, presence of ALUMINUM.)

Notes.—1. A confirmatory test for aluminum should always be tried when the NH_4OH precipitate is small; for the precipitation by NH_4OH of an element whose hydroxide is soluble in NaOH is not very characteristic (lead, antimony, tin, and silicon showing a similar behavior). It is especially necessary to guard against mistaking SiO_3H_2 for $Al(OH)_3$; for the former substance, if not entirely removed by proper dehydration in the process of preparing the solution, may appear at this point.

2. Aluminum chloride, $AlCl_3.6H_2O$, is only slightly soluble in concentrated HCl solutions, and the precipitation is complete when ether is added and the mixture saturated with HCl. 0.5 mg. of aluminum can be easily detected in 30 cc. The test is therefore a delicate one. It is also characteristic; for neither silicon nor zinc nor any of the rarer elements soluble in excess of NaOH giv a precipitate under the same conditions. Chromium givs a violet precipitate, but only when more than 10–20 mg. of it are present.

3. The HCl gas may be readily prepared by dropping H_2SO_4 (s.g., 1.84) from a separating funnel into a bottle containing commercial HCl (s.g., 1.19).

4. The confirmatory test with $Co(NO_3)_2$ depends upon the formation of a blue substance, whose formula is not definitely known; but it is doubtless a compound of the two oxides CoO. and Al_2O_3, and may be simply cobalt aluminate, $Co(AlO_2)_2$. It enables 0.5 mg. Al to be detected, or even 0.2 mg. after a little practis. No other element givs a blue color to the ash. It is essential to have the aluminum present in excess; for otherwise the blue color is obscured by the black oxide of cobalt. Moreover, when sodium or potassium salts are present, the ash fuses together and the test is unsatisfactory. For this reason the sodium salts present should be completely washed out of the NH_4OH precipitate before dissolving it in HNO_3.

Procedure 55.—*Detection of Chromium.*—To the NH_4OH solution (P. 53) add HAc, 1 cc. at a time, till the solution reddens blue litmus paper.

If the solution is colorless, treat it by P. 57.

If it is at all yellow, add about 10 cc. $BaCl_2$ solution, allow the mixture to stand for at least 5 minutes, and filter. (Yellow precipitate, presence of CHROMIUM.)   (Precipitate, P. 56; filtrate, P. 57.)

> *Notes.*—1. The presence of less than 0.5 mg. chromium as chromate in a volume of 50 cc. makes the solution distinctly yellow; and the addition of $BaCl_2$ is therefore unnecessary when the solution is perfectly colorless. It is to be avoided, since $BaSO_4$ may be precipitated and has then to be removed by filtration.   In doubtful cases the color of the solution should be compared with that of water.   The color-test is, of course, not delicate by artificial light.
>
> 2. Since some sulfate may be present, the formation of a white precipitate with $BaCl_2$ does not prove the presence of chromium.   Whether the precipitate is pure white or yellow should therefore by carefully noted.   The yellow color of a small $BaCrO_4$ precipitate is most apparent when the precipitate has settled or when it has been collected on the filter.   If there be sufficient sulfate present to obscure the yellow color of a little $BaCrO_4$, the confirmatory test described in the next procedure will enable the chromium to be detected.

Procedure 56.—*Confirmatory Test for Chromium.*—Pour repeatedly through the filter (P. 55) a hot 5–10 cc. portion of a mixture of 1 volume of HCl with 3 volumes of saturated SO_2 solution.   Evaporate the filtrate in a casserole almost to dryness.   (Green coloration of the solution, presence of CHROMIUM.)

> *Note.*—The green color of $CrCl_3$ is intense enough to enable less than 0.5 mg. of chromium in 1 cc. of solution to be detected.

Procedure 57.—*Detection of Zinc.*—Warm the HAc solution (P. 55) to 50° or 60°, saturate it in a small flask with H_2S, cork the flask, and allow it to stand for 5 or 10 minutes if no precipitate separates at once.   (White flocculent precipitate, presence of ZINC.)

To confirm the presence of zinc, filter through a double filter (made by folding two filter-papers together), wash with a little water, and pour a 5–10 cc. portion of HNO_3 two or three times through the filter. To the solution add a $Co(NO_3)_2$ solution containing 1% Co, as follows: if the H_2S precipitate was small, add from a dropper a number of drops of the $Co(NO_3)_2$ solution equal to the number of milligrams of zinc estimated to be present; if the H_2S precipitate was large, add from a graduate 1 cc. $Co(NO_3)_2$ solution for every 40 mg. of zinc estimated to be present.   Evaporate the mixture in a casserole almost to dryness to expel the acid, neutralize with Na_2CO_3 solution, and add about 1 cc. in excess.   Evaporate to dryness, ignite gently until the purple color due to the cobalt disappears, and allow the casserole to cool.   (Green color, presence of ZINC.)

Notes.—1. ZnS precipitates more rapidly, and in a somewhat more flocculent form, from a warm solution. Very small quantities of zinc (less than 1 mg.) may be missed unless a short time be allowed for the precipitate to coagulate; but since sulfur may then separate, the appearance of a white turbidity is not sufficient proof of the presence of zinc. The precipitate may be allowed to settle in order that the amount of zinc present may be better estimated. A double filter is used, since the ZnS is apt to pass through the filter.

2. The immediate formation of a white flocculent precipitate with H_2S in acetic acid solution is so characteristic as to be a sufficient test for zinc. Manganese is the only other element of this group that forms a light-colored sulfide; and this, owing to its greater solubility in water, does not precipitate from an acetic acid solution. The confirmatory test described in the last paragraph of the procedure is, however, useful when only a small noncoagulating precipitate which may be sulfur results, or when, owing to the presence of a small quantity of other elements, the precipitate is dark-colored.

3. The green compound obtained in the confirmatory test is doubtless a compound of cobalt and zinc oxides, perhaps cobalt zincate, $CoZnO_2$. This compound is formed at comparativly low temperatures in the presence of an alkaline flux. Excess of cobalt must, of course, be avoided; for the black cobalt oxide completely obscures the green color. A somewhat larger proportion of cobalt than is recommended in the procedure may, however, be added without danger, and a much smaller proportion givs satisfactory results.

ANALYSIS OF THE IRON-GROUP.

TABLE VII.—ANALYSIS OF THE IRON-GROUP.

PRECIPITATE PRODUCED BY SODIUM HYDROXIDE AND PEROXIDE:

A. Phosphate absent: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, $[ZnO_2H_2]$.

B. Phosphate present: Also $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, $FePO_4$, $Ca_3(PO_4)_2$, etc.
   Dissolve in HNO_3 and H_2O_2, evaporate, heat with HNO_3 and $KClO_3$ (P. 61).

Precipitate: MnO_2. *Add HNO_3 and sodium bismuthate (P. 62).* —— Violet color: $HMnO_4$.	Solution: *Test a portion for phosphate with $(NH_4)_2MoO_4$ (P. 63).* *A.* Phosphate absent: *add NH_4OH (P. 64).* *B.* Phosphate present: *add NH_4Ac and $FeCl_3$, dilute, boil (P. 65).*			
	Precipitate: *A.* $Fe(OH)_3$. *B.* Basic ferric acetate and $FePO_4$.	Filtrate: *add NH_4OH, pass in H_2S (P. 66).*		
		Precipitate: ZnS, CoS, NiS. *Treat with cold dilute HCl (P. 67).*		Filtrate: Ba,Ca,Sr,Mg. *Treat by P. 81.*
		Solution: $ZnCl_2$, $[CoCl_2]$, $[NiCl_2]$. *Add NaOH and Na_2O_2 (P. 67).*	Residue: CoS, NiS.	
		Solution: Na_2ZnO_2. *Add HAc and H_2S (P. 57).*	Precipitate: $Co(OH)_3$, $Ni(OH)_{2-3}$.	
			.... *Dissolve in acid, evaporate, add NaOH (P. 68).*	
		White precipitate: ZnS.	To one half add KNO_2 and HAc (P. 69).	To other half add KCN, digest, add NaBrO (P. 70).
			Yellow precipitate: $K_3Co(NO_2)_6$.	Black precipitate: $Ni(OH)_3$.

Procedure 61.—*Precipitation of Manganese.*—Transfer the Na_2O_2 precipitate (P. 52) to a casserole, together with the filter if necessary, and add 5–15 cc. HNO_3. If there is still a residue, add gradually with stirring 3% H_2O_2 solution, till the residue is dissolved. Filter to remove the paper, and evaporate the filtrate to 1 or 2 cc. Add 10 cc. HNO_3 (s.g., 1.42), and about 0.5 g. of powdered $KClO_3$, and heat to boiling. (Black precipitate, presence of MANGANESE.)

If there is no precipitate, dilute the solution with 20 cc. water, and treat a part of it by P. 63 and the remainder by P. 64 or P. 65.

If there is a precipitate, add to the mixture 10 cc. HNO_3 (s. g., 1.42) and 1 g. powdered $KClO_3$, cover the casserole, and heat it for 10–15 minutes on a steam-bath. Filter with the aid of suction through an asbestos filter, made by placing in a funnel enough glass-wool to form a wad 1 cm. high, tamping it down gently with the finger, and pouring through it a suspension of asbestos in water enough to form an asbestos layer about 1 mm. thick. Add to the filtrate 0.5 g. $KClO_3$, and heat it to boiling. If more precipitate separates, heat the mixture for 10–15 minutes on a steam-bath, and then filter it through the same asbestos filter. Wash the precipitate two or three times with HNO_3 (s. g., 1.42) which has previously been freed from oxides of nitrogen by warming it with a little $KClO_3$, and treat the precipitate by P. 62. Evaporate the filtrate to about 5 cc., but not further, dilute it with 25 cc. water, and treat a part of it by P. 63 and the remainder by P. 64 or P. 65.

> *Notes.*—1. Pure concentrated HNO_3 does not dissolve hydrated MnO_2; but it may do so in the presence of filter-paper, whereby the HNO_3 is reduced to lower oxides. The action is rapid in the presence of H_2O_2; for the MnO_2 is thereby quickly reduced to $Mn(NO_3)_2$ with evolution of O_2.
>
> 2. By $HClO_3$ in HNO_3 solution (but not by HNO_3 alone) manganous salts are rapidly oxidized to hydrated MnO_2 with formation of chlorin dioxide (ClO_2), which escapes as a yellow gas.
>
> 3. The separation of manganese in this way from the other metals of this group is entirely satisfactory with the exception that a small quantity of iron (up to 1 mg.) may be completely carried down with a large quantity (500 mg.) of manganese.

Procedure 62.—*Confirmatory Test for Manganese.*—To the whole of the $HClO_3$ precipitate (P. 61) if it contains less than 10 mg. Mn, or to 5–10 mg. of it if it is larger, add about 5 cc. HNO_3 and 50–100 mg. solid sodium bismuthate; pour the mixture into a test-tube, and allow the solid to settle. (Purple solution, presence of MANGANESE.)

> *Note.*—This confirmatory test for manganese is usually superfluous, since the precipitation of MnO_2 by $HClO_3$ is highly characteristic. Sodium bismuthate is a trade name for an impure substance which consists largely of a peroxide of bismuth of unknown composition. If it is not available, PbO_2 may be substituted for it; but in that case the mixture must be boiled for 2 or 3 minutes.

Procedure 63.—*Test for Phosphate.*—Add about one-tenth of the HNO_3 solution (P. 61) to three or four times its volume of ammonium molybdate reagent, and heat to 60–70°. (Yellow, finely crystalline precipitate, presence of PHOSPHATE.) If there is no precipitate, or only a very small one, treat the remainder of the HNO_3 solution by P. 64; otherwise by P. 65.

Notes.—1. Phosphate is tested for at this point because a different treatment is necessary when it is present in significant amount, in order to separate from it alkaline-earth elements and to provide for their detection. When phosphate is not present, iron can be separated from nickel and cobalt by NH_4OH (as in P. 64); but when considerable phosphate is present, alkaline-earth elements may also be present and these would be partly or wholly precipitated by NH_4OH as phosphates. (See P. 51, Note 6.)

2. In order that the phosphate test may be delicate and may appear immediately, a large proportion of the molybdate reagent must be used and the solution must be warmed. The precipitate produced by ammonium molybdate, $(NH_4)_2MoO_4$, is ammonium phospho-molybdate, a complex salt of somewhat variable composition; it contains ammonium phosphate and molybdic acid, approximately in the proportion expressed by the formula $(NH_4)_3PO_4.12MoO_3$.

Procedure 64.—*Precipitation of Iron in Absence of Phosphate.*— If phosphate is absent, make the HNO_3 solution (P. 61) strongly alkaline with NH_4OH, using an excess of 3–5 cc. (Dark red precipitate, presence of IRON.) Filter, and wash the precipitate. Treat the filtrate by P. 66. Dissolve the precipitate in HCl, warming if necessary; and to the solution add 3–5 cc. KCNS solution. (Dark red color, presence of IRON.)

Note.—This test may be made in the presence of much HCl, but not in the presence of much HNO_3; for HNO_3 acts on KCNS forming NO_2, and this also gives a deep red color with KCNS. This test for iron is an extremely delicate one; and if only a faint color is obtained, the acids used in the process must be tested for iron. The red color is due to the formation by meta-thesis of ferric thiocyanate, $Fe(CNS)_3$, a slightly ionized substance.

Procedure 65.—*Detection of Iron and Removal of Phosphate when Present.*—If phosphate is present, test one-tenth of the HNO_3 solution (P. 61) for iron, by evaporating it just to dryness, adding 1–2 cc. 12–normal HCl, evaporating again to decompose the HNO_3, diluting to 5 or 10 cc., and adding 5 cc. KCNS solution. (Permanent red color, presence of IRON.) To the remainder of the solution add NH_4OH until the precipitate formed by the last drop does not re-dissolve on shaking. If, owing to the addition of too much NH_4OH, the solution becomes alkaline or a large precipitate separates, make it distinctly acid with acetic acid. Add 15 cc. of a 3–normal solution of NH_4Ac, and, unless the mixture is already of a brownish-red color, add $FeCl_3$ solution, drop by drop, until such a color is produced. Add enough water to make the volume about 100 cc., boil in a 250 cc. flask for 5 minutes, adding more water if a very large precipitate separates, and let the mixture stand for a minute or two. Filter while still hot, and wash with hot water. Add 10 cc. more NH_4Ac solution to the filtrate, boil it again, and collect on a separate filter

any further precipitate. Reject the precipitate. Make the filtrate alkaline with NH$_4$OH, and treat it by P. 66.

> *Notes.*—1. With regard to the test for iron with KCNS and the necessity of removing the HNO$_3$, see P. 64, Note.
>
> 2. This method of separation depends on the facts that, upon boiling an acetic acid solution containing much acetate, ferric iron is completely precipitated in the form of a basic acetate; and that all the phosphate present combines with the iron when it is present in excess, and therefore then passes completely into the precipitate, leaving the bivalent elements in solution. This behavior of the phosphate is due to the fact that the solubility in acids of the phosphates of the trivalent elements is much smaller than that of the phosphates of the bivalent elements.
>
> 3. If upon adding the ammonium acetate the solution becomes of a reddish color, it shows that iron is present in quantity more than sufficient to combine with the phosphate; for a cold solution containing ferric acetate is of a deep red color. If, on the other hand, a colorless solution results (either with or without a precipitate), it shows that there is no excess of iron, and FeCl$_3$ is therefore added. This causes the precipitation of FePO$_4$ as a yellowish white precipitate. Upon boiling, the excess of iron separates completely as a dark red gelatinous precipitate of basic ferric acetate, leaving the supernatant liquid colorless, except when nickel or cobalt is present.
>
> 4. The solution is diluted to at least 100 cc., owing to the large volume of the precipitate; and it is heated in a capacious flask, owing to its tendency to boil over.

Procedure 66.—*Precipitation of Nickel and Cobalt.*—Into the ammoniacal solution (P. 64 or P. 65) pass H$_2$S gas until the mixture after shaking blackens PbAc$_2$ paper held above it. (Black precipitate, presence of NICKEL or COBALT.) Filter, and wash the precipitate with water containing a very little (NH$_4$)$_2$S. (Precipitate, P. 67; filtrate, to detect alkaline-earth elements, P. 81.)

> *Note.*—In precipitating NiS, the use of H$_2$S has the advantage that the nickel is all thrown down at once, while with (NH$_4$)$_2$S some of it usually remains in the solution, giving it a dark brown color. If (NH$_4$)$_2$S be used, the filtrate must be boiled to throw down the unprecipitated nickel, as described in P. 51.

Procedure 67.—*Separation of Zinc from the Nickel and Cobalt.*— Transfer the H$_2$S precipitate (P. 66) with the filter to a casserole, and add 10–30 cc. 1–normal HCl. Digest in the cold for 5 minutes, stirring the mixture frequently, and filter. Treat the residue by P. 68.

Boil the HCl solution until the H$_2$S is completely expelled, add NaOH solution until the mixture is slightly alkaline, transfer to a casserole, cool, and add 0.5–1 g. Na$_2$O$_2$, a small portion at a time. Boil for several minutes to decompose the excess of Na$_2$O$_2$, cool the mixture, and filter. Wash the precipitate and treat it by P. 68,

uniting it with the sulfide residue undissolved by the dilute HCl. Acidify the filtrate with HAc, and test it for zinc by P. 57.

> *Notes.*—1. This treatment with dilute HCl serves to extract almost completely the zinc which may be present in this precipitate, owing to its having been carried down in the Na_2O_2 precipitate as described in P. 52, Note 6. A small proportion of the nickel and cobalt present (5–20%) always dissolves in the dilute HCl, and the subsequent treatment with Na_2O_2 serves to separate these elements from the zinc. This separation is satisfactory when, as in this case, the nickel and cobalt are present in small quantity; for then only an insignificant amount of zinc is carried down with them. When, therefore, the H_2S precipitate is small, it may, instead of being treated with dilute HCl, be dissolved at once in *aqua regia* and the solution treated directly as described in the last paragraph of the procedure.
>
> 2. This procedure must always be followed in order to determin whether or not zinc is present in the substance, unless a satisfactory test for it has already been obtained in P. 57, or unless the original Na_2O_2 precipitate (P. 52) was small.

Procedure 68.—*Solution of the Nickel and Cobalt Precipitates.*— Transfer the sulfide residue undissolved by dilute HCl and the Na_2O_2 precipitate (P. 67), with the filters to a casserole, add 5–15 cc. HCl and a few drops HNO_3, warm until the black precipitate is dissolved, and filter off the paper. Evaporate the solution nearly to dryness to expel most of the acid, add about 5 cc. water, and then NaOH solution, drop by drop, until the mixture is neutral, or until a permanent precipitate just forms. Test one-half of this mixture for cobalt by P. 69, and the remainder for nickel by P. 70.

Procedure 69.—*Detection of Cobalt.*—To one-half of the neutral solution (P. 68) add 5 cc. HAc and then 30 cc. 3–normal KNO_2 solution; and allow the mixture to stand at least half an hour if no precipitate forms sooner. (Yellow, finely divided precipitate, presence of cobalt.) Filter, and wash with KNO_2 solution to which one-sixth its volume of HAc has been added. If the precipitate is very small, incinerate the filter. Introduce a portion of the precipitate, or of the ash, into a borax bead made in the loop of a platinum wire, and heat strongly, adding more of the precipitate or ash if no color is obtained. (Deep blue color, presence of cobalt.)

> *Notes.*—1. The precipitate is potassium cobaltic nitrite, $3KNO_2.Co(NO_2)_3$, or more properly, potassium cobaltinitrite, $K_3Co(NO_2)_6$, since in solution it dissociates into K^+ and the complex anion $Co(NO_2)_6^{\equiv}$. In the formation of this substance the cobaltous salt is oxidized to the cobaltic state by the nitrous acid displaced from its salt by the acetic acid, the cobaltic salt combining as fast as formed with the potassium nitrite.
>
> 2. The precipitate is somewhat soluble in water, but very difficultly soluble in a concentrated KNO_2 solution, owing to the common-ion effect of the potas-

sium-ion. The formation of the $K_3Co(NO_2)_6$ precipitate takes place slowly; but, even when only 0.1–0.2 mg. Co is present, a distinct precipitate is obtained within 10 minutes. The complete precipitation of a large amount of cobalt, however, requires several hours, so that the method is ill adapted for the removal of cobalt before testing for nickel. Moreover, when nickel is present, some of it is carried down with the cobalt; and this is true even when the total amount of nickel is small. For these reasons the test for nickel is made in a separate portion.

3. Nickelous salts are not oxidized by nitrous acid, and are not precipitated by KNO_2 except in a very concentrated solution, when a dark-yellow or dark-red precipitate of potassium nickelous nitrite, $K_4Ni(NO_2)_6$, may separate.
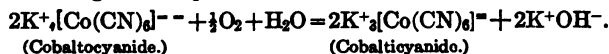
Procedure 70.—*Detection of Nickel.*—To the remainder of the neutralized solution (P. 68) add KCN solution, a few drops at a time, until all or nearly all of any precipitate that may form at first redissolves; then add 0.5–3 cc. more (according to the amount of the KCN precipitate). Heat to 50 or 60° in an open casserole, with frequent stirring, for 5 minutes, or longer if the solution has not become light-colored. Filter off and reject any small precipitate that may remain. To the filtrate, preferably in a test-tube, add freshly prepared, concentrated NaBrO solution (see Note 3) until a piece of filter-paper moistened with KI and starch solutions, when dipped into the solution, is colored blue or brown. Allow the mixture to stand 5–10 minutes and filter. (Brown to black precipitate, presence of NICKEL.)

Wash the precipitate; dissolve it, or a small portion of it if it is large, in 2–3 cc. HNO_3; add 3–5 cc. 10% tartaric acid solution, neutralize with NaOH solution, and add about 2 cc. in excess. Pass in H_2S gas for about 1 minute, filter out any precipitate that may form, and saturate the filtrate with H_2S. Filter again if there is a precipitate. (Brown coloration, presence of NICKEL.)

Notes.—1. The reactions involved in the first test for nickel are as follows: When a little KCN is added to the neutral solution, precipitates of (green) $Ni(CN)_2$ and (dark brown) $Co(CN)_2$ result, unless only small amounts of these elements are present. The addition of more KCN causes the precipitate to dissolve, owing to the formation of soluble complex cyanides, such as

$$K^+_2[Ni(CN)_4]^- \text{ and } K^+_4[Co(CN)_6]^{--}.$$

The complex nickel salt is stable in the air, but the cobalt salt oxidizes very readily according to the equation:

$$2K^+_4[Co(CN)_6]^{--} + \tfrac{1}{2}O_2 + H_2O = 2K^+_3[Co(CN)_6]^{=} + 2K^+OH^-.$$
(Cobaltocyanide.)   (Cobalticyanide.)

The first action of the NaBrO is to decompose the excess of KCN, chiefly with formation of KCNO. It then oxidizes the nickel to the nickelic state, which is then immediately precipitated as brownish-black $Ni(OH)_3$ by the NaOH present. The cobalt, tho already in the cobaltic state, is not precipitated as

6

Co(OH)$_3$, because the complex ion [Co(CN)$_6$] is so slightly ionized into its constituent-ions (Co^{+++} and CN$^-$) that the concentration of the Co^{+++} does not suffice, with the OH$^-$ present, to supersaturate the solution with Co(OH)$_3$.

2. In executing this procedure the following precautions should be observed: A very large excess of the strong KCN solution over that required to redissolve the precipitate should not be added; for the excess must be destroyed by the NaBrO before the nickel can be oxidized and precipitated by it. Yet there must be sufficient KCN added, not only to combine with all the cobalt, but to furnish a moderate excess in order that the oxidation to the cobalticyanide may take place rapidly. Care must also be taken to heat the solution long enough in the air to complete this oxidation before the NaBrO is added; for otherwise the latter reagent after destroying the free KCN will oxidize the decomposable cobaltocyanide with precipitation of Co(OH)$_3$, just as it does the nickelocyanide. The completion of the oxidation by the air is indicated by the disappearance of the dark color in the solution. Finally, one must make sure (by applying the iodide-starch test) that an excess of NaBrO over that required to oxidize both the cyanide and the nickel has been added. If these precautions are observed, there is no difficulty in securing a precipitate with 0.2 mg. of nickel nor in causing 300 mg. of cobalt to remain entirely in solution.

3. The hypobromite reagent is prepared by adding liquid bromin to a known volume of NaOH solution until the solution becomes distinctly red, owing to the presence of excess of bromin; and then adding half as much more NaOH solution. This solution may be filtered through a hardened filter. It decomposes fairly rapidly, with formation of bromate and bromide, and also with evolution of oxygen, and should therefore not be used when more than a few days old.

4. When an alkaline tartrate solution containing a small amount of nickel (even 0.1–0.2 mg. in 20 cc.) is saturated with H$_2$S, a clear brown solution is obtained. With somewhat larger amounts of nickel (10–20 mg.) the liquid is opaque, but runs through a filter very readily. The condition of the nickel in this solution is not known. The presence of the tartrate serves merely to prevent the precipitation of Ni(OH)$_2$ by the NaOH solution, owing to the formation of a complex salt containing the nickel in the anion. The brown color does not appear until the alkaline solution is nearly saturated with H$_2$S, so that care must be taken to use an excess of H$_2$S.

5. This confirmatory test for nickel is not interfered with by moderate amounts of other elements of this group, such as cobalt and iron; for on leading H$_2$S into an alkaline tartrate solution containing these elements, they are completely precipitated as sulfides and may be filtered off, yielding a filtrate which in the absence of nickel remains clear when saturated with H$_2$S, or becomes dark brown when it is present in even small amount.

PRECIPITATION AND ANALYSIS OF THE ALKALINE-EARTH GROUP.

TABLE VIII.—ANALYSIS OF THE ALKALINE–EARTH GROUP.

AMMONIUM CARBONATE PRECIPITATE: $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3.(NH_4)_2CO_3$.
Dissolve in HAc, add NH_4Ac and K_2CrO_4 (P. 82).

Precipitate: $BaCrO_4$. *Dissolve in HCl, evaporate (P. 83).*		Filtrate. *Add NH_4OH and alcohol (P. 84).*		
		Precipitate: $SrCrO_4$. *Treat with $(NH_4)_2Co_3$ (P. 85).*	Filtrate: Ca and Mg salts. *Dilute, add $(NH_4)_2C_2O_4$ (P. 86).*	
Test in flame	*Add HAc, NH_4Ac, and K_2Cr_4O.*		Precipitate: CaC_2O_4. *Dissolve in dilute H_2SO_4, add alcohol (P. 87).*	Filtrate. *Add NH_4OH and Na_2HPO_4 (P. 88).*
Green color: Ba.		Residue: $SrCO_3$. *Dissolve in HAc, add $CaSO_4$*		
	Precipitate: $BaCrO_4$.	Precipitate: $SrSO_4$.	Precipitate: $CaSO_4$.	Precipitate: $MgNH_4PO_4$.

Procedure 81.—*Precipitation of the Alkaline-Earth Group.*—
Evaporate the filtrate from the NH_4OH and $(NH_4)_2S$ precipitate
(P. 51) to a volume of about 10 cc., and filter off the sulfur.

To the cold solution add 15 cc. $(NH_4)_2CO_3$ reagent and 15 cc.
95% alcohol; and, if a large precipitate results, add 15 cc. more of
each of these liquids. Shake the mixture vigorously for 5–10 minutes;
or, let it stand, with occasional shaking, for at least half an hour.
(Precipitate, presence of ALKALINE–EARTH ELEMENTS.)   Filter, and
wash the precipitate with a little $(NH_4)_2CO_3$ reagent, using suction
if the precipitate is large.   (Precipitate, P. 82; filtrate, P. 91.)

Notes.—1. The filtrate from the $(NH_4)_2S$ precipitate is evaporated in order
that the elements of the alkaline-earth group may be precipitated more quickly
and more completely. The evaporation also serves to destroy $(NH_4)_2S$ and to
coagulate any sulfur that may separate. The volume to which the $(NH_4)_2CO_3$
reagent is added should not exceed 10 cc.

2. The $(NH_4)_2CO_3$ reagent is prepared by dissolving 250 g. freshly powdered
ammonium carbonate in 1 liter 6–normal NH_4OH.

3. If the ammonium carbonate and hydroxide were added in only small
excess, the precipitation of $CaCO_3$, $SrCO_3$, and $BaCO_3$ would not be complete,
and additional tests for small quantities of these elements would have to
be made in the filtrate. But, by the use of a concentrated solution of
$(NH_4)_2CO_3$ containing a large excess of NH_4OH (so as to diminish the
hydrolysis of the carbonate into $(NH_4)^+HCO_3^-$ and NH_4OH), the pre-
cipitation may be made practically complete, owing to the greatly increased
concentration of carbonate-ion (CO_3^-).

4. When the concentrations of $(NH_4)_2CO_3$ and NH_4OH are sufficiently great, magnesium is in the cold also completely precipitated. The precipitate, which is in this case a double carbonate, $MgCO_3.(NH_4)_2CO_3.4H_2O$, is, however, fairly soluble in cold water and readily soluble in hot water.

5. From a cold aqueous solution the precipitation of these elements takes place slowly, especially in the case of magnesium and calcium; but it is greatly accelerated by the addition of alcohol and by shaking. Under the conditions recommended in the procedure 0.5 mg. of any of the four elements is easily detected.

Procedure 82.—*Precipitation of Barium.*—Dissolve the $(NH_4)_2CO_3$ precipitate (P. 81) by pouring repeatedly through the filter a 5–15 cc. portion of hot HAc, and evaporate the solution just to dryness, taking care not to ignite the residue.

Add to the residue 3 cc. HAc, 20 cc. 3–normal NH_4Ac, and 15 cc. water; and heat the solution to boiling in a flask. Measure out 8 cc. 3–normal K_2CrO_4 solution, and add it a few drops at a time, heating and shaking after each addition. Finally, heat the mixture at 90–100° for 1 or 2 minutes, shaking at the same time. Filter, even tho the solution appear clear; remove the filtrate, and wash the precipitate thoroly with cold water. (Pale yellow precipitate, presence of BARIUM.) (Precipitate, P. 83; filtrate, P. 84.)

Notes.—1. The solubility in water of the chromates of the alkaline-earth elements increases rapidly in the order, Ba, Sr, Ca, Mg. The difference in solubility of $BaCrO_4$ and $SrCrO_4$ is so great that under the conditions of the procedure 0.5 mg. Ba can be detected, while even 400 mg. Sr giv no precipitate. The amount of K_2CrO_4 added is sufficient to precipitate completely more than 500 mg. of barium.

2. Acetic acid is added to increase the solubility of $SrCrO_4$. By its action the concentration of the chromate-ion is reduced, owing to its conversion partly into hydrochromate-ion and partly into bichromate-ion, according to the reactions:

$$CrO_4^- + H^+ = HCrO_4^-; \text{ and } 2HCrO_4^- = H_2O + Cr_2O_7^-.$$

It is evident that the CrO_4^+ concentration must decrease as the H^- concentration increases. For this reason the presence of an excess of a largely ionized acid (such as HCl or HNO_3) would prevent the precipitation of $BaCrO_4$; but since acetic acid is a slightly ionized acid, and since a large amount of acetate is present, the addition of a considerable excess of acetic acid has but little effect.

3. The K_2CrO_4 is added slowly to the hot solution and the mixture is shaken and heated in the neighborhood of 100° before filtering, since otherwise the precipitate is liable to pass through the filter. By this method of precipitation almost all the barium is precipitated before an excess of K_2CrO_4 is added. This is of importahce since, when much barium is present, as much as 3 mg. Sr may be carried down completely if the K_2CrO_4 reagent is added quickly. If for any reason the filtrate is turbid after two or three filtrations, the precipitate may be coagulated by boiling gently for 1 or 2 minutes. Vigorous

or long-continued boiling is to be avoided, since, owing to loss of acetic acid, $SrCrO_4$ may then separate if much strontium is present. When less than 1 mg. Ba is present it is very difficult to distinguish the faint turbidity in the colored solution; but the pale yellow precipitate can be seen after filtering and washing the K_2CrO_4 out of the filter. The precipitate must be washed thoroly, in order to remove strontium as completely as possible, which otherwise would obscure the flame coloration in the confirmatory test for barium.

Procedure 83.—*Confirmatory Test for Barium.*—Pour repeatedly through the filter containing the K_2CrO_4 precipitate (P. 82) a 5–10 cc. portion of hot HCl, and evaporate the solution just to dryness in a small casserole. Heat a platinum wire having a small loop at one end in a gas flame till it no longer colors the flame, dip it in HCl, touch it to the residue in the casserole, and introduce it again into the flame. (Green color, presence of BARIUM.) If this flame test is inconclusiv, treat the residue by the second paragraph of P. 82. (Yellow precipitate, presence of BARIUM.)

Notes.—1. When the amount of barium present is very small, only a momentary green color is seen as the yellow sodium color which first appears fades away. The only other elements that color the flame green are copper and thallium. Strontium givs a crimson and calcium an orange-red color.

2. If a small quantity of $SrCrO_4$ was precipitated in P. 82, owing to the presence of a very large amount of strontium in the substance or owing to failure to follow the directions, it will not again precipitate in this second treatment; for the quantity of strontium now present in the solution is much less than before. A yellow precipitate obtained in this second treatment is therefore conclusiv evidence of the presence of barium.

Procedure 84.—*Precipitation of Strontium.*—To the filtrate (P. 82), after cooling it, add NH_4OH (s.g., 0.90) slowly until the color of the solution changes from orange to yellow, and then 3 cc. more. Dilute the solution to 60 cc., and add slowly, with constant shaking, 50 cc. 95% alcohol. If a large precipitate forms or if a large precipitate of $BaCrO_4$ separated in P. 82, add 4 cc. 3–normal K_2CrO_4 solution and 10 cc. 95 % alcohol, and shake. (Light yellow precipitate, presence of STRONTIUM.) Filter after 5–10 minutes with the aid of suction; suck the precipitate as dry as possible, but do not wash it. (Precipitate, P. 85; filtrate, P. 86.)

Notes.—1. Under these conditions 0.5 mg. of strontium yields a precipitate; while even 400–500 mg. of calcium or magnesium do not do so. A moderate change in the conditions will not affect this result; but if the concentration of alcohol or K_2CrO_4 is much less than is recommended, the precipitation of strontium may be incomplete; while the addition of larger amounts of alcohol and K_2CrO_4 may cause the precipitation of chromate of calcium or magnesium if much of these elements is present, or of K_2CrO_4 itself, since the latter is not very soluble in alcohol. The confirmatory test should therefore always be tried.

2. When a large quantity of strontium or barium is present, the K_2CrO_4 added in P. 82 may have been so far removed from the solution that the strontium is not at first completely precipitated. In such cases, in order to ensure its complete precipitation, more K_2CrO_4 is added in this Procedure.

3. The precipitate is not washed, since $SrCrO_4$ is fairly soluble in water.

Procedure 85.—*Confirmatory Test for Strontium.*—If the K_2CrO_4 precipitate (P. 84) is small, pour three or four times through the filter containing it a hot mixture consisting of 10 cc. $(NH_4)_2CO_3$ reagent and 5 cc. 3–normal K_2CrO_4 solution. If the K_2CrO_4 precipitate is large, transfer it to a casserole, heat it for 4–5 minutes with 15 cc. of the same mixture, and filter. Wash the precipitate thoroly with cold water. Pour repeatedly through the filter containing it a cold 5–10 cc. portion of 1–normal HAc. Evaporate the solution just to dryness, add 2–3 cc. water, transfer the sloution to a test-tube (pouring it through a very small filter, if it is not perfectly clear), add 3 cc. saturated $CaSO_4.2H_2O$ solution, and heat in a steam-bath (or in a vessel of boiling water) for at least ten minutes. (Fine white precipitate presence of STRONTIUM.)

> *Note.*—The mixture of $(NH_4)_2CO_3$ and K_2CrO_4 converts $SrCrO_4$ into the less soluble $SrCO_3$; but it has no action on any $BaCrO_4$ that may be present, and only very little of any such $BaCrO_4$ dissolves in the subsequent treatment with HAc. Any $CaCrO_4$ present is converted by the mixture into $CaCO_3$, and this dissolves in the HAc; but a solution of a calcium salt givs no precipitate with saturated $CaSO_4$ solution (tho it might, of course, do so with a concentrated solution of another sulfate, like K_2SO_4).

Procedure 86.—*Precipitation of Calcium.*—To the filtrate (P. 84) add 200 cc. water; heat to boiling, and add slowly to the boiling solution 20–50 cc. $(NH_4)_2C_2O_4$ solution; shake, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.) Filter, and wash the precipitate once with water. (Precipitate, P. 87; filtrate, P. 88.)

> *Note.*—The solution is heated to boiling, the ammonium oxalate is added slowly, and the mixture is allowed to stand a few minutes, since otherwise the filtration is slow and CaC_2O_4 may pass through the filter. Moreover, since small amounts of calcium do not precipitate rapidly in the cold, 2 or 3 mg. may escape detection if the mixture is not heated. Under the conditions of the procedure, *i. e.*, in a volume of about 300 cc., 0.5 mg. Ca givs a precipitate within 5 minutes, while 400 mg. Mg do not. If, however, the volume of the solution is much less than 300 cc. and much magnesium is present, some may precipitate, especially if the mixture be allowed to cool to room temperature.

Procedure 87.—*Confirmatory Test for Calcium.*—Treat the $(NH_4)_2C_2O_4$ precipitate (P. 86) with 5 cc. cold H_2SO_4; filter if neces-

sary; add 10–15 cc. 95% alcohol, and let the mixture stand for several minutes. (White precipitate, presence of CALCIUM.)

> *Note.*—1. $CaC_2O_4.H_2O$ is very difficultly soluble in water, but dissolves in dilute solutions of largely ionized acids, owing to the formation by metathesis of unionized $HC_2O_4^-$. $CaSO_4$ is somewhat soluble in dilute H_2SO_4, but is completely thrown out as a flocculent precipitate by the addition of 2 or 3 volumes of alcohol. 1 mg. Ca gives a distinct turbidity at once, 0.5 mg. in 1–3 minutes, and 0.2 mg. within 10 minutes. Even a large amount of magnesium does not interfere with the test. If strontium were present, a small amount of it would dissolve in the H_2SO_4, but only enough to giv a slight turbidity on the addition of alcohol, corresponding to that given by 0.2–0.3 mg. Ca. calcium after standing a few minutes. Therefore anything more than a slight turbidity is a conclusiv proof of the presence of calcium.

Procedure 88.—*Detection of Magnesium.*—To the filtrate from the $(NH_4)_2C_2O_4$ precipitate (P. 86) add 10 cc. NH_4OH (s.g., 0.90) and 25 cc. Na_2HPO_4 solution; cool, and shake the mixture; if no precipitate forms, let the mixture stand for at least half an hour, shaking it frequently. (White precipitate, presence of MAGNESIUM.)

> *Note.*—This test for magnesium depends upon the precipitation of magnesium ammonium phosphate, $Mg(NH_4)PO_4$. This salt is fairly soluble even in cold water, owing chiefly to hydrolysis into NH_4OH and $Mg^{++}HPO_4^-$; and the test is therefore made in a strongly ammoniacal solution. Since the solubility increases rapidly with the temperature, the solution is cooled to the room temperature, or below. In an aqueous solution this substance shows a great tendency to form a supersaturated solution, and it is therefore usually directed to make the test in as small a volume as possible. In the presence of alcohol, however, precipitation takes place rapidly, and even 0.5 mg. Mg givs a distinct turbidity in a solution containing 250 cc. water and 50 cc. alcohol within half an hour. A small precipitate of this kind settles out on further standing and may then be detected by rotating the solution so as to cause the precipitate to collect in the center. Even so small an amount as 3 mg. Ca givs a distinct precipitate of calcium phosphate; it is therefore essential that the calcium be completely precipitated in P. 86.

ANALYSIS OF THE ALKALI-GROUP.

TABLE IX.—ANALYSIS OF THE ALKALI-GROUP.

FILTRATE FROM AMMONIUM CARBONATE PRECIPITATE: NH$_4$, K, Na salts.
Evaporate, ignite, add H$_2$SO$_4$, ignite again (P. 91).

Vapor: NH$_4$ salts.	Residue: K$_2$SO$_4$, Na$_2$SO$_4$. *Add 3 cc. water (P. 91).*	
	To one-third of the solution add Na$_3$Co(NO$_2$)$_6$ (P. 92).	*To the remainder add K$_2$H$_2$Sb$_2$O$_7$ (P. 93).*
	Yellow precipitate: K$_2$NaCo(NO$_2$)$_6$. *Test in flame, view through blue glass.*	Crystalline precipitate: Na$_2$H$_2$Sb$_2$O$_7$; *Test in flame.*
		Yellow color: Na.
	Violet color: K.	

Procedure 91.—*Removal of Ammonium Salts.*—Evaporate the filtrate from the (NH$_4$)$_2$CO$_3$ precipitate (P. 81) to dryness in a small casserole, and ignite the residue, at first gently, then at dull redness, until no more white fumes come off, taking care to heat the sides as well as the bottom of the dish. Cool, moisten the residue with H$_2$SO$_4$ (s.g., 1.84), and ignite again till all the H$_2$SO$_4$ is expelled. After the dish has become cold add 3 cc. cold water, and filter through a very small filter. Test one-third of the filtrate for potassium by P. 92; test the remainder of the filtrate for sodium by P. 93.

Notes.—1. Great care must be taken to remove the ammonium salts completely, since even 1 mg. NH$_4$ would giv a precipitate in the subsequent test for potassium.

2. A brown or black residue of organic matter, coming from impurity in the ammonium salts added in the course of analysis and from the alcohol and filter paper, may remain upon treating the ignited residue with water. Sometimes, owing to the presence of this organic matter, the aqueous solution after the ignition has a brown or yellow color. In such a case the color may be destroyed by adding 1-2 cc. H$_2$SO$_4$ (s.g., 1.84) and 1 cc. HNO$_3$ (s.g., 1.42), evaporating till white fumes of H$_2$SO$_4$ begin to come off, again adding HNO$_3$ (s.g., 1.42) and evaporating, repeating these operations till the H$_2$SO$_4$ becomes light colored, and finally igniting to expel all the H$_2$SO$_4$.

3. Only 3 cc. of cold water are added to the ignited residue, in order that the volume may be small enough to enable the subsequent test for sodium to be applied directly, and in order to leave undissolved a part of the K$_2$SO$_4$ when a large quantity of potassium is present. For the sodium test is more delicate, the less the quantity of potassium salt present.

Procedure 92.—*Detection of Potassium.*—Dilute one-third of the solution (P. 91) to 3–5 cc., and add an equal volume of $Na_3Co(NO_2)_6$ reagent. If no precipitate forms at once, let the mixture stand for at least 15 minutes. Filter, and wash the precipitate thoroly with water. (Yellow precipitate, presence of POTASSIUM.)

Dissolve the precipitate in hot dilute HCl, evaporate to a few drops, dip a clean platinum wire into the solution, and introduce it into a colorless gas flame, viewing the flame through a sufficient thickness of blue cobalt glass to cut off sodium light. (Violet flame, presence of POTASSIUM.)

> *Notes.*—1. The presence of 0.3 mg. K in 5 cc. of solution may be detected within 5 or 10 minutes, and an even smaller amount on long standing. The yellow color of the precipitate is best seen on the filter after washing out the $Na_3Co(NO_2)_6$ thoroly. In the presence of even 0.5–1.0 mg. NH_4 a precipitate is obtained very similar in appearance to that obtained with potassium; but moderate amounts of the alkaline-earth elements do not interfere with the test.
>
> 2. The flame-test for sodium is so much more delicate than that for potassium that the yellow color due to a trace of sodium may completely obscure the color given by a moderate amount of potassium. A sufficient thickness of blue cobalt glass is used to absorb the yellow rays completely, and thus permit the violet rays due to potassium to be seen. Comparativ experiments with known solutions ought always to be made, unless the analyst is perfectly familiar with the appearance of the flames.

Procedure 93.—*Detection of Sodium.*—To the remainder of the solution (P. 91), which should have a volume of 1–2 cc., add 1–2 cc. $K_2H_2Sb_2O_7$ reagent; pour the mixture into a test-tube, and let it stand for at least half an hour, or better over night. (White crystalline precipitate, presence of SODIUM.)

Decant off the solution, wash the precipitate several times with water, and dissolve it in a little HCl. Evaporate the solution to a few drops, and introduce a little of it on a platinum wire into a colorless gas flame. (Brilliant yellow flame, presence of SODIUM.)

> *Notes.*—1. The dipotassium dihydrogen pyroantimonate ($K_2H_2Sb_2O_7$) reagent is prepared by dissolving the salt in water and adding KOH. The alkali must be present, since the pyroantimonate decomposes rapidly in acid solution, and slowly in neutral solution, with precipitation of metantimonic acid ($HSbO_3$). The reagent should be tested occasionally with a solution containing 2–3 mg. Na to make sure that it is in good condition.
>
> 2. In this test, if 2 cc. of the antimonate reagent are added to 1 cc. of solution, 2 mg. Na giv a distinct crystalline precipitate in less than 5 minutes 1 mg. within 30 minutes, and a smaller amount on standing several hours. The precipitate is a heavy crystalline, granular one, and usually adheres in part to the glass, where it can best be seen by tilting the test-tube. Altho in a solution of a pure sodium salt 1 mg. Na is easily detected, yet in an actual

analysis, owing to the presence of potassium salt, it is often difficult to detect less than 2–3 mg. Moreover, certain other elements, even if present in small quantity, giv precipitates; thus a distinct turbidity is produced by even 0.1–0.2 mg. Ca, Ba, or Mg, and by 1–2 mg. Al. These elements giv, however, light, flocculent precipitates which are, very different from the heavy crystalline precipitate obtained with sodium, especially if the mixture has been allowed to stand a few hours. The crystals of the sodium salt may be separated from a flocculent precipitate by shaking the mixture, waiting long enough for the heavy crystals to settle, and decanting off the suspended, flocculent precipitate.

3. In the flame-test the yellow color is to be regarded as a confirmation of the presence of an appreciable amount of sodium in the sample only when a brilliant, large, spreading flame is obtained. Owing to the delicacy of the test, there is always sufficient sodium present to giv a slight yellow color.

SUPPLEMENTARY PROCEDURES.

Procedure 96.—*Detection of Ammonium.*—Place 0.2–0.3 g. of the finely powdered original substance in a 30 cc. round-bottom flask. Add 1 cc. NaOH solution, heat the mixture nearly to boiling, note the odor of the vapor, and hold in it a piece of moist red litmus-paper. (Odor of ammonia or blue coloration of the litmus paper, presence of AMMONIUM.) Add 10 cc. water, insert a cork fitted with a long, wide delivery tube leading to the bottom of a test-tube placed in a vessel of cold water, and distil slowly till about half the water has passed over. To the distillate add a 10% solution of K_2HgI_4 in 3–normal NaOH drop by drop so long as the precipitate increases. (Orange precipitate, presence of AMMONIUM.)

> *Notes.*—1. The orange precipitate produced by the action of NH_3 on alkaline K_2HgI_4 is a complex compound of the composition $HgO.HgNH_2I$.
>
> 2. The test is extremely delicate, a distinct precipitate resulting even with 0.2 mg. NH_4 in 5 cc. solution, and a pronounced yellow color with a much smaller quantity. This fact must be taken into account in estimating the quantity of ammonium present.

Procedure 97.—*Determination of the State of Oxidation of Mercury, Tin, and Iron.*—If mercury, tin, or iron has been found to be present, heat 20–30 cc. 6–normal H_2SO_4 to boiling in a small flask (to expel the air from the solution and flask); drop in 0.5 g. of the finely powdered original substance; and, if solution does not take place at once, boil the mixture for 2–3 minutes, covering the flask loosely with a small watch-glass. Pour 5 cc. portions of the solution (through a filter if it is not clear) into test-tubes containing: *a*, 5 cc. 1–normal HCl (white precipitate, presence of MERCUROUS MERCURY or silver); *b*, 5 cc. $SnCl_2$ solution (white precipitate, presence of MERCURIC MERCURY); *c*, 5 cc. $HgCl_2$ solution (white precipitate, presence of STANNOUS TIN); *d*, 5 cc. $K_3Fe(CN)_6$ solution (blue precipitate, presence of FERROUS IRON); *e*, 5 cc. KSCN solution (red coloration, presence of FERRIC IRON). If a precipitate is produced by HCl in *a*, filter and add the filtrate (instead of fresh portions of the H_2SO_4 solution) to the solutions named under *b* and *c*; and if silver is present in the substance, treat the HCl precipitate with NH_4OH by P. 15.

Notes.—1.   If in preparing the solution for the analysis for basic constituents the substance was dissolved in water or cold dilute HNO_3, the state of oxidation of mercury will have been determined by its presence or absence in the HCl and H_2S precipitate.   But, if the substance was treated with hot or concentrated HNO_3, any mercurous compound present will have been partly or completely oxidized to the mercuric state.

2.   Stannous and ferrous salts oxidize rapidly in the air.   Hence, if the tests for them are to be delicate, the contact with the air must be made as short as possible.

3.   Ferrous and ferric salts show a different behavior also with $K_4Fe(CN)_6$; the former giving a white precipitate (of $K_2FeFe(CN)_6$) which rapidly turns blue in the air and the latter a dark-blue precipitate (of ferric ferrocyanide, $Fe_4(FeC_6N_6)_3$).   Since this reagent produces a precipitate with both kinds of salts, it is less suitable than $K_3Fe(CN)_6$ for distinguishing between them.— The precipitate produced by $K_3Fe(CN)_6$ with ferrous salts is also ferric ferrocyanide.

DETECTION OF THE ACIDIC CONSTITUENTS.

PRELIMINARY TESTS AND GENERAL DIMENSIONS.

Procedure 100.—*Detection of Constituents Yielding Readily Volatil Products.*—Place 0.3 g. of the finely powdered substance in a 50 cc. conical flask, add 2 cc. of water, heat the mixture nearly to boiling, and to the hot mixture add 5 or 6 drops H_2SO_4. Note whether there is an odor or formation of gas bubbles. Insert in the flask a two-hole rubber stopper through which passes a glass rod from which is suspended a drop of $Ba(OH)_2$ solution. (White precipitate, presence of CARBONATE, SULFITE or THIOSULFATE.) During this test and the following ones keep the mixture hot but not boiling, and expose the drop to the vapor for about half a minute.—Replace the drop of $Ba(OH)_2$ solution by a drop of $PbAc_2$ solution. (Black precipitate, presence of SULFIDE.)—Replace the drop by a drop of $Hg_2(NO_3)_2$ solution. (Black precipitate, presence of SULFITE, THIOSULFATE or SULFIDE.)—Replace the drop by a drop of a mixture of a solution of KI with a solution of starch. (Blue coloration, probable presence of NITRITE, HYPOCHLORITE, or IODIDE.)

General Directions in regard to the Analysis for the Acidic Constituents. —If the substance dissolves completely in dilute acid (as used in P. 2) and if the preceding tests show that none of the constituents yielding readily volatil products is present, dissolve 1 g. of the finely powdered substance in 15–25 cc. 1–normal HNO_3 solution, and test portions of the solution as follows: test one fifth for *sulfate* by adding 10 cc. water and 1 cc. $BaCl_2$ solution; test one fifth for *phosphate* by adding an equal volume of $(NH_4)_2MoO_4$ solution (as in P. 115); test one fifth for *halides* by adding 1 cc. $AgNO_3$ solution (as in P. 107); continue to add $AgNO_3$ to this portion as long as a precipitate is produced, and test the filtrate from the precipitate for *chlorate* by adding to it 5 cc. saturated So_2 solution (as in the last part of P. 117); and test the remainder of the HNO_3 solution (in case $AgNO_3$ produced a precipitate) for the *separate halides* by adding an equal volume of NaAc solution (to react with the HNO_3 present) and treating the mixture by P. 110. Test also fresh portions of the original substance for *nitrate* by P. 111, for *borate* by P. 113, and for *fluoride* by P. 114.

If the substance does not dissolve completely in dilute HNO_3, or in any case if the tests described in the first paragraph show the presence of readily volatil constituents, treat fresh portions of the original substance as directed in P. 101–119.

Notes.—1. When the substance is completely decomposed by dilute acids the tests described in the first paragraph of the Procedure show whether or not it contains any of the constituents yielding readily volatil products; and, when none of these constituents is found present, the analysis for acidic constituents can be completed by testing for the other constituents in the simple manner described in the second paragraph of the Procedure. When, however, the substance is not decomposed by dilute acids, some of the acidic constituents might escape detection if tested for in the ways described in the first two paragraphs. With such a difficultly soluble substance it is therefore necessary to use a more powerful decomposing agent. Phosphoric acid is suitable for this purpose, since it is a fairly strong acid whose solution can be made highly concentrated without causing much volatilization or decomposition of the acid. When the substance does not dissolve completely in dilute HNO_3 it is therefore directed to boil it with dilute H_3PO_4 (as described in P. 101) and to condense the vapors which contain all the volatil acids resulting from the decomposition of the substance. This process serves at the same time to separate the acidic constituents of the substance from its basic constituents, thereby facilitating the detection of the acidic constituents.

2. Even with a substance which dissolves completely in dilute acids it is advantageous to employ the distillation process of P. 101 whenever the tests described in the first paragraph of the Procedure show the presence of any of the acidic constituents yielding readily volatil products. For these suspended-drop tests, tho very delicate, do not enable a satisfactory estimate to be made of the proportions in which the constituents are present. Moreover these tests fail to detect certain of the constituents when they are present together (for example, carbonate in the presence of sulfite), and to distinguish between certain of them (for example, between nitrite, hypochlorite or iodide).

DISTILLATION WITH PHOSPHORIC ACID.

TABLE X.—BEHAVIOR OF THE ACIDIC CONSTITUENTS ON DISTILLATION WITH PHOSPHORIC ACID.

Distil the substance with dilute H_3PO_4 (P. 101). Collect the first half of the distillate in $Ba(OH)_2$ solution and the second half in water. To the residue add Cu and distil again, collecting this third distillate in water.

FIRST DISTILLATE	SECOND DISTILLATE	THIRD DIST.	NONVOLATIL RESIDUE
CO_2 from carbonate. SO_2 from sulfite or thiosulfate. Cl_2 from hypochlorite, chlorate, or chloride.* Br_2 from bromide.* I_2 from iodide.* HNO_2 from nitrite. H_2S from sulfide. HCN from cyanide.	HCl from chloride. HBr from bromide. HI from iodide. $HSCN$ from thiocyanate. HCN from ferrocyanide. H_2S from insoluble sulfides. HNO_3 from nitrate. Cl_2 from chlorate or chloride*. Br_2 from bromide.* I_2 from iodide.	SO_2 from sulfate.	HPO_3 from phosphate. HBO_2 from borate. H_2SiO_3 (as a precipitate) from silicate.

* When the substance contains also an oxidizing compound.

Procedure 101.—*Distillation with Phosphoric Acid.*—Place 2 g. of the finely powdered substance and a few glass beads in a 100 cc. round-bottom Jena-glass flask fitted with a rubber stopper, through which pass a straight tube, 20–30 cm. long, leading to the bottom of the flask and a delivery tube. Fasten the flask in an inclined position. Lead the end of the delivery tube through a two-hole stopper into 40 cc. of nearly saturated $Ba(OH)_2$ solution contained in a 100 cc. flask supported in a large beaker of cold water. Boil in a small flask for about a minute a mixture of 25 cc. water and 10 cc. 85% H_3PO_4 (to expel any CO_2 present in it). Pour this mixture into the distilling flask with the aid of a small funnel connected with the long, straight tube. Heat the mixture to boiling, distil till about 10 cc. have passed over, and then remove the distillate. (White precipitate, presence of CARBONATE or some SULFUR–CONTAINING CONSTITUENT.)

Cool the distillate and make it slightly acid with HAc. (Complete or partial solution of the precipitate, presence of CARBONATE; residue (S or BaSO₃), presence in the substance of free SULFUR, SULFIDE, SULFITE, or THIOSULFATE.) If there is a residue, treat one-half of the mixture immediately by P. 102, and separate portions of the remainder by P. 103, 104, 105, and 106. If there is no residue, treat separate portions of the whole distillate by P. 103, 104, 105, and 106.

Introduce the end of the delivery tube of the distilling flask into another receiving flask containing 35 cc. water. Continue the distillation until the liquid becomes sirupy, boils more quietly, and begins to giv off fine white fumes. Treat this distillate as directed in P. 107.

To the contents of the distilling flask, while still warm, add 5–10 g. of copper filings or turnings. Distil for 3–5 minutes longer, collecting the distillate in 15 cc. of water. Note the odor of the distillate, and treat it by P. 112.

Notes.—1. It is necessary to use a Jena-glass flask, since one of ordinary glass is quickly destroyed by the action of hot, concentrated H_3PO_4. The boiling is sometimes violent, especially when much insoluble material is present. The addition of the glass beads serves to reduce the bumping; and placing the flask in an inclined position prevents material from being thrown over into the distillate, which would lead to error in the subsequent tests. In any case in which it seems possible that some of the boiling liquid has been thrown over into the distillate, a small portion of the latter should be tested for phosphate by adding an equal volume of $(NH_4)_2MoO_4$ solution (see P. 115).

2. Phosphoric acid, which is ionized into H^+ and $H_2PO_4^-$ to a moderate extent (about 27% in 0.1 molal solution), displaces almost completely from their salts (unless these are very difficultly soluble) the much less ionized acids, H_2CO_3, HNO_2, H_2S, $HClO$, HCN, HF, and H_3BO_3, and also to a large extent the moderately ionized H_2SO_3. Since all these acids, except HF and H_3BO_3, volatilize readily out of aqueous solution, they pass over almost or quite completely into the first distillate, HClO in the presence of chloride giving Cl_2. The largely ionized acids, HCl, HBr, HI, HSCN, HNO_3, $HClO_3$, $H_3Fe(CN)_6$, and $H_4Fe(CN)_6$, are not found in any considerable proportion in the first distillate, since they are displaced from their salts much less completely, and since in addition they are much less volatil. Of these the first five pass over unchanged and almost completely into the second distillate; for after the H_3PO_4 has become fairly concentrated, the acids are displaced to a greater extent and volatilize more readily in consequence of the higher temperature at which the mixture boils and the smaller proportion of water it contains. From the stronger H_3PO_4 solution HF also passes over in large quantity; but this is not true of H_3BO_3 and H_2SO_4, which volatilize only in insignificant amounts even when the acid has become nearly anhydrous. The three acids, $HClO_3$, $H_4Fe(CN)_6$, and $H_3Fe(CN)_6$, are not volatil as such, but are decomposed by the H_3PO_4 after it becomes fairly concentrated—$HClO_3$ with formation of Cl_2 and HCl, $H_3Fe(CN)_6$ and $H_4Fe(CN)_6$ with formation of free HCN. In regard to the acids that may be present in the two distillates, see also Table X.

3. The barium salts of all the acids passing into the first distillate, except the carbonate and sulfite, remain in solution. Phosphoric acid, if thrown over mechanically, would, however, also giv a precipitate. Sulfur, when present in the free state or when liberated from a polysulfide or thiosulfate, volatilizes with the steam, and givs a turbid appearance to the water condensed in the delivery tube and to the barium hydroxide solution, by which it is little acted on in the cold. Chlorin is converted by the barium hydroxide into barium chloride and hypochlorite; bromin, into bromide, hypobromite, and bromate; and iodin, mainly into iodate and iodide.

4. On acidifying the first distillate slightly with HAc, $BaCO_3$ dissolves, but $BaSO_3$ does not. This difference in behavior is due to the fact that hydrocarbonate-ion (HCO_3^-) is much less ionized than hydrosulfite-ion (HSO_3^-). Sulfur, if present, also remains undissolved. The addition of HAc causes the liberation almost at once of chlorin, bromin, or iodin from a mixture of hypochlorite and chloride, hypobromite and bromide, or iodate and iodide; but bromin is set free somewhat more slowly from a mixture of bromate and bromide.

5. A small precipitate obtained in this procedure (or in the following one) does not prove the presence of carbonate in the mixture unless the prescribed precautions are carefully observed—namely, the boiling of the original H_3PO_4 solution, and avoiding the exposure to the air of the various solutions, especially that of the BaO_2H_2. Even with these precautions, however, it is seldom possible to prevent the absorption of enough CO_2 to produce a slight turbidity.

6. Upon boiling the H_3PO_4 with the copper, H_2SO_4, if present, is reduced to H_2SO_3; and this passes over into the distillate in the form of SO_2 gas. Less than 1 mg. SO_4 can be detected by this process of distillation. The copper should be finely divided and should be added while the liquid is still warm, since on cooling it solidifies to a glassy mass, which consists of pyrophosphoric acid ($H_4P_2O_7$). The heating should be continued for 5–10 minutes; but, if much more prolonged, the contents of the flask change to a solid mass, owing to conversion of the pyro to metaphosphoric acid (HPO_3), which can afterwards be removed only with much difficulty.

7. With reference to the analysis of the first and second distillates, provided for in the subsequent procedures, certain facts are to be noted which in many cases greatly reduce the number of these special tests which it is necessary to make. In the first place, some of the acids are incompatible with each other, so that when certain ones are found, others need not be tested for: thus in the acidified distillate H_2S can not be present with H_2SO_3, HNO_2, or free halogen; HNO_2 and H_2SO_3 can not be associated with each other or with free halogen, etc. Secondly, the nature of the basic elements taken in connection with the solubility of the substance often excludes certain acidic constituents; thus in a substance containing barium and soluble in water or very dilute acid, sulfate can not be present; in a water-soluble substance containing silver, none of the acids precipitated by silver nitrate can be present. Thirdly, the general character or known source of the substance may make many of the tests unnecessary; thus, it is useless to test a mineral for nitrite, sulfite, oxyhalogen salts, simple or complex cyanides, oxalate, or other organic salt. The analyst should, therefore, always consider these aspects of the problem, shortening the procedure in such ways as his knowledge makes possible.

8. For a general statement as to the solubilities of substances in water and dilute acids, see Note 9, P. 2; see also the Table of Solubilities of Slightly Soluble Substances at the end of the book.

7

TABLE XI.—ANALYSIS OF THE FIRST DISTILLATE.

FIRST DISTILLATE.—Precipitate: $BaCO_3$, $BaSO_3$, S. Solution: Barium hypohalites (with halides), $Ba(NO_2)_2$, BaS, $Ba(CN)_2$.

To the whole mixture add HAc (P. 101).

Precipitate: $BaSO_3$, S. Solution: H_2CO_3, Cl_2, Br_2, I_2, HNO_2, H_2S, HCN. Treat portions of the unfiltered mixture as follows:

Add HCl and filter (P. 102).			Add HAc and $CHCl_3$ (P. 103). (Purple color shows IODIN.) (Orange color shows BROMIN.) Treat portions of the aqueous layer as follows:		Introduce 1 cc. into an inverted tube filled with a solution of HCl and urea (P. 104).	Filter, add $Cd(NO_3)_2$ (P. 106).	Treat with NaOH, $FeSO_4$, and $FeCl_3$; boil, add HCl (P. 106).
Residue: S. (Shows SULFIDE OR THIOSULFATE.)	Solution.	Add Br_2.	If the $CHCl_3$ was colorless, add KI and $CHCl_3$.	Add HNO_3, extract with $CHCl_3$.	Gas evolved: N_2. (Shows NITRITE.)	Precipitate: CdS. (Shows SULFIDE.)	Blue precipitate $Fe_4(Fe(CN)_6)_3$. (Shows CYANIDE.)
		Precipitate: $BaSO_4$.*		Chloroform layer: I_2, Br_2, Cl_2. Shake with H_2SO_3.			
		Solution: H_2CO_3.		Water layer: HI, HBr, HCl. Test for separate halogens (P. 110).			
		Distil into $Ba(OH)_2$.	Purple coloration: I_2. (Shows CHLORIN OR NITRITE.)				
		Precipitate: $BaCO_3$. (Shows CARBONATE.)					

* Shows SULFITE OR THIOSULFATE

† The solution is subjected to this treatment only when the previous indications have not led to definit conclusions as to the presence or absence of each of the three halogens

ANALYSIS OF THE FIRST DISTILLATE.

See Table XI, page 90.

Procedure 102.—*Detection of Carbonate and Sulfur-containing Constituents.*—To one-half of the first distillate (P. 101), if there was a residue on adding HAc, add 1–2 cc. HCl. (Residue, presence of free SULFUR, SULFIDE, or THIOSULFATE.)   Filter, and add to the filtrate saturated bromin solution till the liquid becomes slightly yellow.   (White precipitate, presence of SULFITE or THIOSULFATE.) Transfer the mixture to a distilling apparatus such as is used in P. 101, first filtering out the precipitate if it is large, distil for a minute or two, collecting the vapors in 20 cc. saturated $Ba(OH)_2$ solution. (White precipitate, presence of CARBONATE.)   Acidify slightly with HAc.   (Solution of the precipitate, presence of CARBONATE.)

If H_2SO_3 is found in the distillate, treat a fresh portion of the original substance by P. 118, to determin whether it comes from a sulfite or thiosulfate.

> *Notes.*—1. See P. 101, Notes 3–5. Since H_2SO_3 slowly oxidizes to H_2SO_4 in the air, the solution should be treated with HCl at once. If any H_2SO_4 has been formed in this way, it will be precipitated as $BaSO_4$ before the addition of Br_2. Care must be taken to add enough Br_2 to complete the oxidation, since otherwise in the subsequent distillation SO_2 will distil over and might be mistaken for carbonate.
>
> 2. If there is a large precipitate of $BaSO_4$, it is filtered out, since otherwise it is difficult to avoid violent bumping during the distillation. Exposure to the air, and especially to the breath, should, however, be avoided so far as possible, so that CO_2 may not be absorbed from it.
>
> 3. A residue of sulfur may arise from the presence in the substance of free sulfur, of a persulfide, of an ordinary sulfide together with some oxidizing substance, or of a thiosulfate.

Procedure 103.—*Detection of Nitrite and Free Halogen.*—To one-fourth of the first distillate (P. 101), or of what remains of it (P. 102), add 1–2 cc. HAc and 2–3 cc. of chloroform, and shake vigorously. (Purple coloration of the chloroform, presence in the distillate of free IODIN; yellow or orange coloration, of free BROMIN.)

If there is no coloration, pour about a third of the aqueous layer into a test tube, add 1 cc. chloroform and a few drops 1%KI solution, and let the mixture stand for 5 minutes, noting whether the color due to liberated iodin increases.   (Purple color, presence in the distillate of CHLORIN, or, if the color gradually increases, of NITROUS ACID; no color, absence of NITRITE in the substance.)

If there is a coloration after the addition of KI, test a 1 cc. portion of the first distillate (P. 101) for NITRITE by P. 104.

If these tests show the absence of nitrite and the presence of free halogen, but do not warrant definit conclusions as to the presence or absence of each one of the three halogens, proceed as follows: Add 5 cc. HNO_3 to the remaining two-thirds of the aqueous layer, separate the chloroform from it by means of a separating funnel, shake that layer a second and third time with 3 cc. of fresh chloroform, and separate the layers sharply again. Unite the three portions of chloroform, wash it once in the separating funnel by shaking it with about one-third its volume of HNO_3, add the chloroform to an equal volume of H_2SO_3 solution in a separating funnel, shake, draw off and reject the chloroform layer, and test the aqueous layer for bromide and chloride by P. 110.

If free halogen is found present in the distillate, test fresh portions of the original substance for hypochlorite by P. 116 and for chlorate by P. 117.

Notes.—1. For the reactions between the halogens and barium hydroxide and their re-formation on acidifying with HAc, see P. 101, Note 4.

2. The free halogens distribute themselves between the chloroform and water phases. In the case of pure bromin or iodin the ratio of the concentration in the chloroform to that in the water layer is very large and is almost independent of the concentration. This is in accordance with the so-called distribution law, which requires that the ratio of the concentrations of a given molecular species, such as Br_2 or I_2, in the two solvents be constant. When an iodide, like HI, is also present, the proportion of iodin extracted by the chloroform is greatly reduced, since the iodin in the aqueous layer is largely combined with the iodide in the form of the triiodide (HI_3); but it is still sufficient to make the color-test a very delicate one.

3. The characteristic purple color given to chloroform is so delicate a test that even 0.05 mg. of iodin in the solution tested can be detected by this procedure. Bromin may be detected, but only in the absence of iodin, by the orange or yellow color of the chloroform layer when not less than 0.5 mg. of bromin is present in the solution tested. (If a few drops of KI solution be added to one-third of the chloroform layer, the more intense color of the iodin liberated will enable a smaller quantity of bromin to be detected.) Chlorin gives no decided color to the chloroform, but like bromin causes liberation of iodin on the addition of KI. For extracting the halogens from aqueous solutions carbon tetrachloride or carbon bisulfide may be used instead of chloroform; but carbon bisulfide has the disadvantage of being highly inflammable.

4. Nitrous acid, like bromin or chlorin, liberates iodin from KI. The reaction is delicate enough to enable 0.1 mg. NO_2 to be detected in the solution tested. A peculiarity of this reaction is that the nitric oxide which is formed reacts with the iodide, so that a continuous liberation of iodin results. Thus the nitrous acid acts as a catalyzer of the reaction between oxygen and HI. This progressiv liberation of iodin is highly characteristic of nitrous acid, but renders it difficult to estimate the amount of it present. Since this behavior

may not be a conclusiv indication of nitrous acid, a fresh portion of the distillate is tested for it by P. 104.
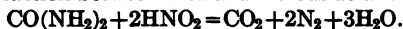
5. If nitrous acid is found in the distillate, it shows the absence of free halogens, since nitrous acid is oxidized by chlorin or bromin very rapidly at room temperature and by iodin during the distillation with phosphoric acid.

6. An aqueous solution of chlorin contains a considerable proportion of HClO and HCl, sufficient to satisfy the equilibrium conditions of the reaction $Cl_2 + H_2O = HClO + H^+ + Cl^-$. Since the proportion present as Cl_2 decreases with decreasing hydrogen-ion concentration, and since the Cl_2 alone dissolves in the chloroform, the quantity of chlorin extracted from a nitric acid solution must, in accordance with the distribution law, be much larger than from an acetic acid solution. In order, however, to extract small amounts of chlorin nearly completely, it is necessary to add chloride as well as the acid.

7. When free halogen is detected by these tests it shows either that the halogen was present in the original substance in the free state, or (what is more common) that it was liberated during the distillation with phosphoric acid from a halide by the action of some oxidizing substance, or from an oxy-halogen salt (such as a hypochlorite, chlorate, bromate, etc.) by spontaneous decomposition or by reaction with some reducing substances. When free halogen is found in the distillate, a portion of the original substance is therefore further tested (by P. 116 and 117) to determin from what source the halogen originated.

Procedure 104.—*Detection of Nitrite.*—If the results of P. 103 show that the first distillate may contain HNO_3, determin its presence or absence as follows: Fill a weighing tube with a 20% solution of urea in HCl, and invert it over a small dish containing more of the same solution. Introduce 1 cc. of the first distillate (P. 101) into the weighing tube by means of a small tube which has one end closed with a rubber nipple and the other end drawn out and bent so as to form a small U. Take care not to introduce an air-bubble at the same time. (Formation of gas, presence of NITRITE.)

Notes.—1. The reaction between urea and nitrous acid is
$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$
The N_2 is liberated in the form of minute bubbles which collect at the top of the tube. When much CO_2 is produced, it also separates as a gas; but a small quantity remains dissolved in the liquid. The amount of nitrite present may be estimated by making a comparativ test with a known quantity of nitrite.

2. This procedure enables 0.1 mg. NO_2 in the 1 cc. of solution tested to be detected; but since such a small portion of the distillate is used, a more delicate test may be desirable. If so, make a larger amount of the distillate slightly alkaline with NaOH, evaporate it to about 1 cc., acidify with a drop or two of HCl, and treat this solution as described in the procedure. In this process, before evaporating the solution, it is made alkaline so as to avoid loss of HNO_2. The mixture is afterwards acidified so that carbonic acid may be expelled from it before it is introduced into the tube.

3. The halogens, chlorin, bromin, and iodin, when dissolved in alkali decompose urea with evolution of nitrogen, but they do not do so when dissolved in concentrated HCl. They do not therefore interfere with the test when carried out as above described.

4. Since all nitrites are at least moderately soluble in water, this test may be made with an aqueous solution or aqueous extract of the original substance. The test should be so made when the nature of the substances present makes it possible that nitrous acid may have been completely decomposed during the distillation with H_3PO_4.

Procedure 105.—*Detection of Sulfide.*—To one-half of what still remains of the first distillate (P. 101), add 2–3 cc. $Cd(NO_3)_2$ solution. (Yellow precipitate, presence of SULFIDE.)

> *Notes.*—1. The presence of H_2S is usually detected in the distillate by its odor; but the precipitation of CdS from a weakly acid solution has the advantage of enabling the amount of sulfide to be approximately estimated. When this test is applied to a strongly acid solution from any other source, sodium acetate should also be added.
>
> 2. A negativ test for H_2S in the first distillate does not prove the absence of sulfide in the original substance, unless the latter has dissolved completely in the dilute H_3PO_4; for some difficultly soluble sulfides, such as CuS, are decomposed only when the H_3PO_4 becomes concentrated, as it does in the latter part of the distillation. It is therefore directed in P. 107 and P. 112 to test also the second and third distillates for sulfide.

Procedure 106.—*Detection of Cyanide.*—Place what remains of the first distillate in a casserole; add 1 cc. NaOH solution, about 0.5 cc. $FeSO_4$ solution (or about 0.1 g. solid $FeSO_4.7H_2O$), and 1 or 2 drops $FeCl_3$ solution; and boil for one minute. To the hot mixture add HCl a few drops at a time until, on shaking, the dark colored precipitate of ferrous and ferric hydroxides is dissolved. Cool the mixture. If a precipitate is not plainly visible, filter, and wash out the filter-paper once with water. (Blue precipitate, presence of CYANIDE.)

> *Notes.*—1. This test is based upon the formation of ferrocyanide by the action of cyanide on ferrous hydroxide and upon the reaction between this substance and the ferric salt whereby ferric ferrocyanide (Prussian blue) is formed, which is difficultly soluble in dilute hydrochloric acid.
>
> 2. A small precipitate is not readily detected in the hot reddish-yellow solution, but is more easily seen in the cold light-colored solution, especially after standing, or when collected on a filter. If the precipitate on the filter is not dark blue, it should be washed with a little hot, dilute hydrochloric acid. With these precautions, 0.2 mg. CN in the solution tested can be detected.
>
> 3. Cyanides may be present in the original substance in the form either of simple or of complex cyanides. The latter are characterized by complex anions (such as $Ag(CN)_2^-$ and $Fe(CN)_6^{--}$). These differ very greatly in their stability towards decomposing agents, the difference depending on the extent to which they are dissociated into the simple ions (Ag^+ and CN^- or

Fe^{++} and CN^-). Ferrocyanides, ferricyanides, and cobalticyanides are so slightly dissociated in this way that scarcely any HCN is produced when dilute HCl, HNO_3, or H_2SO_4 is added to their cold solutions; but almost all the other complex cyanides (such as $KAg(CN)_2$ or $K_2Ni(CN)_4$) are readily decomposed by these acids.—In the distillation with H_3PO_4, not only the simple cyanides, but also nearly all the complex cyanides are decomposed during the first part of the distillation; but a few very stable substances (such as Prussian blue) are completely decomposed only in the second part of the distillation.

4. The following procedure enables 2 mg. cyanide to be detected in the presence of ferro or ferricyanide: Place in a 20 cc. distilling flask provided with a thistle-tube 0.5–1 g. of the original substance, 2 g. powdered $CaCO_3$, and 10 cc. water. Add very gradually through the thistle-tube 2 cc. HCl (enough to decompose some, but not all of the $CaCO_3$). Allow the gas which is evolved to pass into a small test-tube containing 1 cc. NaOH and 5 cc. water. Finally heat the contents of the flask almost to boiling. Test the NaOH solution for cyanide by P. 106.—This separation depends upon the fact that HCN is displaced by H_2CO_3 from simple cyanides and from the relativly unstable complex cyanides, such as $Ag(CN)_2^-$ or $Ni(CN)_4^-$, but not from ferro or ferricyanides.

5. Ferrocyanide and ferricyanide may be detected and distinguished from each other when only one of them is present, by adding a ferric salt to one portion of an aqueous or dilute acid solution, and by adding ferrous salt to another portion of the solution. A ferric salt givs a blue precipitate of ferric ferrocyanide with ferrocyanide, but no precipitate with a ferricyanide. A ferrous salt givs the same blue precipitate (of ferric ferrocyanide) with a ferricyanide; but it also givs with a ferrocyanide a precipitate (of ferrous ferrocyanide), which is white if no ferric salt is present, but which rapidly turns blue in contact with the air.

6. Ferrocyanide and ferricyanide may be detected in the presence of each other by proceeding as follows: Add to an aqueous or dilute solution of the substance $AgNO_3$ and then a moderate excess of NH_4OH. (White precipitate insoluble in NH_4OH, presence of FERROCYANIDE. Orange to red precipitate readily soluble in NH_4OH, presence of FERRICYANIDE.) Filter out and wash the precipitate, and pour over it a little $FeCl_3$ solution. (Blue coloration, presence of FERROCYANIDE.) Acidify the ammoniacal filtrate with HAc, filter out and wash the precipitate, and pour through the filter containing it a little $FeSO_4$ solution. (Orange-red precipitate, which is turned blue by the $FeSO_4$, presence of FERRICYANIDE). This procedure enables 0.2 mg. $Fe(CN)_6$ as either ferro or ferricyanide to be detected when present alone; but the test for ferricyanide is much less delicate in the presence of much ferrocyanide.

TABLE XII.—ANALYSIS OF THE SECOND AND THIRD DISTILLATES.

SECOND DISTILLATE: H₂S, HSCN, HCl, HBr, HI, HNO₃. *Treat separate portions as follows:*

If AgNO₃ *gives a precipitate, treat separate portions as follows:*

					THIRD DISTILLATE: H₂SO₄. Add HCl, BaCl₂, and Br₂ (P. 112).
Add AgNO₃ (P. 107).					
Precipitate: AgCl, AgBr, AgI, AgSCN, AgS, AgCN.	Add Cd(NO₃)₂ (P. 105).	Add FeCl₃ and HNO₃ (P. 108).	Add CHCl₃ (P. 109).		
	Precipitate: CdS. (Shows SULFIDE.)	Red color: Fe(SCN)₃. (Shows THIOCYANATE.)	CHCl₃ layer: I₂, Br₂, Cl₂.* — Purple color: I₂. (Shows CHLORIN.) — If colorless, add KI.		
			Water layer. *Remove free halogen, if present, by repeated shaking with CHCl₃; then add NaAc, HAc, and KMnO₄, and extract with CHCl₃* (P. 110).		
			CHCl₃ layer: purple: I₂. (Shows IODIDE.)	Purple color: I₂. (Shows NITRATE.)	
			Water layer. Add H₂SO₄ and more KMnO₄ and CHCl₃.	Distillate: HNO₃. Add KI and CHCl₃.	
			CHCl₃ layer, orange: Br₂. (Shows BROMIDE.)	Distil with H₂SO₄ and FeSO₄ (P. 111).	Precipitate: BaSO₄. (Shows SULFATE.)
			Water layer. *Boil to expel Br₂, filter, add H₂SO₄, HNO₃ and AgNO₃.*		
			Precipitate: AgCl. (Shows CHLORIDE.)		

* Purple coloration shows IODIN, orange coloration, BROMIN.

ANALYSIS OF THE SECOND AND THIRD DISTILLATES.

See Table XII, page 96.

Procedure 107.—*Detection of Constituents Precipitable by Silver Nitrate.*—To one-eighth of the second distillate add 1 cc. HNO_3 and 1 cc. $AgNO_3$ solution. (White precipitate, presence of CHLORIDE, CYANIDE, or THIOCYANATE; yellowish precipitate, presence of BROMIDE or IODIDE; black precipitate, presence of SULFIDE; no precipitate, absence of all these in this distillate.)

If there is a precipitate, test one-sixth of the second distillate for sulfide by P. 105 (see, however, Note 2), and another sixth for thiocyanate by P. 108; and then test the remainder for free halogen and halides by P. 109 and 110, and for nitrate by P. 111.

If there is no precipitate, test the distillate for nitrate by P. 111.

> *Notes.*—1. All the common silver salts, except the halides, cyanide, thiocyanate, and sulfide are either soluble in water (as are the nitrate, sulfate, chlorate, and fluoride), or dissolve readily in HNO_3 owing to displacement of the weaker acid (as do the phosphate, carbonate, borate, and sulfite). It should be noted, however, that salts of weak acids are not necessarily readily soluble in a strong acid. Thus Ag_2S does not dissolve in dilute HNO_3 because its solubility in pure water is so extremely small that there is only a very minute concentration of S^- ion in the saturated solution, and this can yield, in accordance with the mass-action law, only a relatively small concentration of SH^- and unionized H_2S with the H^+ ion of the HNO_3. Silver cyanide has for another reason a very slight concentration of its anion in its saturated solution; namely, because of the fact that this salt exists in the solution mainly as Ag^+ and $Ag(CN)_2^-$, and scarcely at all as Ag^+ and CN^-.
>
> 2. It is not necessary to test for cyanide in this distillate; for even the insoluble ferro and ferricyanides are decomposed partly, tho not necessarily completely, in the first part of the distillation. It is, however, advisable to test for sulfide unless the substance dissolved completely in the hot dilute H_3PO_4, or unless the $AgNO_3$ precipitate is pure white. For some insoluble sulfides begin to decompose only when the H_3PO_4 becomes concentrated.

Procedure 108.—*Detection of Thiocyanate.*—If $AgNO_3$ produced a precipitate (P. 107), dilute a sixth of the second distillate (P. 101) to 5–10 cc., add 2–3 drops of $FeCl_3$ solution and 2–3 drops of HCl. (Red color, presence of THIOCYANATE.)

> *Notes.*—1. The red coloration arises from the formation by metathesis of $Fe(SCN)_3$, a substance whose degree of ionization is relatively small. The HCl is added to reduce the hydrolysis of the $FeCl_3$ and diminish the color imparted by it to the solution.—A distinct reddish-yellow coloration is produced by 0.1 mg. SCN. A deep red color is obtained when 1 mg. or more is present.
>
> 2. Since in the distillation with H_3PO_4, thiocyanates are destroyed by certain oxidizing agents, such as nitrates, which do not act on it at ordinary temperatures, it is sometimes advisable to apply this test also to a solution of the original substance.

Procedure 109.—*Detection and Removal of Free Halogens.*—If AgNO₃ gave a precipitate in P. 107, to three-fourths of the remainder of the second distillate in a separating funnel add 2–3 cc. chloroform and shake. (Purple color, presence of IODIN; orange or yellow color, presence of BROMIN.)

If the chloroform is colorless, separate it from the aqueous layer. Add to the chloroform layer a few drops of KI solution. (Purple color, presence of CHLORIN, or of BROMIN in small quantity.) If there is no color, treat the aqueous layer left in the separating funnel by P. 110.

If any free halogen is present, add to the mixture in the separating funnel 10 cc. chloroform, shake, and separate the two layers. Repeat the extraction with a fresh 10 cc. portion of chloroform. (Purple color of the chloroform layer and brown color of the aqueous layer, showing slow extraction of iodin, presence of IODIDE.) Test the aqueous layers for halides by P. 110.

If further tests for free bromin or chlorin are necessary, shake the chloroform extracts with 10 cc. water, adding enough H_2SO_3 solution to reduce the halogen, and treat the aqueous layer by P. 110.

> *Notes.*—1. As to these tests see the notes to P. 103.
> 2. As there stated, the proportion of the iodin extracted from the aqueous layer by chloroform is much smaller when iodide is also present, so that some tri-iodide then remains in the aqueous solution after two extractions. Since this behavior itself shows the presence of iodide, it is not necessary to attempt to extract all the iodin before testing for halides by P. 110.

Procedure 110.—*Detection of Halides.*—Place the aqueous layer which is to be tested for halides (P. 109) in a separating funnel; add 3 cc. chloroform, 8 cc. normal sodium acetate solution, 2 cc. HAc, and 1 cc. 1% KMnO₄ solution (in excess of that required to oxidize any H_2SO_3 present), and shake. (Purple color, presence of IODIDE.) If there is a color, pour the mixture into a flask, add 10 cc. more CHCl₃, and then add gradually 1% KMnO₄ solution, shaking after each addition, till the aqueous layer becomes pink. Pour the mixture through a moistened filter to remove the chloroform and precipitated MnO₂, and shake the filtrate once or twice with a fresh 10 cc. portion of chloroform to extract all the iodin.

Place the aqueous solution and 3 cc. chloroform in a separating funnel, add 5 cc. H_2SO_4, and 1 cc. 1% KMnO₄ solution, unless such an excess is already present, and shake. (Yellow or orange coloration of the chloroform, presence of BROMIDE.)

Transfer the aqueous layer to a casserole, add 5–20 cc. 1 % KMnO₄ solution, and boil the mixture 3–5 minutes, or until the volume has been reduced to 10 cc. Filter off the MnO₂, and, if the solution is still pink, add H₂SO₃ solution drop by drop until it is colorless. Dilute the solution to 100 cc., filter if necessary, and add 2 cc. HNO₃ and 1–2 cc. AgNO₃ solution. (White precipitate, presence of CHLORIDE.)

   Notes.—1. This separation is based upon the different rates at which KMnO₄ sets free by oxidation the three halogens from their salts in a solution of definit hydrogen-ion (H⁺) concentration. A dilute solution of acetic acid containing considerable sodium acetate has such a hydrogen-ion concentration that an iodide is immediately oxidized by KMnO₄ with liberation of iodin, while bromide and chloride are not oxidized to an appreciable extent in the time required for the operations. When the H⁺ concentration is increased by the addition of the prescribed quantity of H₂SO₄, the bromide is oxidized very rapidly while the rate of the corresponding reaction for the chloride is still so small at room temperature that scarcely any chlorin is set free. Even when the solution is boiled to expel the bromin, only a small fraction of the chloride present is oxidized to chlorin.
   2. To secure satisfactory results, the directions as to the quantities of the acids added must be followed carefully. The proper quantity of H₂SO₄ is that required to react with all the sodium acetate and to giv in addition an excess equal to about 1 cc. H₂SO₄ per 20 cc. of solution.
   3. A very small precipitate of AgCl obtained at the end of the procedure does not necessarily indicate the presence of chloride in the substance, unless the reagents used have been proved to be entirely free from chloride. Even then a very slight precipitate (corresponding to less than 0.1 mg. Cl) may result from a reaction between the permanganate and chloroform. For these reasons a blank test should be made in any doubtful case.
   4. The yellow color of bromin in 3–5 cc. chloroform enables about 0.5 mg. Br to be detected in this procedure, which corresponds to about 1 mg. Br in the whole of the second distillate.
   5. If HCN, H₂S, or HSCN is present in the distillate, it will be expelled or destroyed by the boiling with KMnO₄ before the final test for chloride with AgNO₃ is applied.

Procedure III.—*Detection of Nitrate.*—To the remainder of the second distillate (after removing any iodide or thiocyanate present by shaking with solid Ag₂SO₄ and filtering) add 3 cc. H₂SO₄ (s.g., 1.84) and 5 cc. saturated FeSO₄ solution. Place the mixture in the apparatus used in P. 101, and distil until only about 5 cc. remain, collecting the distillate in a mixture of 20 cc. water and 1 cc. NaOH solution. Make the distillate acid with H₂SO₄, add 2–3 cc. chloroform, and shake (to make sure that the chloroform remains colorless). Then add a few drops of KI solution, and shake again. (Purple color, presence of NITRATE.)

Notes.—1. In this procedure the nitrate is reduced by the $FeSO_4$ to nitric oxide (NO), which passes over as a gas into the receiver, where it is oxidized by the oxygen of the air to HNO_2, which is then absorbed by the NaOH. When the solution is acidified and KI added, I_2 is liberated by the HNO_2 (see P. 103, Note 4). By this procedure 0.2 mg. NO_3 in the liquid submitted to distillation can be detected.

2. The reaction is highly characteristic for nitrates, since any nitrous acid present passed over completely into the first distillate, and since other oxidizing substances (for example, chlorin or bromin) which might liberate iodin from potassium iodide are reduced by the $FeSO_4$ to compounds which, even if they pass over into the distillate, have no action on KI. The only substances that may interfere are iodide and thiocyanate; and provision is therefore made for first removing these by adding solid Ag_2SO_4, shaking, and filtering.

Procedure 112.—*Detection of Sulfate.*—To the third distillate obtained upon heating with copper (P. 101), add 1–2 cc. HCl, 3–5 cc. $BaCl_2$ solution, and saturated Br_2 solution till the liquid becomes yellow. (White precipitate, presence of SULFATE.)

Notes.—1. By the action of copper in the presence of concentrated H_3PO_4 on sulfates (even on the very difficultly soluble $BaSO_4$) SO_2 is formed. This is oxidized by the Br_2 to H_2SO_4, which then precipitates as $BaSO_4$. In this way 1 mg. SO_4 may be detected. Even when this small amount is present in the substance, only an inconsiderable proportion of it passes into the first and second distillates.

2. Much H_3PO_4 also passes over into the distillate; and the HCl is added to prevent its precipitation as $BaHPO_4$. Too much HCl must not be added since $BaSO_4$ is appreciably soluble in it.

3. When a sulfide is present which has not already been decomposed, sulfur and H_2S may pass into the third distillate, after the acid has become concentrated. The H_2S may be tested for in a portion of the distillate by P. 105.

TABLE XIII.—SUPPLEMENTARY PROCEDURES.

Treat portions of the original substance as follows:

Distil with CH₃OH and H₂SO₄ (P. 115).	Heat with SiO₂ and KHSO₄ (P. 114).	Boil with HNO₃, add (NH₄)₂MoO₄ (P. 115).	*Heat with water, HAc, and PbAc₂ (P. 116).	*Add dilute HNO₃, Na₃AsO₃ (to reduce hypochlorite), and AgNO₃ (P. 117).	† Add Na₂CO₃ solution and filter; to filtrate add Sr(NO₃)₂ and HAc (P. 118).	‡ Fuse with Na₂CO₃, extract with water, filter (P. 119); acidify the filtrate, test portions for chloride, borate, sulfate, fluoride, phosphate, and silicate.
Distillate: B(OCH₃)₃. Collect in CH₃OH and HCl, and add turmeric. Orange color. (Shows BORATE.)	Gases evolved: SiF₄ and H₂O. Deposit on cold part of tube: SiO₃H₂. (Shows FLUORIDE.)	Yellow precipitate: (NH₄)₃PO₄.12MoO₃. (Shows PHOSPHATE.)	Dark brown precipitate: PbO₂. (Shows HYPOCHLORITE.)	Precipitate: AgCl, etc. Reject. Filtrate: AgClO₃. Add H₂SO₄. → Precipitate: AgCl. (Shows CHLORATE.)	Precipitate: SrSO₄, SrSO₃. Treat with HCl, add BaCl₂. → Precipitate: BaSO₄. Filtrate: H₂SO₃. Add Br₂. → Precipitate: BaSO₄. (Shows SULFITE.) Filtrate: SrS₂O₃. Add HCl and heat. → Precipitate: S. (Shows THIOSULFATE.)	

* These tests are made when free halogen was found in the first or second distillate.

† These tests are made when H₂SO₄ was found in the first distillate.

‡ These tests are made only when the substance is not completely decomposed by hot concentrated acids.

Procedure 113.—*Detection of Borate.*—Place 1–2 g. of the finely powdered substance in the distilling apparatus used in P. 101, and add 10 cc. of methyl alcohol (CH_3OH) and two or three glass beads. Pour in carefully 3 cc. H_2SO_4 (s.g., 1.84), and distil off the alcohol, collecting it in a mixture of 5 cc. CH_3OH and 3 cc. HCl (s.g., 1.20). Make the distillate up to 18 cc. with CH_3OH, cool, and add five drops of a saturated solution of turmeric in ethyl alcohol. (Red or orange color, presence of BORATE.)

> *Note.*—Methyl alcohol reacts with boric acid to form methyl borate $B(OCH_3)_3$ which is a readily volatil liquid. The color given by turmeric to a solution of boric acid in methyl alcohol and strong hydrochloric acid is so intense that the test is very delicate if the proportions given are reproduced. The presence of 1 mg. BO_2 in the substance distilled may readily be detected. To estimate roughly the quantity present, the color may be compared with that given by adding the turmeric solution to known quantities of borate dissolved in a mixture of 3 cc. HCl (s.g., 1.20) and 15 cc. CH_3OH.

Procedure 114.—*Detection of Fluoride.*—Mix 0.2 g. of the dry, finely powdered substance with twice its weight of powdered $KHSO_4$ and with 10–20 mg. dry, finely powdered or precipitated SiO_2. Blow a thick-walled bulb $1\frac{1}{2}$–2 cm. in diameter at the end of a glass tube of 5–8 mm. bore. Place the mixture in the bulb (not using more of it than will one-third fill the bulb). Heat the bulb carefully until the $KHSO_4$ is melted, taking care that the mixture does not froth up into the tube. Continue to heat the bulb and the lower part of the tube until there is a deposit of a solid substance or of condensed acid 3 or 4 cm. above the bulb. After it has cooled, cut off the tube close to the bulb. Dip the tube several times in water, dry it in a flame, and heat it strongly. (White deposit in the middle part of the tube and etched surface at the lower end, presence of FLUORIDE.)

> *Notes.*—1. This test depends on the following reactions:
> $$4HF + SiO_2 = SiF_4 + 2H_2O.$$
> $$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$
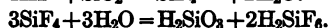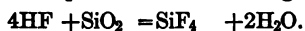
Some of the HF liberated by the molten $KHSO_4$ volatilizes and takes the silica required for the first reaction from the glass, thus producing the characteristic etched surface in the lower part of the tube. The SiF_4 gas and the water-vapor liberated react in the cooler part of the tube according to the second equation (forming a white ring of solid silicic acid and fluosilicic acid, H_2SiF_6). The reaction is reversed at higher temperatures, so that the deposit may be driven up the tube by heating. This white deposit is the most characteristic part of the test for fluoride. A deposit of SO_3 and H_2SO_4 may also form in the upper part of the tube, and might be mistaken for, or interfere with, the test

for small amounts of fluoride, if the final washing with water is omitted. This procedure enables 0.5 mg. F to be easily detected.

2. The test fails with certain minerals which are not decomposed by fusion with KHSO₄. Such cases are provided for by the treatment described in P. 119.

3. In distilling a fluoride with H₃PO₄ by P. 101, much of the HF reacts with the glass, but enough of it passes into the second distillate to enable 2–3 mg. F in the substance to be detected, if the whole distillate be tested with NaAc and CaCl₂ as described in P. 119.

4. Fluoride is often tested for by heating the solid substance in a platinum crucible with H₂SO₄ alone and detecting any HF evolved by its etching action on a watch glass coated with wax through which markings have been made. This test has the disadvantage that in the presence of silica or silicate, which is very often present in minerals, it is unreliable owing to the conversion of the HF to SiF₄ by the reaction given in Note 1.

Procedure 115.—*Detection of Phosphate.*—To 0.1–0.2 g. of the finely powdered substance add about 5 cc. HNO₃. If the substance does not dissolve, boil the mixture for 2 or 3 minutes, and filter. Add to the filtrate an equal volume of (NH₄)₂MoO₄ solution, and allow it to stand 5 to 10 minutes. (Yellow precipitate, presence of PHOSPHATE.)

Notes.—1. The yellow precipitate produced is a complex compound, ammonium phosphomolybdate, of a composition varying somewhat with the conditions, but approximating that required by the formula (NH₄)₃PO₄.12MoO₃.

2. In order that the test may be delicate, a large proportion of the (NH₄)₂MoO₄ must be present to reduce the solubility of the precipitate; and a short time must be allowed for the formation of the complex phosphomolybdate. This is promoted by gentle warming; but in a hot solution arsenate or silicate may giv rise to a similar yellow precipitate, while in the cold the reaction is given only by phosphate. By this test 0.1 mg. PO₄ may be easily detected. The great delicacy of this test should be borne in mind in estimating the quantity of phosphate present.

Procedure 116.—*Detection of Hypochlorite.*—If free halogen was found (in P. 103) to be present in the first distillate, treat 0.5 g. of the powdered substance mixed with 5 cc. water, or 5 cc. of the alkaline solution, as follows: Add HAc, a few drops at a time, until the solution is acid. Filter if there is much residue, add 2–3 cc. PbAc₂ solution, heat the mixture to boiling, and let it stand for ten minutes. (Brown precipitate, presence of HYPOCHLORITE.)

Notes.—1. Hypochlorites are commonly met with either in alkaline solution or in the form of a powder (for example, in bleaching powder). Since they are prepared by the action of chlorin on alkali, chloride is ordinarily present in nearly equivalent amount. When the solid powder is treated with water, the hypochlorite passes into solution; and from it the unionized HClO is liberated upon the addition of the more largely ionized acetic acid. Chlorin is also formed until the equilibrium-conditions of the reaction

$$HClO + Cl^- + H^+ = Cl_2 + H_2O$$
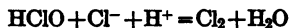
are satisfied. When in neutralizing with HAc litmus paper is used, the paper will soon be bleached if hypochlorite is present; but the color at the first instant or on the edges of the bleached portion can usually be observed.

2. This test depends upon the oxidation of the lead salt to lead dioxide (PbO_2) by the hypochlorite. The reaction takes place so slowly in the cold that not less than 10 mg. ClO in 5 cc. solution can be detected at room temperature, even if the mixture be allowed to stand a few minutes. But when the mixture is heated the limit of detectability is about 0.5 mg. in 5 cc. The solution is acidified with HAc, since oxidation does not take place in the presence of a strong acid, such as HNO_3.

3. Peroxides in alkaline solution react instantaneously with lead salts, forming PbO_2; but this reaction does not take place in the presence of HAc, even on boiling. Therefore in the above procedure a peroxide will not be mistaken for a hypochlorite. Peroxide and hypochlorite, moreover, cannot exist together, since they react very rapidly with formation of oxygen.

4. This test for hypochlorite may be made even more delicately in alkaline solution, provided peroxides are known to be absent. If the solution is only slightly alkaline, a small white precipitate of $Pb(OH)_2$ or $PbCO_3$ is first formed; but this turns brown if hypochlorite is present when the mixture is heated and allowed to stand. The delicacy is of course diminished by the presence of a large amount of $Pb(OH)_2$ or $PbCO_3$; but 1 mg. ClO can be detected in the presence of even 2 or 3 g. of these substances, provided an excess of the lead salt is still present in the solution and the mixture is boiled vigorously, preferably in a casserole.

5. Hypobromite in alkaline solution or bromin in HAc solution also oxidizes lead salts to PbO_2. Hypobromite is, however, so unstable that it will not be met with except in a solution freshly prepared from bromin and alkali. In a doubtful case the halogens may be extracted by chloroform from an acid solution, and tested for by P. 109 and 110.

Procedure 117.—*Detection of Chlorate.*—If free halogen was found (in P. 103 or P. 109) to be present in the first or second distillate, treat 0.5 g. of the substance in the cold with 50 cc. water and 10 cc. HNO_3. (If hypochlorite is present as shown by P. 116, reduce it by adding Na_3AsO_3 solution in excess.) Add $AgNO_3$ solution as long as a precipitate forms and then about 5 cc. more. Shake the mixture and filter off the precipitate. To the filtrate add 5 cc. saturated SO_2 solution, heat the mixture, or allow it to stand five minutes. (White precipitate, presence of CHLORATE (or BROMATE).)

Notes.—1. In this procedure chlorate is reduced to chloride by the H_2SO_3. The reaction is not instantaneous; but it is so rapid in the presence of a large excess of H_2SO_3 that at room temperature 1 mg. ClO_3 gives a distinct precipitate of AgCl within 5 minutes, even in a volume of 100 cc.

2. If iodate is present, $AgIO_3$ is precipitated upon the first addition of $AgNO_3$, along with the silver halides; but if bromate is present, some of it remains in the solution and shows the same behavior as chlorate. If necessary to distinguish between them, the final precipitate with $AgNO_3$ may be treated as follows: Suspend it in 25 cc. water, pass in H_2S until the mixture is satu-

rated with it, heat to boiling, filter off the precipitated Ag_2S, boil the filtrate till the H_2S is expelled, and test it for bromide and chloride by P. 110.

Procedure 118.—*Detection of Sulfite and Thiosulfate.*—If in P. 102 the first distillate was found to contain H_2SO_3, add 0.5 g. of the finely powdered original substance to 5 cc. water and 1–5 cc. Na_2CO_3 solution, shake the mixture, filter out any precipitate or residue, and add to the solution 3 cc. $Sr(NO_3)_2$ solution. Then at once add HAc slowly, at the last a few drops at a time, until the precipitate of $SrCO_3$ dissolves on shaking, or until the solution reacts acid to litmus. Heat the mixture to boiling, add a drop or two of HAc if a flocculent precipitate forms, and let the mixture stand 15 minutes. (No precipitate, absence of SULFITE.)

Filter out the $Sr(NO_3)_2$ precipitate, wash it once with a little cold water, pour a portion of 3–4 cc. HCl two or three times through the filter, and add to the solution 5 cc. $BaCl_2$ solution. (If a precipitate of $BaSO_4$ forms, filter it out.) Then add to the solution saturated Br_2 solution till the liquid is slightly yellow. (Precipitate, presence of SULFITE.)

To the filtrate from the $Sr(NO_3)_2$ precipitate, add 1–2 cc. HCl (s.g., 1.20), heat the mixture to boiling, and let it stand overnight. White turbidity or yellow precipitate, presence of THIOSULFATE.)

Notes.—1. Na_2CO_3 is added at the beginning of this procedure to separate from the acidic constituents in question any basic constituents that may be present. All the basic constituents, except arsenic, potassium, sodium, and ammonium, are precipitated by it from solutions of their salts, and most of their slightly soluble compounds are metathesized by it; thus $BaSO_3$ is converted into $BaCO_3$. In some systems of analysis most of the acidic constituents are tested for in a solution prepared by boiling the solid substance with Na_2CO_3 solution, filtering, and neutralizing the filtrate.

2. The addition of the Na_2CO_3 solution and the subsequent neutralization of it by HAc also serve to giv a solution of small H^+ concentration, which is essential for a satisfactory separation of sulfite and thiosulfate. When the H^+ concentration is large, $SrSO_3$ dissolves and the thiosulfate decomposes with formation of sulfur; but in HAc solution the latter reaction is negligible, even on heating in the presence of a considerable excess of the acid. $SrSO_3$ separates as a crystalline precipitate, slowly in the cold when present in small quantity, but much more rapidly when the mixture is heated. The procedure enables 1 mg. SO_3 in an initial volume of 10 cc. to be easily detected.

3. Upon the addition of a moderate excess of HCl over that required to react with all the NaAc present, the thiosulfate decomposes with the separation of sulfur. When 10 cc. of solution are treated by the above procedure, a precipitate forms within 30 minutes with 3 mg. S_2O_3, and on standing over night with 1 mg. S_2O_3.

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Procedure 119.—*Detection of the Acidic Constituents in Undecomposed Substances.*—If the substance is not completely decomposed by acids (as shown in P. 101 and 115) heat 1 g. of the finely powdered substance with HNO_3, filter out and wash the residue, dry it, separate from the filter, and mix it with 5–10 g. dry Na_2CO_3 in a platinum crucible (or in a porcelain crucible, if reducible metals may be present in it.) Cover the crucible and heat it over a powerful burner for 5–10 minutes. If a perfectly clear fusion does not result, add more Na_2CO_3, and heat again. Cool, place the crucible in a casserole, boil it with water till the fused mass is disintegrated, and filter, rejecting the residue.

To a portion of the filtrate add HNO_3 till it is distinctly acid, and test portions of the solution for CHLORIDE by adding $AgNO_3$, for PHOSPHATE by P. 115, and for SULFATE by adding $BaCl_2$ solution.

Test another portion of the filtrate for BORATE by evaporating it to complete dryness, adding H_2SO_4 (s.g., 1.84) drop by drop, and treating the mixture by P. 113.

Test a third portion of the filtrate for FLUORIDE as follows: add 5 – 10 cc. NaAc solution and 5 cc. $CaCl_2$ solution, and allow the mixture to stand 10–15 minutes. (White precipitate, presence of FLUORIDE.) To confirm its presence, filter out, wash, and dry the precipitate, and test it by P. 114.

If silicate needs to be tested for, evaporate a portion of the solution, heat the residue at 100–125° till it is perfectly dry, add HCl, and boil gently. (White residue, presence of SILICATE or SILICA.) To confirm its presence, treat the residue by P. 5.

Notes.—1. Fusion with Na_2CO_3 metathesizes nearly all insoluble compounds in the way described in the notes to P. 7.

2. If basic elements that may be reduced to the metallic state (those of the silver, copper, and tin groups) may be present in the insoluble residue, it must be fused in a porcelain instead of a platinum crucible. It is, however, less desirable to use a porcelain crucible, since it is more difficult to attain the high temperature necessary, and since it is attacked by the flux and silicate is thereby introduced into the solution.

3. In minerals or metallurgical products undecomposed by acids, it is usually necessary to test only for silicate, chloride, sulfate, phosphate, borate, and fluoride, since other acidic constituents are scarcely ever present.

4. The formation of a precipitate in a solution acidified with HAc distinguishes fluoride from all other acidic constituents except sulfate and oxalate. The test is delicate enough to enable 0.2 mg. F in 10 cc. solution to be detected.

APPENDICES

PREPARATION OF THE REAGENTS

ACIDS.

Acetic, 6–normal: Mix 350 cc. 99.5% acid with 650 cc. water.

Hydrochloric, 12–normal: Use the C. P. acid of commerce of s. g. 1.19.

Hydrochloric, 6–normal: Mix 12–normal HCl with an equal volume of water.

Hydrofluoric, 48 per cent.: Use the pure acid sold in ceresin bottles.

Nitric, 16–normal: Use the C. P. acid of commerce of s. g. 1.42.

Nitric, 6–normal: Mix 380 cc. HNO_3 (s. g., 1.42) with 620 cc. water.

Phosphoric, 85 percent.: Use the C.P. acid of commerce.

Sulfuric, 96 percent.: Use the C. P. acid of commerce of s. g. 1.84.

Sulfuric, 6–normal: Pour 96% H_2SO_4 into five times its volume of water.

Sulfurous, saturated: Saturate water at 20–25° with SO_2 gas made by dropping 96% H_2SO_4 into hot $NaHSO_3$ solution.

BASES.

Ammonium hydroxide, 15–normal: Use the C.P. product of commerce of s. g. 0.90.

Ammonium hydroxide, 6–normal: Mix 400 cc. 15–normal NH_4OH with 600 cc. water.

Barium hydroxide, saturated: Heat 60 g. $Ba(OH)_2.8H_2O$ with 1000 cc. water, cool to 15°, decant or filter.

Sodium hydroxide, 6–normal: Add to 250 g. NaOH enough water to make the volume 1000 cc.

AMMONIUM SALTS.

Acetate, 3–normal: Mix equal volumes of 6–normal HAc and 6–normal NH_4OH; or dissolve 250 g. of the solid salt in enough water to make the volume 1000 cc.

Carbonate: Dissolve 250 g. freshly powdered ammonium carbonate in 1000 cc. 6–normal NH_4OH, and filter if there is a residue.

Chloride, 1–normal: Add to 54 g. NH_4Cl enough water to make the volume 1000 cc.

Molybdate: Dissolve 75 g. of the pure ammonium molybdate of commerce in 500 cc. water, pour the solution into 500 cc. 6–normal HNO_3, and let the mixture stand till the precipitate is dissolved.

Monosulfide, 6–normal: Pass H_2S gas into 200 cc. 15–normal NH_4OH in a bottle immersed in running water or in iced water until the gas is no longer absorbed; then add 200 cc. 15–normal NH_4OH and enough water to make the volume 1000 cc.

Oxalate, 0.5 normal: Dissolve 35 g. $(NH_4)_2C_2O_4.H_2O$ in 1000 cc. water.

Polysulfide, 6–normal: Digest one liter of ammonium monosulfide with 25 g. flowers of sulfur for some hours and filter.

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OTHER SALTS.

Name of Salt	Formula and formula-weight	Concentration	Grams per liter
Barium chloride	BaCl$_2$.2H$_2$O (244)	1-normal	120
Cadmium nitrate	Cd(NO$_3$)$_2$.4H$_2$O (308)	1-normal	150
Calcium chloride	CaCl$_2$.6H$_2$O (219)	1-normal	110
Calcium sulfate	CaSO$_4$.2H$_2$O (172)	saturated	2
Cobalt nitrate	Co(NO$_3$)$_2$.6H$_2$O (291)	1% cobalt	50
Ferric chloride	FeCl$_3$.6H$_2$O (270)	1-normal	90
Ferrous sulfate	FeSO$_4$.7H$_2$O (278)	saturated	200
Lead acetate	Pb(C$_2$H$_3$O$_2$)$_2$.3H$_2$O (379)	1-normal	190
Mercuric chloride	HgCl$_2$ (271)	0.2-normal	25
Potassium chromate	K$_2$CrO$_4$ (194)	3-normal	290
Potassium cyanide	KCN (65)	1-normal	65
Potassium ferricyanide	K$_3$Fe(CN)$_6$ (329)	1-normal	110
Potassium ferrocyanide	K$_4$Fe(CN)$_6$.3H$_2$O (422)	1-normal	105
Potassium iodide	KI (166)	1-normal	165
Potassium nitrite	KNO$_2$ (85)	3-normal	250
Potassium permanganate	KMnO$_4$ (158)	1-per cent.	10
Potassium thiocyanate	KSCN (97)	1-normal	100
Silver nitrate	AgNO$_3$ (170)	0.1-normal	17
Sodium acetate	NaC$_2$H$_3$O.3H$_2$O (136)	1-normal	135
Sodium arsenite	NaAsO$_2$ (130)	1-normal	130
Sodium carbonate	Na$_2$CO$_3$ (106)	1-normal	55
Sodium phosphate	Na$_2$HPO$_4$.12H$_2$O (358)	1-normal	120
Strontium nitrate	Sr(NO$_3$)$_2$ (212)	1-normal	105

SPECIAL REAGENTS.

Bromin, saturated solution: Shake liquid bromin with water and decant the aqueous solution.

Hydrogen peroxide, 3 per cent.

Magnesium ammonium chloride, 1-normal in MgCl$_2$: Dissolve 100 g. MgCl$_2$.6H$_2$O and 100 g. NH$_4$Cl in water, add 50 cc. 15-normal NH$_4$OH, and dilute to 1000 cc.

Potassium pyroantimonate: Add 20 g. of the best commercial salt to 1000 cc. boiling water, boil for a minute or two till nearly all the salt is dissolved, quickly cool the solution, add about 30 cc. 10% KOH solution, and filter.

Sodium cobaltinitrite: Dissolve 250 g. NaNO$_2$ in 500 cc. water, add 150 cc. 6-normal HAc and 25 g. Co(NO$_3$)$_2$.6H$_2$O, let the mixture stand over night, filter or decant the solution, and dilute it to one liter.

Sodium hypobromite: Prepare this reagent not more than a few days before using by adding liquid bromin to 6-normal NaOH solution till the mixture becomes distinctly red, and then adding half as much more NaOH solution. Filter, if necessary, through a hardened filter.

Stannous chloride, 1-normal: Dissolve 115 g. $SnCl_2.2H_2O$ in 100 cc. 12-normal HCl, dilute to 1000 cc., and keep in bottles containing granulated tin.

Turmeric: Shake turmeric powder with 95% alcohol and filter.

Urea: Dissolve 200 g. urea in 1000 cc. 6-normal HCl.

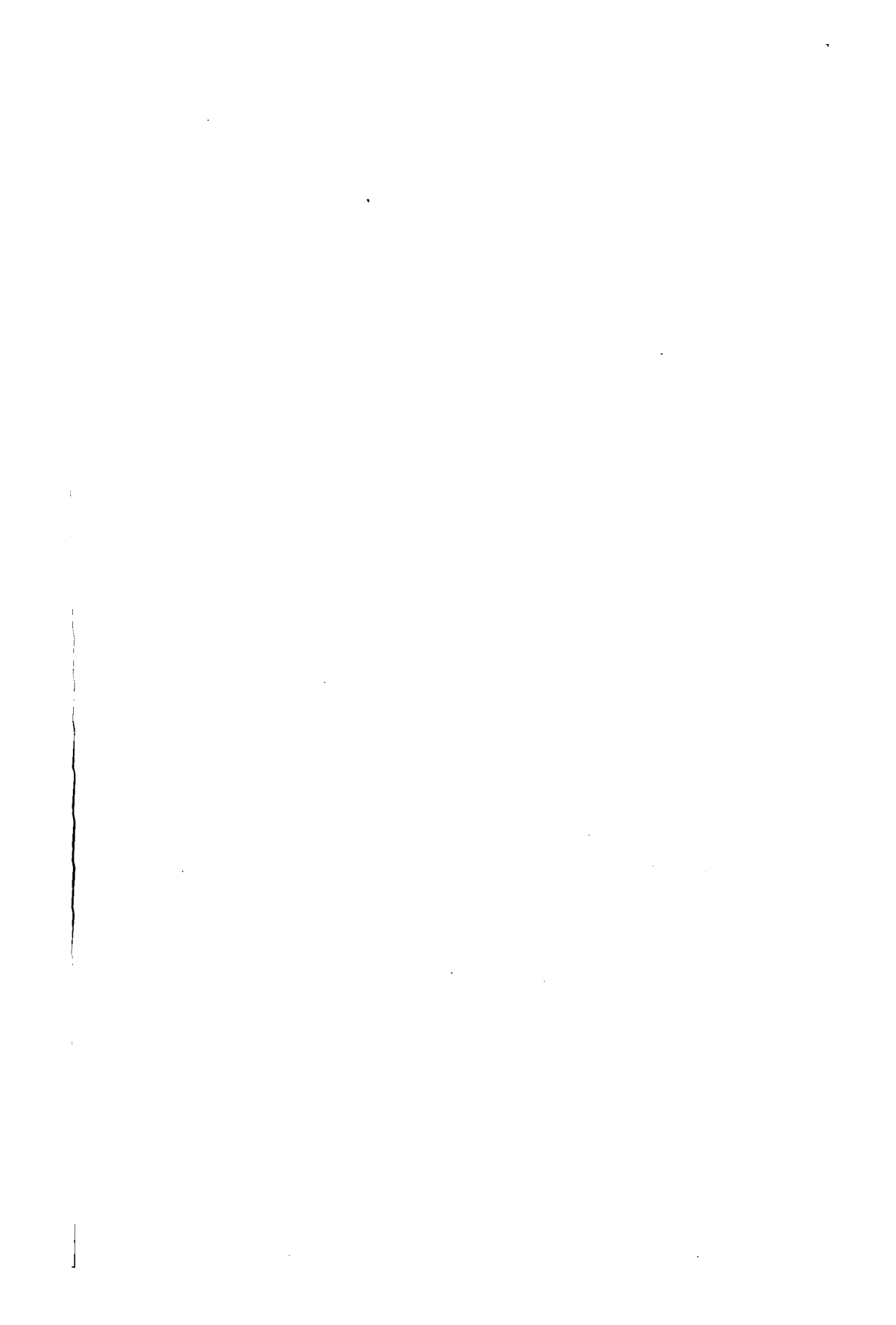## ATOMIC WEIGHTS OF THE COMMON ELEMENTS.

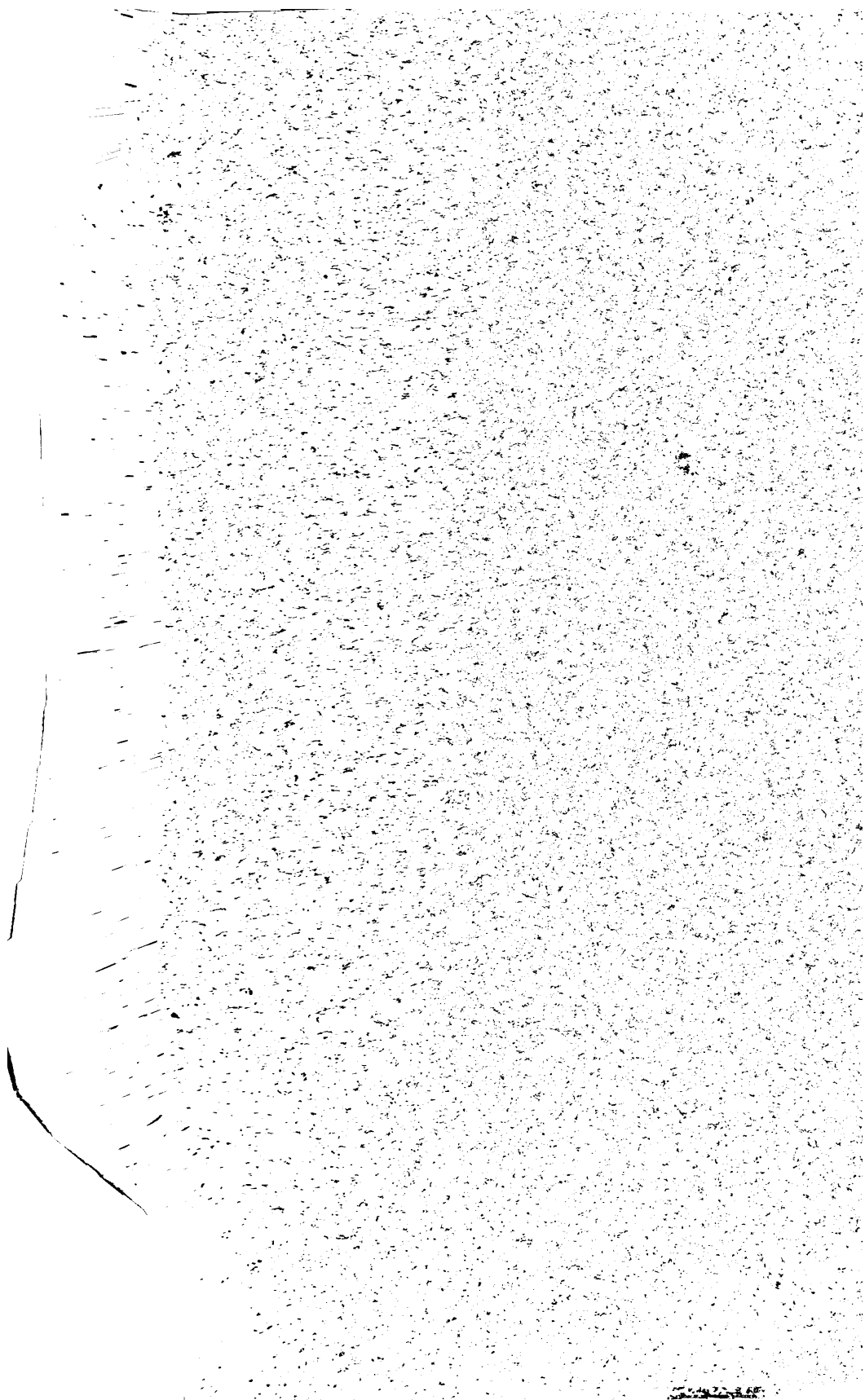|						
Aluminum.......	Al	27.1	Iron............	Fe	55.84
Antimony........	Sb	120.2	Lead...........	Pb	207.10
Arsenic..........	As	74.96	Magnesium	Mg	24.32
Barium..........	Ba	137.37	Manganese.......	Mn	54.93
Bismuth.........	Bi	208.0	Mercury.........	Hg	200.6
Boron...........	B	11.0	Molybdenum.....	Mo	96.0
Bromine.........	Br	79.92	Nickel..........	Ni	58.68
Cadmium........	Cd	112.40	Nitrogen.........	N	14.01
Calcium.........	Ca	40.07	Oxygen..........	O	16.00
Carbon..........	C	12.00	Phosphorus	P	31.04
Chlorine.........	Cl	35.46	Potassium........	K	39.10
Chromium.......	Cr	52.0	Silicon..........	Si	28.3
Cobalt...........	Co	58.97	Silver............	Ag	107.88
Copper..........	Cu	63.57	Sodium..........	Na	23.00
Fluorine.........	F	19.0	Strontium........	Sr	87.63
Gold............	Au	197.2	Sulfur...........	S	32.07
Hydrogen........	H	1.008	Tin.............	Sn	119.0
Iodine..........	I	126.92	Zinc............	Zn	65.37

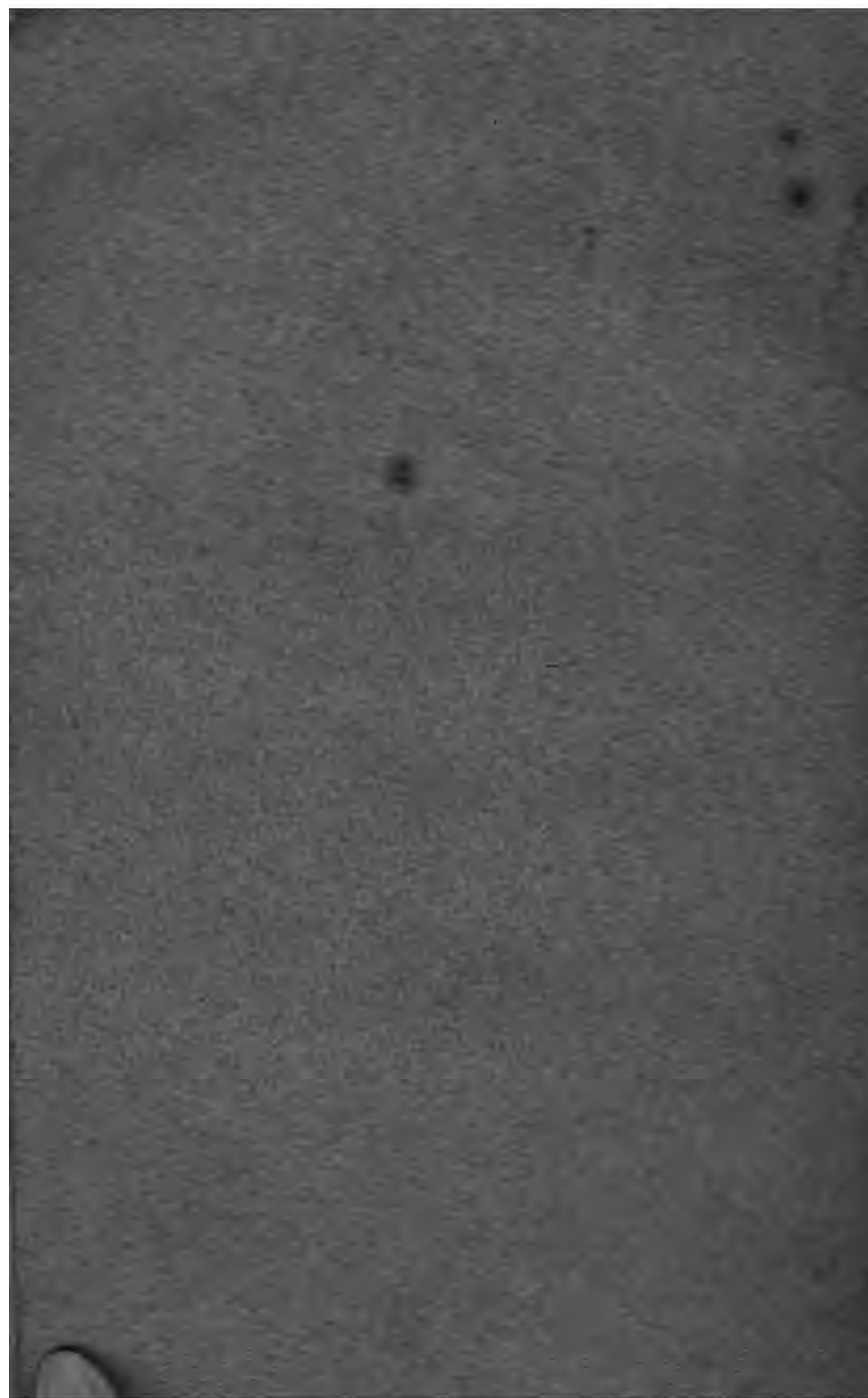## SOLUBILITIES OF SLIGHTLY SOLUBLE SUBSTANCES.

The numbers in the table show the solubility in milli-equivalents per liter at 20°. The letters v.s. (very soluble) denote a greater solubility than 1-normal.

	Mg	Ca	Sr	Ba	Pb	Ag
Chloride	v.s.	v.s.	v.s.	v.s.	70.	0.01
Bromide	v.s.	v.s.	v.s.	v.s.	45.	0.0005
Iodide	v.s.	v.s.	v.s.	v.s.	2.6	0.00002
Thiocyanate	v.s.	v.s.	v.s.	v.s.	28.	0.0008
Sulfate	v.s.	30.	1.2	0.02	0.28	50.
Chromate	v.s.	60.	12.	0.03	0.0003	0.16
Hydroxide	0.3	45.	·130.	450.	0.2	0.18
Fluoride	2.8	0.4	1.9	18.	5.	v.s.
Oxalate	5.	0.09	0.5	0.8	0.012	0.24