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FOREWORD

This little volume is the outgrowth of the *Lecture Notes on Qualitative Analysis*, by the late Professor Henry B. Hill, which has served a wide field of usefulness for almost half a century. A revision of Professor Hill's book at this time is hardly justifiable. Professor Hill's widow has, however, kindly consented to allow me to utilize certain portions of the *Lecture Notes* which could be made of service in the preparation of this volume. The principal parts so selected are the compilations on properties of acids and bases, which originally constituted the first twenty-five pages of Professor Hill's book. The Introduction also, with a few changes and additions, is taken from Professor Hill's volume.

There has been no attempt to depart from the beaten paths of Elementary Qualitative Analysis. In fact, such a divergence would not be desirable, notwithstanding the fact that not a few teachers crave for their own sake a new system of analysis. Elementary Qualitative Analysis should serve as a guide to direct the student in the beginning, and it is, therefore, always new to him. A wideawake teacher should always be able to find new suggestions and better methods of performing the same task.

The volume presents, however, certain new methods that will not be found in any other book on analysis. These methods have been thoroughly tried out, and have been used for a number of years in the laboratories of Ohio University.

I am glad to acknowledge in this connection, that this little volume would never have appeared, had it not been for the inspiration, kindly suggestions, and criticisms of Dr. William B. Bentley. Some of the new methods are the result of his many years' experience in teaching this subject.

No attempt is made to treat the theoretical phase of the subject. Experience seems to indicate that a knowledge of careful manipulation and a clear notion of the methods of separation are the first essentials for an elementary course in analysis.

This should be followed by a course emphasizing the application of the laws of electrolytic equilibrium and mass action. Courses in Physical Chemistry usually supply this requirement. The student will find it profitable to study carefully such works as Ostwald's *Foundations of Analytical Chemistry*, or Volume I of Steiglitz's *Qualitative Analysis*.

A comparative description of those compounds of bases and acids which are commonly found or used in analysis is first given, and afterwards a method of separation, which experience has proved to be sufficiently simple and accurate, is briefly explained. This method of procedure from the properties of compounds to the methods of separation will also serve to show the way in which the more difficult problems of analysis must be solved.

No tables for analysis have been given, since their use is of questionable advisability, and, if used, are much better drawn up by the student himself. The description of the properties of the acids and bases should be studied during the analysis of the unknown.

For more complete description and detail, the student is referred to such standard works as Prescott and Johnson's *Qualitative Analysis*, Newth's *Manual of Chemical Analysis*, and Steiglitz's *Qualitative Analysis, Laboratory Manual*, Volume II. The *Tables of Properties of Inorganic Substances* by Sergeblom will be found helpful.

J. R. M.

ATHENS, O.,
May, 1917.

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Qualitative Chemical Analysis

INTRODUCTION

QUALITATIVE ANALYSIS is that branch of chemistry which treats of the recognition of elements or their compounds. It demands a thorough study and comparison of the several elements and their compounds, of the phenomena exhibited by them under various conditions, and the determination of the particular conditions essential to the manifestation of each. It is advisable, at first, to take into consideration only the more common compounds, and to leave for subsequent study all rare elements and all but a few of the compounds of carbon (organic substances).

The phenomena exhibited by a substance under various conditions are termed its *reactions*. The conditions under which reactions are studied may be divided into two classes: those dependent upon solution, and those independent of it; the two modes of examination are known as the *wet* and the *dry way*. In either case any known substance which is used in effecting a reaction is called a *reagent*.

Reactions in the *dry way* are dependent upon volatilization, or chemical change effected by heat. The nature of these changes will be sufficiently clear after a study of the reactions described in the preliminary examination.

In the *wet way* a reagent is used to effect solution or to determine a metathesis. Experience has shown that when the solutions of two substances are mixed, and a compound insoluble under the existing conditions can be formed by metathesis, this insoluble compound is formed; or when a substance volatile under the existing conditions can be formed, that it is formed and escapes. An insoluble substance separating from solution is called a *precipitate*. If the precipitate settles readily, the liquid may be decanted, or, in any case, it may be separated by filtration, when the liquid is called the *filtrate*. Inasmuch as the completeness of the separation of those substances which are precipitated by a reagent from those which are left in solution depends upon the insolubility of the precipitate, all the conditions which may affect its solubility must be known and considered.

A *general reagent* is used to precipitate a number of substances, a *special reagent* as a test for a single substance. Some special reagents give no precipitate, but cause a change of color. The precipitate thrown down by a general reagent always requires further examination, and it is better to submit to a confirmatory test the precipitate caused by a special reagent. A precipitate or reaction is said to be characteristic when no further test is needed.

There are two things essential to success in qualitative analysis: (1) *the accurate observation of phenomena and* (2) a *correct interpretation of their significance*, neither of which can be attained without conscientious work in the laboratory. By studying the reactions of known substances, taking care to observe everything which takes place, however small it may seem, the power of observation will be educated, and it will soon be possible to determine what is accidental and what essential, and experience will show what is the meaning of each reaction observed.

In this book it is supposed that the student already has a good knowledge of general chemistry. Such knowledge is essential, and may be gained by the aid of any good text-book on chemistry. Experience in laboratory work and manipulation is on all accounts desirable.

It is best to begin with the study of the bases, and, taking each element by itself, to compare the properties of the different members. The description of the properties of bases is intended as a guide in this work.

After a thorough study of the properties of a group of bases, a method of separation should be devised and compared with that given in course of analysis. The members of the group must then be separated from each other, taking care that the facts upon which the method of separation is based are well understood, and the sources of error distinctly recognized. The separation of the group as a whole from the other groups must then be considered, and the conditions necessary for complete separation clearly made out. After the basic groups have been studied in order, and each of the bases can be detected with certainty, a similar method should be followed with acids, taking as a guide the description of the properties of acids, and the methods given for their detection.

The student will then be prepared to make complete analyses. He should begin with simple salts, and proceed gradually to complex mixtures and insoluble substances, in every case proving the presence or absence of each base and acid which he has studied. In the analysis of such compounds the reactions in the dry way should first be observed. Here the significance of each reaction may be learned, as before, by practice upon known substances, or the reactions of a substance may be carefully observed, and its composition afterward determined by analysis in the wet way. The correct interpretation of reactions in the dry way requires long practice. Great care must be taken to distinguish between those reactions which are so decisive that they may be taken as tests for the presence or absence of certain substances, and those which are proofs or indications of presence, if observed, but from whose non-appearance no negative conclusions can be drawn.

GENERAL DIRECTIONS

As far as practical work is concerned, it will be necessary to give here only a few general directions and point out a few common errors. *Neatness* and *cleanliness* are absolutely necessary. The reagents must be carefully preserved from contamination. The stoppers of the bottles must not be misplaced, nor laid down while the reagent is used. The reagent bottles should be kept clean and plainly labeled; they should be conveniently arranged, and the order of arrangement never changed.

The quantity of a substance taken for analysis should be small. This facilitates the manipulation, and, unless carried to extreme, affords better practice.

Each reagent must be added cautiously, in quantity just sufficient. Too little fails to effect complete precipitation, and separation; too much is often quite as objectionable. *If the first few drops of a reagent cause a precipitate, more must be added until a drop allowed to run into the solution gives no further precipitate. The filtrate* should also be tested with a few drops of the reagent in confirmation. In using an acid or an alkaline solution the reaction on test-paper will show when an excess has been added. In the use of a few reagents the necessary quantity can be learned by experience alone. In any case, *the reagent must be thoroughly mixed with the solution by shaking or stirring.*

If a solution is moderately concentrated, the precipitation is usually immediate; but in dilute solutions it often takes place only after some time. If separation is to be effected, time should be allowed for complete precipitation. Occasionally half an hour, or even several hours, are necessary; but more frequently five or ten minutes will be found sufficient. *Heat* almost always facilitates precipitation; in a few cases, however, which are mentioned in the course of analysis, a reagent must be used in the cold.

In filtering, the filter must be evenly folded and carefully fitted to the funnel. For rapid filtration a creased or star filter is better, and in any case a *hot solution filters more rapidly.* Precipitates must be thoroughly washed, though only the first part of the wash water should be saved with the filtrate. If the precipitate is granular and settles readily, it may be advantageously washed by decantation before it is collected on a filter. A precipitate may be removed from the filter with a small spatula, or by washing it off with a stream of water, and removing by decantation most of the water. A precipitate may be readily dried by supporting the filter over a hot sand-bath, either in the funnel or on a triangle.

In fusions the well-dried substances should be intimately mixed in a mortar; the crucible containing the mixture should be supported just *above the point of the blue cone of the lamp flame.* The removal of the fused mass from a platinum crucible is much facilitated by setting it, while cooling, upon a thick, cold bit of metal.

In blowpipe work full time must be allowed for reduction on charcoal. With borax but little substance must be used, and care must be taken to get a good oxidizing or reducing flame, as the case may be.

It is essential that concise and accurate notes should be kept of all laboratory work. They should record the reactions, the conditions under which they take place, and the conclusions drawn from them. In other words, *they should give in order what is done, what is observed, and what is inferred. These notes should be taken as the work is done*, and are of value only as they are a truthful record of fact.

Blank pages are left for notes in making the preliminary tests. Any good note-book will serve for note writing in case of the unknown. The student should always present his notes when the report of his unknown is made. If his notes present a true record of his work, they will assist the instructor in pointing out the probable difficulties, and assist him in giving suggestions for the second analysis.

If careful notes are taken, the laboratory guide will soon be discarded except in cases of reference.

BASES

GROUP I

Sulphides and carbonates soluble:
Na, K, Li, H_4N, *Cs*, *Rb*.

GROUP II

Sulphides soluble, carbonates insoluble:
Ba, Sr, Ca, Mg.

GROUP III

Sulphides not formed in wet way. $(H_4N)_2S$ precipitates hydrates:
Al_2 Cr_2, *Th*, *Zr*, *G*, *Y*, *E*, *Ce*, *La*, *D*, *Cb*, *Ta*.

GROUP IV

Sulphides not formed in acid solutions, but precipitated in alkaline:
Fe, Fe_2[1], Ni, Co, Mn, Zn, *U*, *V*, *Te*, *In*.

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[1] Is precipitated as FeS.

GROUP V

Sulphides formed in acid solutions, insoluble in alkaline:

Ag, Hg, Hg_2, Pb, Cu, Cd, Bi, *Rh*, *Os*, *Ru*, *Pd*.

GROUP VI

Sulphides formed in acid solutions, soluble in alkaline.

As, Sb, Sn, Sn^{IV}, *Au*, *Pt*, *Ir*, *W*, *Mo*, *Te*, *Se*.

PROPERTIES OF BASES

GROUP I. Na, K, Li, H_4N Mg

Metals.—Na, K, Li. Soft, very fusible, and lighter than water. Oxidize rapidly in air, or in water setting free H_2. H_4N. Known only in combination, as it is decomposed, when set free, into 2 NH_3 and H_2.

Oxides.—Na_2O and K_2O absorb water eagerly from the air, Li_2O unites with water readily, $(H_4N)_2O$ unknown.

Hydrates.—NaOH and KOH are deliquescent, LiOH sparingly soluble, and H_4NOH known only in solution.

Sulphides.—All soluble.

Chlorides.—LiCl is deliquescent, the rest readily soluble. K_2PtCl_6, and $(H_4N)_2PtCl_6$ are quite insoluble in water, or HCl, more insoluble in alcohol. The other double chlorides with Pt are soluble.

Carbonates.—Li_2CO_3 sparingly soluble, the other neutral carbonates readily soluble, K_2CO_3 deliquescent.

$KHCO_3$ and $NaHCO_3$ are less soluble than the neutral salts, $LiHCO_3$ more soluble.

Sulphates.—Na_2SO_4, $(H_4N)_2SO_4$, and Li_2SO_4 very soluble, K_2SO_4 less so. The acid salts of the form $MHSO_4$ are all more soluble than the neutral.

Chromates.—All soluble. The salts of the form M_2CrO_4 give a yellow solution, of the form $M_2Cr_2O_7$ a red.

Phosphates.—All Na, K, and H_4N salts soluble. Na_2HPO_4 precipitates Li_3PO_4 insoluble in water, quite soluble in H_4NCl, and soluble in acids.

Oxalates.—All soluble, KHC_2O_4 not readily.

Tartrates.—Salts of the form $M_2C_4H_4O_6$ all soluble. $KHC_4H_4O_6$ and $H_4NHC_4H_4O_6$ are sparingly soluble in cold water. $HC_2H_3O_2$ does not increase the solubility, though they are soluble in mineral acids, or in an alkaline solution. The other acid salts readily soluble.

Cyanides.—Soluble in water, the salts readily decomposed in solution.

Ferrocyanides.—All soluble.

GROUP II. Ba, Sr, Ca, Mg

Metals.—Harder than metals of Gr. I. Ba, Sr, and Ca oxidize rapidly in air or water, Mg slowly in moist air, or water at 100°.

Oxides.—Combine with water to form hydrates.

Hydrates.—BaO_2H_2 is soluble, SrO_2H_2 less so; CaO_2H_2 sparingly soluble, and the solubility decreased by heat. MgO_2H_2 is insoluble in water though soluble in solutions of H_4N salts. All are readily soluble in acids. NaOH precipitates the hydrates of the group; Ba, Sr, and Ca hydrates only from concentrated solutions. H_4NOH precipitates only MgO_2H_2, that partially, or not at all, in presence of H_4NCl.

Sulphides.—BaS, SrS, and CaS are soluble; MgS decomposes water, and therefore is not formed in the wet way.

Chlorides.—$BaCl_2$ and $SrCl_2$ readily soluble, $CaCl_2$ and $MgCl_2$ deliquescent. $MgCl_2$ in solution is partially decomposed by evaporation to dryness.

Carbonates.—Carbonates of the form $M''CO_3$ insoluble in water, soluble in acids. $CaCO_3$ and $SrCO_3$ are slightly soluble in H_4NCl, $BaCO_3$ more markedly, $MgCO_3$ readily. Na_2CO_3 precipitates Ba, Sr, and Ca as carbonates, Mg as basic carbonate. $(H_4N)_2CO_3$ precipitates Ba, Sr, and Ca completely, Mg partially in concentrated solutions, or not at all in presence of H_4NCl. The salts of the form $M''H_2(CO_3)_2$ are soluble; on boiling their solutions the neutral carbonates are precipitated.

Sulphates.—$BaSO_4$ and $SrSO_4$ are insoluble, $CaSO_4$ sparingly soluble in cold water, less in hot, $MgSO_4$ readily soluble. Mineral acids increase the solubility of $BaSO_4$ but slightly, of $SrSO_4$ and $CaSO_4$ very decidedly. In strong H_2SO_4 all these are soluble, forming acid salts $M''H_2(SO_4)_2$, decomposed by water with formation of $M''SO_4$.

Chromates.—$BaCrO_4$ insoluble in water or $HC_2H_3O_2$ soluble in HCl or HNO_3. $SrCrO_4$ quite soluble in water, readily in $HC_2H_3O_2$, $CaCrO_4$ and $MgCrO_4$ soluble in water.

Phosphates.—Of the three classes of phosphates, those of the form $M''_3(PO_4)_2$ are insoluble; those of the form $M''_2H_2(PO_4)_2$ are practically insoluble in water, though the Ba and Sr salts are markedly soluble and the Ca salt somewhat soluble in H_4NCl. The salts of the form $M''H_4(PO_4)_2$ are soluble in water. The insoluble salts are soluble in acids. In neutral solution Na_2HPO_4 precipitates phosphates of the form $M''_2H_2(PO_4)_2$, in an H_4NOH solution Ba, Sr, and Ca precipitated in the form $M''_3(PO_4)_2$. Mg is precipitated by Na_2HPO_4 in presence of H_4NCl and H_4NOH as $Mg_2(H_4N)_2(PO_4)_2$, insoluble in water, though soluble in acids.

Oxalates.—Neutral oxalates of the form $M''C_2O_4$ insoluble in water, soluble in mineral acids. MgC_2O_4 is soluble in H_4NCl.

Tartrates.—Neutral salts of Ba, Sr, and Ca insoluble in water, soluble in mineral acids, or NaOH; more or less soluble in H_4NCl. $MgC_4H_4O_6$ sparingly soluble in water, readily soluble in H_4NCl.

Cyanides.—Soluble in water, the solutions decomposed by heat.

Ferrocyanides.—$Ba_2Fe(CN)_6$ sparingly soluble, the rest soluble.

GROUP III. $\underline{Al_2}$, $\underline{Cr_2}$ $\underline{Fe}$

Metals.—Al white, ductile, fusible, and does not readily oxidize. It is soluble in HCl, in dilute

H_2SO_4, or in NaOH, with difficulty in HNO_3. Cr very hard and infusible.

Oxides.—Insoluble in water; before ignition they are soluble in acids, after ignition insoluble. Fusion with Na_2CO_3 and KNO_3 converts Al_2O_3 into soluble $Na_6O_6Al_2$ and Cr_2O_3 into Na_2CrO_4.

Hydrates.—Insoluble in water, soluble in acids, or NaOH. Cr_2 precipitated from NaOH solution by boiling as $Cr_2O_6H_6$, Al_2 is not. Both slightly soluble in H_4NOH, the solubility of $Al_2O_6H_6$ diminished by presence of H_4NCl. On heating the solution the dissolved hydrates are precipitated.

Sulphides.—Not formed in the wet way Al_2S_3 decomposes water, liberating H_2S and forming $Al_2O_6H_6$. $(H_4N)_2S$ precipitates $Al_2O_6H_6$ and $Cr_2O_6H_6$ with evolution of H_2S.

$$Al_2Cl_6+3(H_4N)_2S+(6H_2O+Aq)=$$
$$Al_2O_6H_6+3H_2S+ (6H_4NCl+Aq).$$

Chlorides.—Soluble, Al_2Cl_6 deliquescent.

Carbonates.—Normal salts unknown. Na_2CO_3 or $(H_4N)_2CO_3$ precipitate essentially $Al_2O_6H_6$ and $Cr_2O_6H_6$ with escape of CO_2.[1]

Sulphates.—Soluble. Most commonly found with K_2SO_4 as alums.

Phosphates.—Salts of the form $(M_2)^{vi}H_{12}(PO_4)_6$ are soluble, the other phosphates insoluble in water, soluble in acids or NaOH; the Cr_2 salts precipitated on boiling the NaOH solution.

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[1] $(Al_2Cl_6 + 3Na_2CO_3 + 3H_2O + Aq) =$
$Al_2O_6H_6 + 3CO_2 + (6NaCl + Aq)$.

Oxalates.—The normal Al_2 salt insoluble, the Cr_2 salt soluble.

Tartrates.—Readily soluble in water. From their solutions $Al_2O_6H_6$ and $Cr_2O_6H_6$ cannot be precipitated.

Cyanides.—$Cr_2(CN)_6$ insoluble in water, slowly soluble in KCN.

GROUP IV. Fe, Ni, Co, Mn, Zn

Metals.—Fe, Ni, Co, Mn, hard, fuse only at high temperatures; Zn soft, readily fusible, boils at red heat. Mn and Fe oxidize readily in moist air, Co and Ni do not. All soluble in acids.

Oxides.—All insoluble in water, soluble in acids, though FeO and Fe_2O_3 dissolve very slowly after ignition. MnO_2 dissolves in HCl with evolution of Cl_2.[1]

Hydrates.—Insoluble in water, soluble in acids. FeO_2H_2, white, rapidly turning green or black, and MnO_2H_2 flesh-colored, turning brown, are soluble in H_4NCl; NiO_2H_2, pale green, and CoO_2H_2, pink, are soluble in H_4NOH or H_4NCl; ZnO_2H_2, white, is soluble in H_4NOH, NaOH, or H_4NCl. H_4NOH and NaOH precipitate the hydrates,— with Co a blue basic salt in the cold, but the hydrate on boiling. $Mn_2O_4H_2$, brown, $Ni_2O_6H_6$, black, CoO_6H_6, black, and $Fe_2O_6H_6$, red

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[1] $(MnO_2 + 4HCl + Aq) = (MnCl_4 + 2H_2O + Aq)$. The solution then gently heated; $(MnCl_4 + Aq) = (MnCl_2 + Aq) + Cl_2$.

brown, are insoluble in water or H_4NCl, but soluble in acids.

Sulphides.—Insoluble in water or in solutions of the hydrates or sulphides of Gr. I. When moist they are oxidized upon exposure to the air, some of them, at least, turning into soluble sulphates. FeS, black, MnS, flesh-colored, soluble in dilute acids; ZnS, white, soluble in dilute mineral acids, insoluble in $HC_2H_3O_2$; NiS, black, CoS, black, insoluble in cold dilute acid, soluble in strong hot HCl or HNO_3. The sulphides are not precipitated by H_2S from acid, or, at best, partially from neutral solutions, except ZnS, which is precipitated from solution in $HC_2H_3O_2$. Fe_2S_3 cannot be formed in the wet way. From solutions of Fe_2 salts $(H_4N)_2S$ precipitates FeS with separation of S.[1] In acid solutions H_2S converts Fe_2 salts into Fe.[2] $(H_4N)_2S$ precipitates the other members as hydrated sulphides.

Chlorides.—All readily soluble, $ZnCl_2$ very deliquescent.

Carbonates.—Neutral salts $M''CO_3$ insoluble in water, soluble in acids. $FeCO_3$ soluble, $MnCO_3$ slightly soluble in H_4NCl; $NiCO_3$ and $CoCO_3$ are soluble in H_4NCl or H_4NOH; $ZnCO_3$ soluble in NaOH, H_4NCl, or H_4NOH. From solutions of Fe_2 salts soluble carbonates precipitate essentially $Fe_2O_6H_6$ with evolution of CO_2. From solutions containing other members of the group Na_2CO_3

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[1] $(Fe_2Cl_6 + 3\,(H_4N)_2S + Aq) = 2FeS + S + (6H_4NCl + Aq)$.

[2] $(Fe_2Cl_6 + H_2S + Aq) = S + (2FeCl_2 + 2HCl + Aq)$.

precipitates basic carbonates; $(H_4N)_2CO_3$ precipitates similar basic salts, those of Ni, CO, and Zn being soluble in an excess.

Sulphates.—All readily soluble.

Phosphates.—Salts of the form $M''H_4(PO_4)_2$ soluble, of the forms $M''_2H_2(PO_4)_2$ and $M''_3(PO_4)_2$ insoluble in water, soluble in acids, more or less soluble in solutions of the soluble salts of the same member of the group. The Mn salts are soluble in H_4NCl; the Ni and Co salts in H_4NCl or H_4NOH; the Zn salts in H_4NCl, H_4NOH, or NaOH. Na_2HPO_4 added in excess precipitates members of the group in the form $M_3(PO_4)_2$.

Oxalates.—The neutral salts insoluble in water, soluble in acids. The Ni and Co salts readily soluble in H_4NOH; ZnC_2O_4 soluble in H_4NOH, H_4NCl, and NaOH.

Tartrates.—$ZnC_4H_4O_6$ and $NiC_4H_4O_6$ insoluble in water, soluble in acids or NaOH; $MnC_4H_4O_6$ and $FeC_4H_4O_6$ sparingly soluble in water, readily soluble in NaOH; $CoC_4H_4O_6$ and $Fe_2(C_4H_4O_6)_3$ soluble in water, the solutions not precipitated by NaOH, or Na_2CO_3.

Cyanides.—With the exception of the Fe_2 salt, which is unknown, the cyanides are all insoluble in water and soluble in KCN. $Ni(CN)_2$ and $Co(CN)_2$ are also soluble in H_4NOH, $Zn(CN)_2$ in H_4NOH or NaOH. From the solutions in KCN $Ni(CN)_2$ and $Zn(CN)_2$ are reprecipitated by neutralizing the KCN with acids. The solutions of the other cyanides in KCN contain (in the case of Mn and Co only after heating or exposure to air) $K_4Fe(CN)_6$, $K_6Mn_2(CN)_{12}$, and $K_6Co_2(CN)_{12}$ from which acids do not separate the simple cyanides, and from which Fe, Mn, and Co cannot be precipitated by ordinary reagents.

Ferrocyanides.—Insoluble in water, decomposed by NaOH into hydrate of the metal, and $Na_4Fe(CN)_6$. $Zn_2Fe(CN)_6$, white, $Ni_2Fe(CN)_6$, greenish white, $Co_2Fe(CN)_6$, green, $FeK_2Fe(CN)_6$, white, rapidly turning blue, and $(Fe_2)_2(Fe(CN)_6)_3$, blue, insoluble in HCl; $Mn_2Fe(CN)_6$, reddish white, soluble in HCl. All are decomposed by heating with H_2SO_4 diluted with $\frac{1}{3}$ its volume of water; HCN evolved, and sulphates left.

GROUP V. Ag, Hg, Pb, Cu, Cd, Bi

Metals.—Bi brittle, Ag and Pb soft, Cu and Cd harder, Hg liquid at ordinary temperatures. Exposed to the air Ag, Bi, and Hg do not oxidize, Pb, Cu, and Cd not readily. All but Ag oxidize rapidly at high temperatures. HNO_3 is the best solvent for all, though Cd dissolves in any acid. HCl does not act upon Ag, Hg, Pb, or Bi, and acts upon Cu only in presence of O. Hot concentrated H_2SO_4 dissolves all but Pb, which it affects but little.

Oxides.—Ag_2O, brown, slightly soluble in water readily soluble in H_4NOH and in solutions of chlorides, cyanides, or hyposulphites or in HNO_3.

HgO, yellow or red, and Hg_2O, black, insoluble in water, soluble in HNO_3. PbO, reddish yellow, CuO, black, Cu_2O, red, CdO, brown, and Bi_2O_3, yellow, in solubility are like the hydrates.

Hydrates.—Ag and Hg form no hydrates. PbO_2H_2 is practically insoluble in water, though alkaline to test paper, readily soluble in $NaOH$. CuO_2H_2, blue, and $Cu_2O_2H_2$, orange yellow, insoluble in water, slightly soluble in cold $NaOH$, soluble in H_4NCl, or in H_4NOH. On boiling CuO_2H_2 with $NaOH$ it is converted into CuO, the small amount dissolved in the cold being precipitated; CdO_2H_2, white, insoluble in water, soluble in H_4NOH; BiO_3H_3, white, insoluble in water or H_4NOH. All these hydrates readily soluble in acids.

From solutions containing members of the group, $NaOH$ precipitates Ag, Hg, and Hg_2 as oxides, the rest as hydrates, PbO_2H_2 soluble in an excess; H_4NOH precipitates Ag as oxide, Hg and Hg_2 as insoluble amine compounds, the rest as basic salts or hydrates, the Ag, Cu, and Cd precipitates being soluble in an excess.

Sulphides.—Insoluble in water, cold dilute acids or solutions of the hydrates or sulphides of Gr. I.; all except HgS and Hg_2S soluble in hot dilute HNO_3. HgS, black, Ag_2S, black, CuS, black, and Bi_2S_3, black, may be completely precipitated from solutions containing HCl unless present in very great excess. PbS, black, and CdS, yellow, are not completely precipitated, if much HCl is present. Hg solutions are precipitated by H_2S first white, then yellow, the color changing to brown red, and becoming black only with excess of H_2S. The change of color is due to the formation of various insoluble compounds of HgS with undecomposed Hg salt.

Chlorides.—AgCl insoluble in water or acids, soluble in H_4NOH and in solutions of chlorides, cyanides, or hyposulphites. Hg_2Cl_2 insoluble in water but gradually decomposed by boiling with water, HCl, or solutions of chlorides; H_4NOH converts it into $(Hg_2)_2H_4N_2Cl_2$, black, insoluble in water or H_4NOH. $PbCl_2$ crystalline, sparingly soluble in cold water, still less soluble in dilute HCl, soluble in hot water, in concentrated HCl, or in NaOH. $BiCl_3$ is soluble in a small quantity of water, more water separates BiOCl, white, insoluble in water, soluble in acids. $HgCl_2$ and $CuCl_2$ soluble in water, $CdCl_2$ deliquescent.

Carbonates.—Neutral salts insoluble in water, soluble in acids. Ag_2CO_3 and $CuCO_3$ are readily soluble in H_4NOH, $PbCO_3$ soluble in NaOH. From solutions containing members of the group, Na_2CO_3 precipitates carbonates, generally basic, insoluble in an excess; $(H_4N)_2CO_3$ precipitates Hg and Hg_2 as insoluble amine compounds, the rest as carbonates or basic salts, the Ag and Cu salts being readily soluble in an excess.

Sulphates.—$CuSO_4$ and $CdSO_4$ readily soluble; $HgSO_4$ and $Bi_2(SO_4)_3$ decomposed by water, giving insoluble Hg_3SO_6 yellow, and $Bi_2H_4SO_8$

white; Ag_2SO_4 sparingly soluble; $PbSO_4$ insoluble in water, much more soluble in strong acids, readily soluble in NaOH, or in solutions of some H_4N salts, especially $H_4NC_2H_3O_2$ and $(H_4N)_2C_4H_4O_6$.

Phosphates.—Salts of the forms $M''_2H_2(PO_4)$ and $M''_3(PO_4)_2$ are insoluble in water, soluble in HNO_3, many of them in H_4NCl. Ag_3PO_4 and the Cu salts are soluble in H_4NOH, the Pb salts in NaOH. From solutions of the members of the group, Na_2HPO_4 precipitates Ag as Ag_3PO_4, and, if added in excess, the rest in the form $M''_3(PO_4)_2$.

Oxalates.—Insoluble in water, soluble in HNO_3. $Ag_2C_2O_4$ and CuC_2O_4 soluble in H_4NOH; PbC_2O_4 soluble in NaOH.

Chromates.—Ag_2CrO_4, brick red, insoluble in water, soluble in H_4NOH, or HNO_3; Hg_2CrO_4, red, and $Bi_2(CrO_4)_3$, yellow, insoluble in water, soluble in HNO_3; $PbCrO_4$ bright yellow, insoluble in water or $HC_2H_3O_2$, soluble in NaOH, with difficulty in HNO_3. $CuCrO_4$, brown, soluble, and $HgCrO_4$ sparingly soluble in water.

Tartrates.—The Cu, Cd, and Hg_2 salts sparingly soluble in water, the rest insoluble. $CuC_4H_4O_6$ is readily soluble in NaOH; $PbC_4H_4O_6$ soluble in $H_2C_4H_4O_6$ or in NaOH.

Cyanides.—$Hg(CN)_2$ soluble in water, the rest insoluble in water, soluble in HNO_3, except AgCN. In KCN AgCN, $Cu(CN)_2$, $Cd(CN)_2$ are soluble, $Pb(CN)_2$ and $Bi(CN)_3$ insoluble. KCN added to solutions of Hg_2 salts precipitates Hg, forming $Hg(CN)_2$ in solution.

Ferrocyanides.—$Pb_2Fe(CN)_6$ and $Cd_2Fe(CN)_6$ insoluble in water, soluble in HNO_3; $Ag_4Fe(CN)_6$, white, $Cu_2Fe(CN)_6$, red brown, $Bi_4(Fe(CN)_6)_3$, white, insoluble in acids, or H_4NOH.

GROUP VI. As, Sb, Sn

Metals.—As and Sb brittle, Sn soft and malleable. As volatilizes without fusion; Sb and Sn fuse readily. As oxidizes at ordinary temperatures, all oxidize readily when heated. As and Sb are hardly attacked by HCl, Sn is easily dissolved. HNO_3 oxidizes all three, Sn and Sb without solution. HCl with HNO_3 dissolves all.

Oxides.—As_2O_3 sparingly soluble, Sb_2O_3 and Sb_2O_5 slightly soluble in water; the rest insoluble in water. All soluble in HCl or HCl with HNO_3. As_2O_3 readily soluble in NaOH. SnO_2 is often insoluble in HCl, but rendered soluble by fusion with NaOH. SnO and Sb_2O_3 heated in air give SnO_2 and Sb_2O_4. As_2O_5 and Sb_2O_5 when heated become As_2O_3 and Sb_2O_4.

Hydrates.—H_3AsO_3 known only in solution or in its salts, H_3AsO_4 soluble. $HSbO_3$ slightly soluble in water. The other hydrates are insoluble in water, soluble in HCl or NaOH. The Sn^{IV} hydrates more readily soluble in KOH than in NaOH; one modification of it insoluble in acids, and with great difficulty soluble in KOH.

Sulphides.—Insoluble in water or dilute acids, readily soluble in solutions of the hydrates or sulphides of Gr. I. If dissolved in soluble sulphides they form sulphur salts,[1] or if in solutions of the hydrates, a mixture of sulphur salt with oxygen salt.[2] On adding acid to either of the solutions the original sulphide is reprecipitated.[3] SnS dissolved in yellow $(H_4N)_2S$ precipitated as SnS_2. As_2S_3, yellow, insoluble in strong HCl, soluble in $(H_4N)_2CO_3$; Sb_2S_3 and Sb_2S_5, orange, SnS, brown, SnS_2, yellow, are soluble in strong HCl, insoluble in $(H_4N)_2CO_3$. As^v in acid solution is slowly reduced by H_2S and precipitated as As_2S_3.

Chlorides.—$AsCl_3$, $SbCl_5$, $SnCl_4$ volatile liquids; $SbCl_3$, $SnCl_2$ solids. All decomposed by water; $SnCl_2$ and $SnCl_4$ slowly or when treated with a large amount. $SbCl_3$ gives at once SbOCl insoluble in water, soluble in acids; $AsCl_3$ gives As_2O_3 as the chief product.

Hydrides.—AsH_3 and SbH_3, gaseous, are formed when a soluble As or Sb compound is treated with Zr and dilute H_2SO_4. They are decomposed

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[1] $As_2S_3 + (3(H_4N)_2S + Aq) = (2(H_4N)_3AsS_3 + Aq)$.

[2] $As_2S_3 + (6NaOH + Aq) = (Na_3AsO_3 + Na_3AsS_3 + 3H_2O + Aq)$.

[3] $(2(H_4N)_3AsS_3 + 6HCl + Aq) = As_2S_3 + 3H_2S + (6H_4NCl + Aq)$.
$(Na_3AsO_5 + Na_3AsS_3 + 6HCl + Aq) = As_2S_3 + (6NaCl + 3H_2O + Aq)$.

below red heat into Sb or As and H_2. Passed into $AgNO_3$, AsH_3 precipitates Ag and leaves H_3AsO_3 in solution[1]; SbH_3 precipitates $SbAg_3$.[2]

Tartrates.—$(SbO)KC_4H_4O_6$ soluble in water. The presence of $H_2C_4H_4O_6$ in sufficient quantity prevents the precipitation of basic Sb salts by water.

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[1] $AsH_3 + (6AgNO_3 + 3H_2O + Aq) = 3Ag_2 + (6HNO_3 + H_3AsO_3 + Aq)$.

[2] $SbH_3 + (3AgNO_3 + Aq) = SbAg_3 + (3HNO_3 + Aq)$.

SPECIAL TESTS FOR THE BASES

GROUP I. Na, K, Li, and NH_4 Radical

Sodium.—Make a loop on a clean platinum wire around the point of a lead pencil. Place one drop of a solution of a sodium salt upon a watch glass. Dip the platinum wire into this solution and insert it in the edge of a low-burning Bunsen flame. The sodium salt will undergo volatilization and will partially decompose. The sodium particle being heated to incandescence imparts a deep persistent yellow color to the flame. Look at the flame through the cobalt glass. Result? Then observe through the spectroscope. See that the slit adjustment of the spectroscope is not too wide. Observe the color and the position of the band. As small an amount of sodium as $\frac{1}{3,000,000}$ milligram will respond to this test. Report sodium *only* when the flame is an intense yellow and lasts for some time. The wire must be repeatedly cleaned by dipping it into con. HCl and heating till no characteristic tests are observed. A thorough cleaning of the wire must follow every test. Do not insert the wire in the reagent bottle.

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Potassium and Lithium.—Follow exactly the same test as for sodium. Observe the difference in behavior. Note that the most characteristic test for potassium is the pale violet or lilac color observed through the cobalt glass. The intense crimson band in the spectroscope just to the left of the sodium band is the most characteristic test for lithium.

Make a solution containing a few drops of the sodium, lithium, and potassium solutions used in the preceding tests and observe as before. Note: The blue glass filters out all light rays except the violet, indigo, and blue. Thus sodium and lithium are intercepted. Since sodium emits only monochromatic light, it will be entirely filtered out, except when the capacity of the glass is exceeded by a great excess of sodium, in which case the flame will appear blue.

Ammonium.—Make a stiff paste by mixing a little water with some dry calcium hydroxide and a few drops of NaOH in a 100 c.c. beaker. To this add a few drops of NH_4Cl or NH_4NO_3 solution. Place a strip of moist litmus paper on the bottom of a clean watch glass and place on the beaker. Heat very gently to avoid spattering. NH_3 is formed and with the moisture in the litmus paper forms NH_4OH, which turns the paper blue. Be careful that no $Ca(OH)_2$ comes into contact with the litmus paper. In testing for ammonium, it is best to make a blank test to prove that the water is free from ammonia which is often present due

to organic matter. (Ask instructor for test solution.)

Ammonium Carbonate Group, or GROUP II. (Ba, Sr, Ca, and Mg)

Barium.—To five c.c. of a soluble salt of Ba, add a few c.c. of NH_4Cl and enough NH_4OH to impart a distinct odor on shaking; warm and add $(NH_4)_2CO_3$ until precipitation is complete. Stir and let stand until the precipitate settles. Filter. Note.—Always test the first few c.c. of the filtrate with the precipitant in order to make sure that the precipitation is completed. If a precipitate appears, more of the reagent is added and the solution is refiltered. Test filtrate with Na_2HPO_4. Result? Dissolve the precipitated carbonate in 2 or 3 c.c. of $HC_2H_3O_2$ and divide into two unequal parts, (a) and (b). To (a), the smaller portion, add a few c.c. of $CaSO_4$ solution. An immediate white precipitate should appear, $BaSO_4$. To (b) add K_2CrO_4 until precipitation is complete. Warm, stir a few minutes, and filter. To the filtrate, add NH_4OH until alkaline, and $(NH_4)_2CO_3$. No precipitate should appear, thus proving that K_2CrO_4 completely precipitated Ba from the solution as $BaCrO_4$.

Strontium.—With a Sr solution repeat the direction given for Ba, except part (a), treated with $CaSO_4$, should stand ten minutes. Note exactly how Sr differs from Ba. To a fresh Sr

solution add a few c.c. of dil. sulphuric acid. Warm and let stand for ten or twelve minutes. Filter and test filtrate with ammonium oxalate after having added ammonium hydroxide until odor is pronounced on shaking. There should be no precipitate as the sulphuric acid should have precipitated the Sr completely as $SrSO_4$.

Calcium.—With a solution of calcium chloride or other soluble salt of calcium, repeat the same test as was used for Sr. Dil. H_2SO_4 does not completely precipitate Ca from solution as $CaSO_4$, since it is partially soluble and is found in the filtrate by adding NH_4OH until alkaline and $(NH_4)_2C_2O_4$. This is a delicate test for Ca, as CaC_2O_4 is very insoluble. It will be seen that Ca is not entirely separated from Ba and Sr unless the solution is so dilute that it will pass into the filtrate as $CaSO_4$.

Magnesium.—To 5 c.c. of a soluble salt of Mg, add a few c.c. of NH_4Cl, NH_4OH, $(NH_4)_2CO_3$, and HNa_2PO_4 dilute with water. If the precipitate is heavy, pour out all but a small portion, dilute with water and view by transmitted light. Note the crystalline appearance of the precipitate ($MgNH_4PO_4$). Since the precipitate is crystalline, it is often necessary to scratch the side of the containing vessel with a stirring rod to hasten the formation of crystals, as the little particles of glass thus separated act as nuclei. Gentle heat and long standing may often be necessary if the solution is dilute. How does Mg differ from Ba,

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Sr, and Ca? How is Ba detected in the presence of the other members of this group? How detect Ca in the presence of Ba, Sr, and Mg?

Make solution containing 5 c.c. of each member of this group. Add a few drops of dil. HCl. Result? Warm and pass H_2S into the solution. Result? Boil to expel H_2S and add a few c.c. of NH_4OH, then $(NH_4)_2S$. Result? These results should prove that the chlorides and sulphides in both acid and alkaline solution are soluble under the conditions of the experiment. Now add a few c.c. of ammonium carbonate. A white precipitate is obtained and ammonium carbonate is the group reagent. (Ask instructor for test solution.)

GROUPS III and IV. Al, Cr, Fe, Co, Ni, Mn, and Zn or $(NH_4)_2S$ Group

Chromium.—To about 5 c.c. of a soluble salt of chromium add a few drops of ammonium chloride, heat almost to boiling, and add ammonium hydroxide until odor is pronounced. Observe the color of the precipitate. Filter and spread the filter paper on a triangle, place on a porcelain dish, and dry above a low lighted flame. Dissolve the dry precipitate in a few drops of concentrated nitric acid. The acid should be slowly dropped on all parts of the precipitate. Then add a small quantity of water in order to wash all of the solution from the paper. Add a pinch of $KClO_3$ to

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the acid solution and boil until yellow. The basic chromium is oxidized to acid chromium. Add sodium hydroxide until alkaline and divide into two parts, (a) and (b). To (a) add $HC_2H_3O_2$ until acid to test paper, and then $Pb(C_2H_3O_2)_2$. Yellow $PbCrO_4$ is formed. To (b) add dilute nitric acid, then ammonium hydroxide in excess. Shake and warm; no visible results should be obtained with chromium salts. With an Al salt, a white gelatinous precipitate, soluble in sodium hydroxide, is formed. $Al(OH)_3$ is also soluble in a bead made of microcosmic salt, $NaNH_4HPO_4$. In this way aluminum hydroxide may be distinguished from SiO_2, which is insoluble in the bead. Aluminum hydroxide may be further confirmed by moistening a small amount with $Co(NO_3)_2$ and heating on a platinum wire. The bead assumes a blue color due to the formation of Al_2O_3CoO.

Aluminum.—With a solution of an aluminum salt follow the direction given for chromium. Notice that no visible result is obtained for aluminum under direction (a).

GROUP IV. (Fe, Co, Ni, Mn, and Zn)

With a solution of a ferric salt, follow the same directions given for Al and Cr, noting that NaOH completely precipitates reddish brown ferric hydroxide from the solution of ferric salt. Dilute 1 c.c. of a ferric salt to about 10 c.c. and add about three

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drops of KCNS; a blood-red coloration is obtained. This is a delicate test for iron and can be made in *general solution*. Make a solution containing about 5 c.c. each of a chromium, aluminum, and a ferric salt. Add a few c.c of dil. HCl, heat, and pass H_2S into the solution. No precipitate should be obtained. Why? Boil to expel H_2S, and add ammonium hydroxide to complete precipitation. Filter and add a few drops of ammonium sulphide to the filtrate. No precipitate should appear, showing that with ammonium hydroxide the precipitation was complete.

Cobalt.—To about five c.c. of a soluble salt of cobalt, add a small amount of ammonium chloride, ammonium hydroxide, and ammonium sulphide until precipitation is complete. Warm, shake, and let stand a few minutes. Filter, wash, and add dil. HCl to the black precipitate, CoS, on the filter paper. The precipitate does not dissolve. MnS and ZnS are soluble in dil. HCl and are thus separated from CoS and NiS. Make a borax bead on a loop of platinum wire. Touch the bead to the CoS so that a small quantity adheres, and fuse in the outer flame. Note the deep blue color. Dissolve the CoS in aqua regia, using one and one half c.c. of con. HCl and one half c. c. of con. HNO_3. If more than the above quantity of aqua regia is used to effect the solution, the excess should be removed by evaporation. Add NaOH until alkaline, a blue green precipitate, $Co(OH)_2$, is formed. Filter, wash with a little hot water,

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and dissolve in a concentrated solution of KCN. (Solution is prepared by dissolving a piece about as large as a small pea in about 3 c.c. of water.) Caution—Pour the solution on the precipitate in such a manner as to come into contact with the entire precipitate. Wash the adhering liquid from the filter paper with 2 or 3 c.c. of hot water, allowing the wash water to run into the KCN solution. Add to the KCN solution 3 or 4 c.c. of NaOH, and then bromine water until color of bromine just appears. Boil. No jet black precipitate should appear as this would show the presence of nickel. Filter and test with borax bead. If a brown precipitate appears do not report nickel.

Nickel.—Follow the same directions as for Co. Notice that a jet black precipitate is formed when bromine water is added in excess and the solution boiled. The precipitate is $Ni(OH)_3$. With the borax bead, nickel shows a violet color when hot and a reddish brown when cold.

Manganese.—To a solution of a soluble salt of manganese, add ammonium chloride, ammonium hydroxide, and ammonium sulphide. A pink or flesh-colored precipitate appears. Warm, shake, filter, and wash. Do not let the MnS stand long in contact with the air. It undergoes oxidation to Mn_2O_3, $MnSO_4$ and a little free S. The $MnSO_4$ is soluble and passes into the filtrate. Dissolve the MnS in a little dil. HCl, and add NaOH to the solution. $Mn(OH)_2$ is precipitated and turns

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brown when exposed to the air, forming $Mn(OH)_3$ or $MnO(OH)_2$. Place a very small quantity of the precipitate on a bead composed of Na_2CO_3 and KNO_3, and fuse in outer flame. The manganese compounds are oxidized and forms Na_2MnO_4 and K_4MnO_4, which are a robin-egg blue in color. This affords a very delicate test for Mn. Report Mn. only by the bead test.

Zinc.—To a solution of a soluble salt of zinc, add ammonium chloride, ammonium hydroxide, and ammonium sulphide. Warm. White ZnS is precipitated. Filter, wash, and dissolve, in a few c.c. of dilute HCl. To the liquid, add sodium carbonate solution until effervescence completely ceases. Boil and filter. Wash the precipitated carbonate into the tip of the filter paper and dissolve in two or three c.c. of $HC_2H_3O_2$. Wash out the adhering solution with one c.c. of water, and squeeze the remaining liquid from the paper. The solution and the wash water together should not exceed four or five c.c. Pass H_2S into the top of the test tube containing the solution for one or two seconds, not allowing the generator tube to touch the liquid. Move the test tube slightly and observe the formation of the white precipitate ZnS at the top of the solution. Shake and observe again. Add a few drops of dilute HCl. The precipitate should entirely dissolve and leave the solution clear. This shows that the precipitate is ZnS and not free sulphur.

Prove that a few drops of NaOH first precipitate

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$Zn(OH)_2$ which dissolves in a slight excess of the reagent, forming $Zn(ONa)_2$.

Compare with **manganese.** Prove that sodium carbonate forms a precipitate with soluble salts of manganese which, dissolved in a moderate quantity of acetic acid, does not give a precipitate with H_2S. Therefore the presence of Mn does not interfere with the test for zinc just outlined.

Make a solution containing 5 c.c. each of Co, Ni, Mn, and Zn solutions. Add a few drops of dil. HCl, warm, and pass H_2S into the solution. Notice that no precipitate forms. What does this signify? Boil to expel the H_2S and add ammonium hydroxide and ammonium sulphide until precipitation is complete. Filter and test filtrate with ammonium carbonate. Does a precipitate appear? What does this show? Ask instructor for test solution.

GROUPS V AND VI. (Ag, Hg′, Pb. Hg″, Bi, Cu, Cd, As, Sb, and Sn, or H_2S Group)

Silver.—To 5 c.c. of $AgNO_3$ add a little dil. HCl. Shake and filter, wash the precipitate on the filter paper with boiling water, and dissolve in cold ammonium hydroxide. Add dil. HNO_3 to the ammoniacal solution. A white precipitate, AgCl, should appear.

Mercurous Mercury.—To 5 c.c. of $HgNO_3$ add a little dil. HCl; shake and filter. Wash with hot water and add ammonium hydroxide to the white

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precipitate, HgCl, on the filter paper. A black residue will be left on the paper. This is a test for a mercurous salt. Filter and test filtrate with dilute nitric acid, to prove that HgCl is insoluble in ammonium hydroxide.

Lead.—To 5 c.c. of $Pb(NO_3)_2$, add a little dil. HCl. Filter and wash the precipitate with cold water. Save the filtrate (a). Dissolve the precipitate in boiling water. Compare the result with Ag and Hg. Add a few drops of dil. H_2SO_4 and a finely divided white precipitate, $PbSO_4$, will be observed. Agitate the precipitate and notice that it settles quickly. Pass through the filtrate (a) H_2S. A brick-red precipitate, $PbCl_2PbS$, first forms but changes into a brown or black precipitate, PbS, especially on dilution. Filter and dissolve the precipitate in 2–3 c.c. of boiling dilute HNO_3. Dilute with water and add 1–2 c.c. of dil. H_2SO_4, and observe the characteristic appearance of the precipitate as before. Lead sulphate is soluble in $NH_4C_2H_3O_2$ and may be precipitated from the solution as black PbS with H_2S. This is a confirmation test for lead. To the filtrate from the lead sulphate, add ammonium hydroxide. With NH_4OH how do Bi and Cu behave? Pass H_2S into the ammoniacal solution. How does Cd behave if present? To a mixture of 5 c.c. each of the nitrates of Ag and Hg, add dil. HCl and filter. Pass H_2S into filtrate. How do they differ from Pb?

Mercuric Mercury.—To 5 c.c. $Hg(NO_3)_2$ add

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about 1 c.c. of dil. HCl, warm and pass H_2S into the solution until precipitation is complete. Filter and try to dissolve in boiling dilute HNO_3. How does this differ from PbS? Dissolve the HgS in 2–3 c.c. of con. HCl and a very small quantity of $KClO_3$. Boil off the chlorine fumes. Dilute with water to about 5 c.c. and add one piece of bright copper wire about one-fourth inch in length. (The wire is brightened by heating in a few c.c. of dil. HNO_3 in a test tube.) The copper is coated with mercury, giving a silver luster when rubbed with a cloth. For further confirmation, place in a small tube sealed at one end and heat. Small globules of mercury will collect on the cold parts of the tube which can be best observed by the aid of a hand lens.

Bismuth.—To 5 c.c. of bismuth nitrate add a few c.c. of dil. HCl, warm and pass H_2S into the solution for some time. Filter and dissolve in about 3 c.c. of boiling dil. HNO_3. Add two or three drops of dil. H_2SO_4. Result? How does bismuth differ from lead with this reagent? Add ammonium hydroxide until the odor is pronounced on shaking. Heat and observe the white flocculent precipitate, bismuth hydroxide. Filter and wash repeatedly with small amounts of hot water. Try to wash into the apex of the filter. Dissolve in 1 c.c. of con. HCl, pouring it on the precipitate drop by drop. Squeeze out all adhering liquid from the filter paper into the test tube. Boil to one drop and pour the solution of $BiCl_3$ into a beaker half

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full of water. Watch the result when the drop comes into contact with the water and further mingles as it sinks to the bottom. A blue white or smoky precipitate, BiOCl, should be formed. Report bismuth only when this result is obtained.

Copper.—To 5 c.c. of Cu $(NO_3)_2$ add a few drops of dil. HCl, heat and pass into solution, H_2S. Filter and dissolve the black precipitate, CuS, in 3 c.c. of boiling dil. HNO_3. Add one or two drops of dilute sulphuric acid. Result? Compare with Pb. Add ammonium hydroxide to the solution until a deep blue color is obtained. Observe that there is no precipitate. How is copper separated from bismuth? Decolorize the blue solution by adding small amounts of KCN at a time (caution). Pass H_2S into the top of the test tube for 1 or 2 seconds. Do not let the gas bubble into the liquid. No precipitate should appear.

Cadmium.—With a solution of cadmium nitrate follow the same process as for copper. Observe that a yellow precipitate, CdS, is formed when H_2S is passed into the top of the test tube. (Ask instructor for explanation.) A dark precipitate masking the yellow CdS will result if too much H_2S is used.

GROUP VI. (As, Sb, and Sn)

Arsenic.—Acidify 5 c.c. of a Na_3AsO_3 solution with dil. HCl, warm and pass H_2S into the solution until a yellow flocculent precipitate is obtained. Filter and thoroughly wash with small amounts

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of water. Treat the precipitate As_2S_3 on the filter paper with four or five c.c. of warm ammonium sulphide. Puncture the bottom of the filter paper and catch the liquid in a test tube. If any precipitate remains undissolved continue the treatment with the same liquid until all is dissolved. Wash out the adhering solution with a little water, allowing it to run into the ammonium sulphide solution. Dilute the solution with an equal volume of water and then slowly add dil. HCl with constant stirring until a yellow precipitate appears. Filter and thoroughly wash, first with hot and then with cold water. Dissolve the precipitate As_2S_3, in cold ammonium carbonate, using the same method for effecting solution as above. (Contrast with Sb and Sn.) Add dil. HCl until effervescence ceases, and observe that the same flocculent yellow precipitate As_2S_3 again appears. Spread filter out on triangle, place on evaporating dish, and dry above a low lighted Bunsen burner. Ignite a small portion and note the garlic-like odor.

Antimony.—With 5 c.c. of $SbCl_3$ follow the same direction as for As and note that Sb_2S_3 will not dissolve in cold ammonium carbonate. The orange red precipitate is washed free from ammonium carbonate and dissolved by repeated treatment with con. HCl and a very small quantity of $KClO_3$. The filter paper is washed and squeezed with stirring rod until free from all adhering liquid. Boil to remove the chlorine

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fumes. There should not be more than 2 c.c. of solution at this point. Dilute with an equal quantity of water and add four or five bright card teeth (Fe). Boil and observe the black flecks of free antimony and also the dark deposit on the card teeth. If the above results do not appear, add a few drops of dil. HCl diluted with one c.c. of water and continue boiling. Filter off the card teeth and liberated Sb and dissolve by repeated treatment in 5 c.c. of warm tartaric acid, $H_2C_4H_4O_6$, with a few drops of dil. HNO_3. After solution is largely affected, acidify with dil. HCl and pass H_2S into the top of the test tube. Observe the orange red precipitate of Sb_2S_3.

Tin.—With 5 c.c. of $SnCl_2$ (the solution is already acid with HCl) follow the direction given for antimony up to and including the treatment with card teeth. Yellow ammonium sulphide must be used to dissolve SnS which passes into solution with much more difficulty than As_2S_3 or Sb_2S_3. The yellow ammonium sulphide must be hot and digested with the precipitate for about ten minutes. The card teeth do not cause the separation of metallic tin, but only reduce $SnCl_4$ to $SnCl_2$ which being soluble remains in solution. After having filtered off the Sb, the solution of $SnCl_2$ is diluted and tested with a few c.c. of $HgCl_2$. A very fine white glistening precipitate, HgCl, is formed, due to the reduction of $HgCl_2$. If much Sn is present, the reduction is carried further and dark Hg is deposited.

$$HgCl_2+SnCl_2=2\mathit{HgCl}+SnCl_4$$
$$2HgCl+SnCl_2=2\mathit{Hg}+SnCl_4$$

Make a solution containing 3 c.c. each of the following: $Pb(NO_3)_2$, $Hg(NO_3)_2$, $Bi(NO_3)_2$, $Cu(NO_3)_2$, and $Cd(NO_3)_2$. Warm and pass hydrogen sulphide into the solution until precipitation is complete. Filter and thoroughly wash. Prove that none of the sulphides of the above metals are soluble in ammonium sulphide. To prove this fact conclusively, these sulphides should be digested for ten minutes in a hot solution of ammonium sulphide, filtered, and the filtrate tested with dil. HCl. Let the acid run down the side of the test tube and note the effect when the first drop comes into contact with the solution. No precipitate should be obtained, only a deposit of free sulphur. Note that the colors of all of the sulphides of Groups V and VI are brown or black except As_2S_3 and CdS (yellow) and Sb_2S_3 (orange-red).

Ask instructor for test solutions, one for Gr. V and one for Gr. VI.

Notes

PRELIMINARY SURVEY OF THE GROUPS

The bases may be divided into six groups as follows: Group I consists of Na, K, Li, and the ammonium radical NH_4. Since all salts of this group are more or less soluble in water, we have no group reagent which precipitates them as a whole. We therefore resort to spectroscopic and flame tests for Na, K, and Li and make a special test for the NH_4 group.

Group II consists of those elements, Ba, Sr, Ca, and Mg, whose carbonates are insoluble and whose sulphides are soluble in water. $(NH_4)_2CO_3$ in the presence of NH_4Cl and NH_4OH completely precipitates Ba, Sr, and Ca as carbonates. Mg may be found in the filtrate by adding HNa_2PO_4, forming a crystalline precipitate, $MgNH_4PO_4$.

Groups III and IV consist of Fe, Al, Cr, Co, Ni, Mn, and Zn, and may be taken collectively as the $(NH_4)_2S$ group. $(NH_4)_2S$ in the presence of NH_4OH and NH_4Cl precipitates Fe, Co, Ni, Mn, and Zn (Gr. IV) as sulphides and Al, Cr (Gr. III) as hydroxides. However, it is somewhat more convenient to precipitate Fe, Al, and Cr as hydroxides with NH_4OH in the presence of NH_4Cl.

The other members of these groups are not thus precipitated but are found in the filtrate by adding $(NH_4)_2S$ and separating by special methods.

Groups V and VI comprise those elements whose sulphides are insoluble in dilute HCl. The sulphides of Group VI (As_2S_3, Sb_2S_3 and SnS) are soluble in $(NH_4)_2S$, and are thus separated from Group V (Ag, Hg′, Pb, Hg″, Bi, Cu, and Cd). H_2S precipitates all the members of both groups as sulphides, but since AgCl, HgCl, and $PbCl_2$ (partially) are precipitated by dilute HCl, it is more convenient to filter off the precipitated chlorides and analyze them separately.

SYSTEMATIC ANALYSIS OF THE BASES

GROUPS V AND VI

Note. In **original** solution always take 2 or 3 c.c. in t.t. and test with blue litmus; if acid, do not add more than 2 or 3 c.c. of dil. HCl more than is necessary to precipitate Ag, Hg′, and Pb (partially). Sometimes Sb, Bi, and Sn are precipitated by dil. HCl, as oxychlorides, SbOCl, BiOCl, and SnOCl, but a small excess of dil. HCl dissolves them. Therefore it is best, when original solution is used, to filter a few c.c. (if a precipitate is already present), and test with a few drops of dil. HCl; if a precipitate appears which dissolves in slight excess of acid, Ag and Hg are absent and Sb, Bi, or Sn is present. In case a precipitate forms and dissolves in excess of dil. HCl, do not use more than 2 or 3 c.c. dil. HCl to about 40 to 50 c.c. of original solution. The oxychlorides if precipitated do no harm, since they are changed to sulphides on addition of H_2S.

To 50–75 c.c. of original solution add cold dil. HCl, drop by drop, shake after each addition and allow P. to settle until the supernatant liquid is clear. Add one more drop of HCl, letting it run down the sides of the t.t. to insure complete precipitation of AgCl.(1)[1]

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[1] Numbers in parentheses refer to notes at end of each group.

Filter off HCl P. and wash once with cold distilled water, letting it run into filtrate, F. Set aside. Analyze P. ($AgCl$, $HgCl$, or $PbCl_2$) as follows: pour boiling water (40–50 c.c.) on the precipitate, using about 10 c.c. each time. Divide the wash water into three parts (a), (b), and (c), and test as follows:

To (a) add a few drops of dil. H_2SO_4—W. P. $PbSO_4$ settles easily.

To (b) add a little K_2CrO_4—Y. P. $PbCrO_4$.

To (c) add H_2S—B. P. PbS.

Which do you like best?

If a residue is left on the filter paper add a few c.c. of NH_4OH, pouring it over precipitate two or three times. Add dil. HNO_3 to the ammoniacal wash water until acid. W. P. shows $AgCl$, curdy if in large quantities, and opalescent if in small quantities.

$AgCl + 2NH_4OH = AgCl(NH_3)_2 + H_2O$.

$AgCl(NH_3)_2 + 2HNO_3 = AgCl + 2NH_4NO_3$.

If a **black** residue is left on the filter paper, insoluble in NH_4OH, it is Hg′. $2HgCl + 2NH_4OH = Hg_2NH_2Cl + NH_4Cl + H_2O$.

Analyze general F. as follows: It is already acid with HCl, used in slight excess (1–2 c.c.) in precipitating $AgCl$, $HgCl$, or $PbCl_2$(2).

Place F. in 100 c.c. flask and heat nearly to boiling. Pass H_2S into solution two or three minutes, or until the solution smells strongly of the gas after shaking. Allow P_1 to settle (may contain sulphides of Sn, Sb, As, Hg″, Pb, Bi, Cu, or Cd). Note color (3). Pour off liquid through a filter paper, leaving P_1 (H_2S) in flask (4). Boil P_1 with 40–50 c.c. of water and pour through filter paper as before with liquid first poured off. Set this F_1 aside for Groups IV–I. Repeat the washing four times in exactly the same way, throwing the wash water away. Wash all P_1 now from the flask into filter paper and let water drain off. Now puncture bottom of filter paper with stirring rod and wash P_1 into t.t. with about 5 or 6 c.c. of yellow $(NH_4)_2S_x$; warm occasionally and let digest for at least ten minutes. Filter and wash P_1 once with about 10 c.c. of hot water, letting it run into ammonium sulphide solution. Set P_1 (sulphides of Hg'', Pb, Bi, Cu, and Cd) aside. Analyze this solution as follows: Add 4 or 5 c.c. of dil. HCl, letting it run down side of the t.t. and shaking after each addition of a few drops (5). A yellow or orange P_2 shows As_2S_3, Sb_2S_3, or SnS_2 present, usually flocculent, while free sulphur is more granular. Boil and filter. The boiling prevents the Sb_2S_3 from dissolving in the next reagent, $(NH_4)_2CO_3$. Explain.

Wash P_2 two or three times with hot water. Let cool thoroughly and add 10 or 12 c.c. of cold $(NH_4)_2CO_3$, pouring it over P_2 several times. As_2S_3 dissolves; Sb_2S_3 and SnS_2 do not. Filter. To F_2 thus obtained add dil. HCl drop by drop, letting it run down the side of the t. t. Effervescence will finally cease, and a yellow flocculent precipitate denotes As_2S_3. If confirmation is needed scrape off the As_2S_3 from the filter paper and place on charcoal and heat. Note the garlic-like odor.

Free the $P_2(Sb_2S_3,SnS_2)$ of $(NH_4)_2CO_3$ by washing and dissolve in 3 c.c. of con. HCl, using **a very little $KClO_3$,** if solution cannot otherwise be obtained. Repeat this treatment several times, using the same solvent. Squeeze liquid out of filter paper into solution and boil down to expel chlorine fumes. Dilute to about 5 c.c. (If a W. P. SbOCl appears, it will do no harm) and add 4 or 5 bright card teeth (Fe), and boil for several minutes,—a dark granular deposit shows pure Sb. What other purpose may the card teeth serve in this connection? Filter off dark deposit and save filtrate for Sn. Wash deposit once with a few c.c. of hot water and dissolve in 5 c.c. of $H_2C_4H_4O_6$ to which are added 5 drops of dil. HNO_3. Continue treatment with same solution, warming occasionally, until Sb is dissolved. Acidify with 2 or 3 drops of dil. HCl and pass H_2S in top of t.t. for 2 or 3 seconds. Do not let generating tube touch liquid. An orange precipitate is Sb_2S_3. Test filtrate from dark antimony deposit for Sn by adding $HgCl_2$, a W. P. HgCl, sometimes mixed with gray Hg, shows Sn present. $SnCl_2 + 2HgCl_2 = SnCl_4 + \mathbf{2HgCl}$, W.P.

$$SnCl_2 + 2HgCl = SnCl_4 - \mathbf{2Hg}, \text{ B. P.}$$

Analyze P_1 (free from As, Sb, and Sn) by placing filter paper with P_1 underneath in a porcelain dish and add about 8–10 c.c. of dil. HNO_3, boil for one-half minute. All sulphides present dissolve except HgS, which is black and heavy (6).

This dark residue, HgS, is filtered off (save F_3 for Pb, Bi, Cu, and Cd), washed in hot water, and dissolved in 2 or 3 c.c of con. HCl with a **very little $KClO_3$**. Boil off chlorine fumes. Dilute to 5 or 6 c.c. and divide into two parts, (a) and (b). To (a) add a few drops of $SnCl_2$, a W. P. often becoming dark shows Hg present. To (b) add a bright piece of Cu wire about one-half inch in length (made bright by warming in a few drops of dil. HNO_3 in a t.t.). The Cu becomes coated with Hg, if present. The Cu is placed in a small bulb tube and heated; Hg sublimes on the sides of the tube in minute particles, best seen by aid of a magnifying glass.

Analyze F_3 (7) (may contain nitrates of Pb, Bi, Cu, and Cd) as follows: Evaporate in a porcelain dish after adding 1 c.c. of dil. H_2SO_4 until dense white fumes of H_2SO_4 appear. HNO_3 will now be all removed since HNO_3 boils at about 120° C. and H_2SO_4 fumes at 250° C. The HNO_3 has a solvent action on $PbSO_4$ if not removed. Place in t.t. 3 or 4 c.c. of water and add a few drops of dil. H_2SO_4, rinse porcelain dish with solution and return to t.t. A W. P. Pb SO_4 indicates Pb (8). Filter and add NH_4OH until odor is pronounced. A white flocculent precipitate indicates $Bi(OH)_3$ and a *blue* coloration Cu. Filter off $Bi(OH)_3$ and confirm for Bi by dissolving in 1 c.c. of con.

HCl. Repeat process with same solvent until all precipitate is dissolved. Rinse with 1 c.c. of water, squeeze out all adhering liquid, and evaporate to **one drop** and pour into a beaker half full of water—a cloudy or smoky precipitate is BiOCl. Decolorize the blue solution containing Cu by adding small amounts of KCN (caution!) at a time. Remove KCN from bottle with a strip of paper. The Cu and Cd form complex ions with the KCN; K $[Cu(CN)_2]$ and K_2 $[Cd\ (CN)_4]$ respectively. Pass H_2S into top of t.t. A yellow precipitate shows CdS. The complex ion of $K[Cu(CN)_2]$ is not decomposed by H_2S. A small amount of Cu may not show a blue coloration with NH_4OH. A small portion of the filtrate from $Bi(OH)_3$ is acidified with $HC_2\ H_3O_2$ and a few drops of $K_4\ Fe\ (CN)_6$ added. A reddish brown precipitate or coloration is $Cu_2Fe(CN)_6$.

NOTES

1. Pour 2 or 3 c.c. of the original solution in a test tube and test with blue litmus paper. If acid, do not add more than 1 or 2 c.c. of dilute HCl more than is necessary to precipitate Ag, Hg^I, and Pb (partially). Sometimes Sb, Bi, and Sn are precipitated by HCl as oxychlorides, SbOCl, BiOCl, and SnOCl, but a slight excess of dil. HCl dissolves them. It is best when the *original solution* is used to filter a few c.c. (if a precipitate is already present), and test with a few drops of dilute HCl; if a precipitate appears which dissolves in a slight excess of acid,

Ag and Hg are absent and Sb, Bi, or Sn is present. In case a precipitate forms and dissolves in excess of dilute HCl, do not use more than 2 or 3 c.c. of dilute HCl to about 40 to 50 c.c. of original solution. The oxychlorides if precipitated do no harm, since they are changed to sulphides on addition of H_2S.

2. If lead is present in moderate quantities, a partial precipitation is obtained on addition of dilute HCl. If only a *small* quantity is present, no precipitate will be obtained with HCl. In either case it will be found and entirely precipitated by dilute H_2SO_4 further along in the analysis of this group.

3. If the precipitate with H_2S is yellow, As or Cd is present; if orange, Sb is present. If the precipitate is yellow and entirely dissolves in yellow ammonium sulphide, Cd is absent, and As and possibly Sb are present. Since the sulphides are precipitated in order of their solubilities, it is often possible to observe a yellow or orange color appearing in the presence of a black precipitate.

4. It is advisable to dilute a few c.c. of the H_2S filtrate to three or four times its volume and again treat with H_2S. If a precipitate appears, dilute the entire filtrate and pass in H_2S until precipitation is complete. Cd is easily lost in this group, if an excess of dilute HCl is added in the beginning of the analysis. In such cases Cd will appear in the next group with Zn.

Boil off the H_2S from the filtrate *at once.* Oxidation of H_2S may occur and Ba and possibly Sr will be lost at this time, if the filtrate is allowed to stand.

5. If As, Sb, and Sn are absent, it is not necessary to treat the H_2S precipitate with $(NH_4)_2S_x$. Since

this fact is not usually known at this time, it will be necessary to treat the H_2S precipitate with this reagent as usual; but the next treatment with dilute HCl will reveal the presence or absence of this group. Notice the effect of the first drop of HCl as it runs down the side of the test tube and mingles with the solution. If a yellow or orange precipitate more or less flocculent appears, some of the members of this group are present. If only a white precipitate (free S) appears, Group VI is absent.

The yellow $(NH_4)_2S_x$, used in the separation of Group VI from group V, is best prepared as needed by dissolving a quantity of sulphur about the size of a grain of wheat in about 10 c.c. of ordinary ammonium sulphide.

6. Free S with particles of sulphides of this group held mechanically is often found. The S is more or less waxy and often floats. The boiling should not be prolonged or the dilute HNO_3 will become concentrated and oxidize the black HgS to white $Hg(NO_3)_2\,2HgS$.

7. Test a few drops of F_2 in a test tube with a few drops of dilute H_2SO_4. If a white precipitate forms and easily settles, Pb is indicated. The entire filtrate should be treated as given in the text, if a precipitate with H_2SO_4 is obtained, otherwise it may be omitted.

8. $PbSO_4$ is heavy and easily settles, leaving a clear supernatant liquid. It is usually finely divided and tends to climb up the sides of the test tube when agitated. If the solution and precipitate are placed in a small beaker and whirled, the $PbSO_4$ will collect at the center in the bottom. Confirm for Pb by dis-

solving in a strong solution of $NH_4C_2H_3O_2$, acidifying with $HC_2H_3O_2$ and treating with a few drops of $K_2 CrO_4$. Yellow $PbCrO_4$ should appear.

9. If a brown precipitate appears on addition of H_2S in testing for Cd, it may be Pb, Bi, or Cu, but more especially Fe (coming from the H_2S generator). In any case the yellow CdS will be masked. Filter and thoroughly wash the precipitates, and treat with 2 c.c. of warm dilute HCl. Repeat treatment with same acid two or three times. CdS, if present, is dissolved. Add about 2 gms. of $NaC_2H_3O_2$ to the HCl solution and pass H_2S into top of test tube. A yellow precipitate will appear if Cd is present.

GROUPS III AND IV

Always test for Fe in general solution (1). A few c.c. are boiled with Br_2 water in order to oxidize any ferr**ous** salt to ferr**ic** salt. A few drops of KSCN give a permanent blood-red coloration, if Fe is present. Always boil general filtrate from Groups V and VI to expel H_2S before testing for members of Groups III and IV (2).

If Fe was found in original solution, add a few drops of Br_2 water and boil. Add NH_4Cl (1 c.c. to about every 5 c.c. of solution), heat almost to boiling, and add NH_4OH with stirring, vigorous shaking will do no harm, until odor of ammonia is pronounced. Filter quickly (3). Note color of precipitate.

The P_1 [may contain $Fe(OH)_3$, reddish brown, $Cr(OH)_3$, blue green, and $Al (OH)_3$, white and gelatinous] is washed twice with hot water on filter paper, letting first wash water run into filtrate. Concentrate F_1 by evaporation to 8 or 10 c.c. and set aside for Groups IV, II, and I.

Analyze P_1 as follows: Spread filter paper on triangle, place on dry evaporating dish, and heat on gauze about 6 or 8 inches above low lighted Bunsen burner until perfectly dry. This serves two purposes, it drives off NH_4OH, which is not easily washed out, and removes water which would otherwise dilute the con. HNO_3 next added. Fold up filter paper and place in funnel. Dissolve P_1 in 1 or 2 c.c. of con. HNO_3, pouring it on the filter so as to moisten all parts of the precipitate. Wash once to remove adhering liquid, press filter paper, and boil solution with a little $KClO_3$ until **yellow** (4).

To the solution boiled in $KClO_3$, add an excess of NaOH. Fe is precipitated as $Fe(OH)_3$, if present; Al and Cr become $Al(ONa)_3$ and Na_2CrO_4 respectively—both in solution.

Filter off the $Fe(OH)_3$ and divide filtrate into two parts, (a) and (b). Dilute (a) to 4 or 5 c.c., acidify with acetic acid, and add a few drops of $Pb(C_2H_3O_2)_2$ **a yellow precipitate,** $PbCrO_4$, indicates the presence of Cr. If the precipitate is white it is due to sulphates or other impurities and Cr is absent.

To (b) add dil. HNO_3 until acid, then NH_4OH until alkaline, a white gelatinous precipitate may be $Al(OH)_3$. Make a blank test for Al and compare with precipitate just obtained. Sometimes a silicate comes down here, which resembles $Al(OH)_3$ very closely. It is best to make a **blank** test with NaOH and HNO_3 in order to prove that the reagents are not in fault (5).

Analyze F_1 (may contain Co, Ni, Mn, Zn with Groups I and II) as follows: Place in 100 c.c. flask, heat to boiling, add $(NH_4)_2S$ (6) until after shaking odor of reagent is strong. Shake vigorously for one or two minutes, let stand two or three minutes longer. Filter quickly using a creased filter paper. When the last of the solution is poured on the filter paper, begin adding hot water, containing a few drops of $(NH_4)_2S$ (this prevents the MnS from oxidizing to soluble $MnSO_4$). Allow first wash water to run into filtrate, F_2 (7). Set F_2 aside for Groups I and II. After the P_2 has been thoroughly washed, puncture the filter paper while full of water and wash P_2 into beaker with cold water. Add 3 or 4 c.c. of con. HCl (this makes dil. HCl since water is already present). MnS and ZnS are dissolved, if present. Filter off P_3(this should be black if CoS or NiS is present). Save F_3 for Mn and Zn. Test black residue on filter paper with borax bead, using very little precipitate and heating in inner flame. Deep blue indicates Co; violet while hot and reddish brown when cold indicates Ni in absence of Co. To test for Ni, in presence of Co, dissolve P_3 (CoS and NiS) in a very little con. HCl (1½ c.c.) and con. HNO_3 (½ c.c.). Add NaOH in slight excess, $Ni(OH)_2$ and Co $(OH)_2$

are precipitated, if present. Wash these precipitates in tip of filter paper with hot water and dissolve in a hot concentrated solution of KCN (caution!), made by dissolving a piece of KCN about the size of a pea in about 2 c.c. of water. Repeat process with same KCN solution until all parts of the precipitate have been moistened. Wash out all adhering liquid into KCN solution, using about 1 c.c. of water at a time (8).

Add to KCN solution 3 or 4 c.c. of NaOH, then Br_2 water **in excess** or until solution is yellow; boil, Ni, if present, is precipitated as $Ni(OH)_3$—jet black. Confirm with borax bead, heating in **outer** flame (9).

Test F_3 for Mn and Zn as follows: Divide into two parts, (a) and (b). To (a) add NaOH and boil, if a blue-green precipitate forms, more or less light in beginning, and turning brown on exposure to air, it indicates Mn. Confirm by fusing in a bead, made of Na_2CO_3 and KNO_3,—a robin's egg blue is K_2MnO_4 or Na_2MnO_4.

To (b) add Na_2CO_3 solution until quite alkaline, boil, filter, and wash; dissolve in a little acetic acid and pass H_2S into top of t.t. for 2 or 3 seconds; shake, if a white precipitate, ZnS, appears, Zn is present (10).

NOTES

1. A small quantity of Fe is often carried over mechanically by the H_2S generator. It is therefore best to test for Fe in the original solution.

H_2S reduces ferric compounds to ferrous. The H_2S must be expelled and the solution boiled with Br_2 water.

A further test for Fe may be made by adding a few drops of $K_4Fe(CN)_6$ to a few c.c. of the original solution. A deep blue indicates Fe.

2. Certain organic acids, oxalates, and phosphates interfere with the tests for Groups IV, III, and II. It is therefore necessary to test for these substances at this time and, if present, to analyze according to "Tests for Groups IV, III, and II in the Presence of Phosphates and Oxalates, etc."

3. If the original solution contains much free HCl, it is not necessary to add but little, if any, NH_4Cl since the addition of NH_4OH forms NH_4Cl with the free HCl already present. The NH_4Cl prevents Mn and Mg from partially precipitating with NH_4OH; also prevents the formation of colloidal solutions.

The NH_4OH precipitate may contain some Mn, especially if allowed to stand, but since provision is made for its detection under these conditions (see note 4), it does not interfere with the tests for Fe, Al, and Cr.

4. At this point the solution sometimes becomes black or brown due to Mn, mostly in the form of MnO_2. Mn may also be precipitated as $Mn(OH)_2$, quickly oxidizing to brown $Mn\ (OH)_3$, along with $Fe\ (OH)_3$ when NaOH is added. If suspected it is best to use the Na_2CO_3 and KNO_3 bead test.

5. Al compounds may be dissolved by NaOH from the bottle. Make a microcosmic bead with a small quantity of the precipitate. SiO_2 whirls around in the bead and does not dissolve, while with Al_2O_3 the bead remains clear.

6. Do not use yellow ammonium sulphide to precipitate the members of this group. It is advisable to test the $(NH_4)_2S$ solution for a sulphate. It is evident that Ba and possibly Sr will be lost if a sulphate is found.

$(NH_4)_2S$ may be entirely dispensed with and H_2S passed directly into the solution made strongly alkaline with NH_4OH.

7. Acidify F_2 *at once* with $HC_2H_3O_2$ and boil to expel H_2S. This prevents the oxidation of ammonium sulphide to ammonium sulphate, the absorption of CO_2 from the air, and also precipitates any colloidal NiS which is sometimes indicated as a brown coloration. The filtrate should be concentrated to about 15 to 20 c.c. and filtered. More or less free S usually separates out on boiling with $HC_2H_3O_2$.

8. The direction for preparing and using KCN solution at this point must be carefully followed. It is always better to wash a precipitate two or three times with a little water each time than to wash *once* with several c.c. of water.

9. If the precipitate formed by the addition of Br_2 water is brown instead of *black*, it may be due to $Mn(OH)_3$ which gives an amethyst with borax bead and may be easily mistaken for Ni. If the precipitate is brown, test with Na_2CO_3 and KNO_3 bead for Mn.

10. Cd if lost in Group V may come down in Group IV with ZnS (white), thus giving a yellow appearance and masking the Zn. In such a case, add 3 or 4 drops of dilute HCl which dissolves the ZnS only. Filter. Add 1 or 2 gms. of $NaC_2H_3O_2$ to filtrate, and pass H_2S into top of test tube. If Zn is present a *white* precipitate, ZnS, is obtained.

GROUP II

The filtrate from the preceding groups is concentrated to about 15 c.c. (1). If NH_4Cl has already been added in the separation of Groups III and IV, render alkaline with NH_4OH, heat almost to boiling (but not boiled) and add $(NH_4)_2CO_3$ with stirring until precipitate seems no longer formed (2). Let settle and filter. Test the filtrate with one or two drops of the precipitant, $(NH_4)_2CO_3$, to make sure that the precipitation is complete. If a precipitate occurs, more of the precipitant must be added until the supernatant liquid is clear.

Filter and add Na_2HPO_4 to a small portion of the filtrate. Save the remainder of the filtrate for Group I. If a *crystalline* precipitate appears it is $MgNH_4PO_4$. If no precipitate, Mg is absent (3).

Wash the precipitated carbonate with hot water, saving first wash water if general solution is used. Dissolve in 2 or 3 c.c. of warm $HC_2H_3O_2$ pouring it on the filter so that all the precipitate is dissolved. Pour the same acetic acid solution on the paper again if the precipitate is not completely removed by the first treatment. Wash the adhering liquid from the filter paper with a few c.c. of water, letting it run into the filtrate. The volume of filtrate should be about 5 c.c. To a small portion (1 c.c.) (a), add a few drops of $CaSO_4$,—an **immediate** white precipitate is $BaSO_4$; a **tardy** precipitate is $SrSO_4$ (4). If an immediate precipitate is obtained, remove the Ba from (b) by adding K_2CrO_4; shake well, warm, and let precipitate settle. The supernatant liquid should be an orange red. Filter through a double filter paper. Wash once with hot water, letting it run into filtrate.

Always test all filtrates with precipitant to make sure that enough reagent has been added.

To the orange red filtrate add NH_4OH until alkaline, then $(NH_4)_2CO_3$. Ca and Sr are precipitated as carbonates, if present.

If a precipitate occurs, filter and wash on filter paper until free from color and dissolve in 2 c. c. of acetic acid, using same acid repeatedly until all precipitate is dissolved. Test a small portion, (a) 1 c.c. with $CaSO_4$, letting it stand 8 or 10 minutes with occasional warming and shaking. If a precipitate appears it is $SrSO_4$. To remainder (b) of solution add 1 or 2 c.c. dil. H_2SO_4 to remove Sr.(5). Warm and let stand 15 minutes. Filter and test filtrate for Ca by adding NH_4OH until strong odor is recognized, and a few drops of $(NH_4)_2C_2O_4$; a white precipitate shows CaC_2O_4.

NOTES

1. If an excess of ammonium salts have accumulated from Groups III and IV, the filtrate should be evaporated to dryness and ignited in a porcelain crucible until all the ammonium salts are expelled. Dissolve in 4 or 5 c.c. of water and proceed with the analysis.

If no NH_4Cl has been added in the analysis of the preceding groups, and the addition of HN_4OH above causes any precipitate to form, NH_4Cl should be added drop by drop until a clear solution is obtained. This precipitate, which may appear on the addition of NH_4OH when NH_4Cl is absent, is an evidence of the presence of Mg, which is partially precipitated by NH_4OH in the absence of NH_4Cl.

Ba and Sr are often lost during the analysis of the previous groups. This is largely due to the oxidation of H_2S and $(NH_4)_2S$. If the precautions are carefully followed as previously given, little difficulty will be experienced.

2. If no precipitate is obtained with $(NH_4)_2CO_3$, see note (3) for methods of testing for traces of Ba, Sr, and Ca.

3. The filtrate from the $(NH_4)_2CO_3$ precipitate may contain *small* quantities of Ba, Sr, and Ca. A slight precipitate (especially if not crystalline) with HNa_2PO_4 may, therefore, not be due to Mg. In a fresh portion Ba and Sr should be tested for and removed with dilute H_2SO_4. Filter, make alkaline with NH_4OH and add $(NH_4)_2C_2O_4$ to remove Ca. Mg may be tested for, after filtering off the CaC_2O_4, with HNa_2PO_4. Warm and scratch the sides of the test tube to start crystallization. Explain.

Sr may be detected in the H_2SO_4 precipitate by moistening with a few drops of con. HCl, warming and holding in edge of flame on platinum wire. Sr gives a crimson flame.

4. An immediate precipitate with $CaSO_4$ usually indicates Ba; a tardy precipitate Sr. However, relative concentrations must be taken into consideration. If a large quantity of Sr is present with a small quantity of Ba, a precipitate may appear very soon. On the other hand, a small concentration of Ba may require a little time before a precipitate appears. In case of doubt it is advisable to add a fraction of a drop of K_2CrO_4, held on end of stirring rod to part (b). Carefully observe the effect as the surfaces of the two liquids come in contact. A cloudy yellow precipitate indicates Ba; if only a yellow coloration, Ba is absent.

5. Ca, if present in relative large quantities, is partially precipitated as $CaSO_4$ along with $SrSO_4$, which is completely precipitated. Any excess of H_2SO_4 must be entirely neutralized with NH_4OH before testing for Ca. It is, therefore, necessary to add only 1 or 2 c.c. of dilute H_2SO_4, or the solution will be rendered so dilute on adding NH_4OH that a precipitate for Ca will be difficult to observe.

If Ba or Sr are not completely removed, they will appear with Ca, or be reported when Ca is absent.

GROUP I

This group consists of the elements Li, Na, K, and the ammonium radical, NH_4. Since all the salts of this group are more or less soluble there is no group reagent which precipitates them as a whole. The color of the flame and the spectroscope are used to test for K, Na, and Li. A special test is made for the ammonium radical, NH_4, in the original solution.

It is not necessary to remove Mg in testing for Na, K, and Li. If, however, the amount of the salts of these metals is desired, its removal is necessary.

Mg, if present, may be removed before testing for members of Group I as follows: Evaporate filtrate from Ba, Sr, and Ca and ignite in evaporating dish until free from ammonium salts; dissolve in a little water and add $Ba(OH)_2$; $Mg(OH)_2$ is precipitated; filter and remove Ba from filtrate by heating to boiling and adding dil. H_2SO_4. $BaSO_4$ is filtered off and filtrate evaporated to dryness and ignited in a porcelain crucible. The residue consists of salts of Na, K, and Li.

Na is best recognized by the intensity and duration of the yellow flame. Also by a bright yellow band in the spectroscope. K is best recognized through the cobalt glass, giving a reddish-violet coloration. The yellow rays from the Na and the crimson rays from Li do not pass through the blue grass. K also gives a red band in the extreme left in spectroscope. Li gives a crimson flame which may be recognized by the naked eye; also gives a red band in the spectroscope, between the Na and K, and a little nearer the Na band.

Test for NH_4 in original solution by making a stiff paste with dry $Ca(OH)_2$ in a small beaker. Place a strip of moist red litmus paper on the bottom of a clean watch glass and place on beaker, heat gently (avoid spattering); NH_3, if present, is evolved and acts on the moist litmus, turning it blue.

ACIDS

GROUP I

Ba Salts insoluble in water.

1. Acids decomposed in acid solution by H_2S.

M_2CrO_4
M_3AsO_3
H_3AsO_4
M_2SO_3
$M_2S_2O_3$
HIO_3

2. Acids not decomposed in acid solution by H_2S.

a. Ba Salts soluble in HCl.

H_3PO_4
H_3BO_3
$H_2C_2O_4$
HF
$H_2C_4H_4O_6$
M_2CO_3
H_4SiO_4
HPO_3
$H_4P_2O_7$
H_3PO_3

b. Ba Salts insoluble in HCl.

H_2SO_4
H_2SiF_6

GROUP II

Ba Salts soluble, Ag Salts insoluble in water.

HCl
HBr
HI
HCN
$H_4Fe(CN)_6$
$H_6Fe_2(CN)_{12}$
H_2S
HNO_2
$HClO$
$HClO_2$
H_3PO_2

GROUP III

Ba and Ag Salts soluble in water.

HNO_3

$HClO_3$

$HClO_4$

$HC_2H_3O_2$

$HCHO_2$

PROPERTIES OF ACIDS

GROUP I. 1. M_2CrO_4, M_3AsO_3, H_3AsO_4, M_2SO_3, $M_2S_2O_3$

Chromates.—Salts generally insoluble in water, the most important soluble salts being those of Gr. I., Sr, Ca, Mg, and the normal salts of Mn and Zn. The acid is unknown, since it breaks upon liberation from its salts into H_2O and CrO_3; it also gives no salts of the form $MHCrO_4$. If acid be added to a solution of M_2CrO_4 it turns from yellow to red with the formation of a salt of the form $M_2Cr_2O_7$,[1] further addition of acid sets CrO_3 free.[2] If H_2SO_4 is used the CrO_3 separates as a red mass, or in red needles. CrO_3 heated with H_2SO_4 loses oxygen and becomes $Cr_2(SO_4)_3$,[3] with HCl it gives Cr_2Cl_6, water and Cl_2.[4] Organic matter or reducing agents, like H_2S or SO_2, effect a similar change, $2CrO_3$ becoming Cr_2O_3.[5] Or in

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[1] $(2K_2CrO_4 + H_2SO_4 + Aq) = (K_2Cr_2O_7 + K_2SO_4 + H_2O + Aq)$.

[2] $(K_2Cr_2O_7 + H_2SO_4 + Aq) = (2CrO_3 + K_2SO_4 + H_2O + Aq)$.

[3] $4CrO_3 + 6H_2SO_4 = 2Cr_2(SO_4)_3 + 6H_2O + 3O_2$.

[4] $(2CrO_3 + 12HCl + Aq) = (Cr_2Cl_6 + 6H_2O + Aq) + 3Cl_2$.

[5] $(2CrO_3 + 6HCl + 3H_2S + Aq) = (Cr_2Cl_6 + 6H_2O + Aq) + 3S$.

any case the change of CrO_3 to Cr_2O_3 is accompanied by a corresponding change of color from red to green. $BaCrO_4$ and $PbCrO_4$, yellow, insoluble in water or in $HC_2H_3O_2$. Ag_2CrO_4, brick red, soluble in HNO_3 or H_4NOH.

Arsenites.—The salts of Gr. I. are soluble, the neutral salts of the other groups insoluble in water, though many are soluble in H_4NCl. The acid is unknown, although acid salts of the forms MH_2AsO_3 and M_2HAsO_3 are known. From acid solutions of all salts H_2S readily precipitates As_2S_3, yellow. Oxidizing agents convert the salts into arseniates. $Cu_2H_2(AsO_3)_2$ is green, insoluble in water, soluble in acids, and soluble in NaOH. On warming the NaOH solution $Cu_2O_2H_2$, orange yellow, is precipitated, Na_3AsO_4 being left in solution. $Mg_3(AsO_3)_2$ and $Ba_3(AsO_3)_2$ insoluble in water, soluble in acids, or H_4NCl; Ag_3AsO_3, pale yellow, insoluble in water, soluble in H_4NOH or HNO_3.

Arseniates.—The salts resemble the phosphates closely. Of the neutral salts only those of Gr. I. are soluble. The acid is solid, soluble in water. From acid solutions of its salts H_2S at first precipitates nothing, but on long standing, or more quickly on warming, it is reduced and As_2S_3 is precipitated. SO_2 reduces it quite rapidly to arsenious acid with formation of H_2SO_4; H_2S then at once precipitates As_2S_3. $Ba_3(AsO_4)_2$ and $Mg_3(AsO_4)_2$ are insoluble in water, soluble in acids. Ag_3AsO_4, red brown, insoluble in water, soluble in

H_4NOH or HNO_3. $Mg_2(H_4N)_2(AsO_4)_2$, insoluble in water or H_4NCl, soluble in acid, is formed when H_4NOH, H_4NCl, and $MgSO_4$ are added to aqueous solutions of arseniates. A solution of $(H_4N)_2MO_4$ in HNO_3 gives no precipitate in acid solutions of arseniates in the cold, but gives a yellow precipitate on boiling.

Sulphites.—The neutral salts are all insoluble or sparingly soluble in water; of the acid salts many are soluble, though many are decomposed by boiling their solutions, neutral salts being formed. The acid is unknown. From its salts stronger acids liberate SO_2,[1] soluble in water; in this solution H_2S forms $H_2S_5O_6$ with separation of S. SO_2 is a powerful reducing agent but is itself reduced by nascent H with formation of H_2S.[2] $BaSO_3$ is insoluble in water, soluble in HCl; from this solution Cl_2 or Br_2 precipitate $BaSO_4$.

Hyposulphites.—Most of the salts are soluble in water. The acid is unknown. Stronger acids liberate from its salts SO_2 and S. The same decomposition[3] takes place when HCl is added to solutions of its salts, though slowly in dilute solutions. With H_2S in acid solutions, or with nascent hydrogen the reactions are the same as with the sulphites. BaS_2O_3, insoluble in water, soluble in HCl. $Ag_2S_2O_3$, white, insoluble in water, soluble in solutions of hyposulphites;

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[1] $(Na_2SO_3+2HCl)=(2NaCl+H_2O+SO_2)$.

[2] $SO_2+3H_2=H_2S+2H_2O$.

[3] $(Na_2S_2O_3+2HCl+Aq)=(2NaCl+H_2O+SO_2+Aq)+S$.

blackens on heating, Ag_2S being formed. PbS_2O_3, insoluble in water, soluble in solutions of hyposulphites, forms PbS on heating.[1]

Group I. 2. (a) H_3PO_4, H_3BO_3, $H_2C_2O_4$, HF, M_2CO_3, H_4SiO_4, $H_2C_4H_4O_6$; (b) H_2SO_4

Phosphates.—Salts of the forms M_3PO_4 and M_2HPO_4 insoluble except those of Gr. I., salts of the form MH_2PO_4 soluble. All the insoluble salts are soluble in acids, and these solutions are precipitated by H_4NOH; the precipitate is usually a phosphate of the form M_3PO_4. $Ba_3(PO_4)_2$ and $Ca_3(PO_4)_2$, insoluble in water, are soluble in HCl and in $HC_2H_3O_2$. Ag_3PO_4, pale yellow, insoluble in water, is soluble in H_4NOH or HNO_3. From aqueous solutions of the phosphates $MgSO_4$, after adding H_4NCl and H_4NOH, precipitates $Mg_2(H_4N)_2(PO_4)_2$, insoluble in water or H_4NCl, soluble in acids. In acid solutions of the phosphates $(H_4N)_2MO_4$ dissolved in HNO_3 gives a yellow precipitate in the cold, insoluble in water or in dilute acids, if $(H_4N)_2MO_4$ be in excess, readily soluble in excess of phosphate.

Borates.—Only the salts of Gr. I. are readily soluble in water, though many salts insoluble in water are soluble in H_4NCl. The acid is separated from its salts by stronger acids; soluble in water, the solution turning turmeric paper red, best seen when the paper is dried at 100°. This red color

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[1] $PbS_2O_3+H_2O=PbS+H_2SO_4$.

is changed to greenish black when moistened with Na_2CO_3. H_3BO_3 partially volatilized by evaporation of its solution. Its alcoholic solution burns with a green flame. The Ba and Ca salts are insoluble in water, soluble in HCl, $HC_2H_3O_2$, or H_4NCl. The Mg salt readily soluble in H_4NCl.

Oxalates.—Almost all the neutral salts, except those of Gr. I., are insoluble in water, soluble in acids. H_4NOH precipitates the acid solutions of many of the salts insoluble in water, those of Ba, Sr, and Ca completely. All the salts are decomposed by ignition; the residue consists of carbonate, oxide, or metal. The acid, readily soluble in water, is decomposed when heated by itself or with strong H_2SO_4 into CO_2, CO, and H_2O.[1] With the dry salts H_2SO_4 gives the same reaction, first setting the acid free, then decomposing it. The acid or its salts warmed with dilute H_2SO_4 and MnO_2 give off CO_2, $MnSO_4$ and water being formed.[2] BaC_2O_4 is insoluble in water, soluble in HCl. CaC_2O_4 is insoluble in water or $HC_2H_3O_2$, soluble in HCl. $Ag_2C_2O_4$, insoluble in water, soluble in H_4NOH or HNO_3, is decomposed with explosion on ignition, Ag being left. The salts of Gr. II. are decomposed on boiling with a concentrated solution of Na_2CO_3 with formation of the corresponding carbonates and $Na_2C_2O_4$ in solution.

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[1] $H_2C_2O_4 = H_2O + CO_2 + CO$.

[2] $(H_2C_2O_4 + H_2SO_4) + MnO_2 = (MnSO_4 + 2H_2O) + 2CO_2$.

Fluorides.—Salts of Gr. I. readily soluble, as also Al_2F_6, Cr_2F_6, Fe_2F_6, AgF, HgF_2. The rest are sparingly soluble or insoluble in water. HF is liberated from its salts by strong H_2SO_4 as a gas readily soluble in water, the solution characterized by its power of dissolving SiO_2 or its compounds (glass). A fluoride mixed with silicates or SiO_2 gives, on heating with strong H_2SO_4, SiF_4, fuming in the air, and giving with water H_4SiO_4, gelatinous.[1] Fluorides not decomposed by H_2SO_4 must be fused with mixed Na_2CO_3 and K_2CO_3. BaF_2 and CaF_2, as precipitated, are gelatinous and transparent, soluble in hot HCl, though with difficulty, soluble in H_4NCl.

Tartrates.—The neutral salts of Grs. I. and III. as well as of Fe_2 and Co readily soluble in water. The acid is very soluble in water, and its presence prevents partially or wholly precipitation with NaOH, H_4NOH, Na_2CO_3, or $(H_4N)_2CO_3$. The acid and its salts char on heating, giving off an odor like burnt sugar. $BaC_4H_4O_6$ insoluble in water, soluble in HCl or H_4NCl. $CaC_4H_4O_6$ insoluble in water, soluble in HCl or $HC_2H_3O_2$, quite soluble in H_4NCl, readily soluble in cold NaOH, reprecipitated gelatinous on boiling; $Ag_2C_4H_4O_6$, white, insoluble in water, soluble in H_4NOH or HNO_3; blackens immediately on boiling from separated Ag. $KHC_4H_4O_6$ is sparingly soluble in cold water, $HC_2H_3O_2$ or $H_2C_4H_4O_6$ readily

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[1] $(3SiF_4+4H_2O+Aq)=H_4SiO_4+(2H_2SiF_6+Aq)$.

soluble in mineral acids or solutions of hydrates of Gr. I.

Carbonates.—The neutral salts are all insoluble in water, except those of Gr. I.; the acid salts are generally soluble, though, if their solutions are boiled, all but those of Gr. I. are decomposed, and neutral salts precipitated. The acid is unknown, since it breaks up upon liberation from its salts into water and CO_2, a gas heavier than air, quite soluble in water. CO_2 gives with CaO_2H_2 $CaCO_3$ white. $BaCO_3$ insoluble in water, soluble in acids. Ag_2CO_3, white, insoluble in water, soluble in H_4NOH or HNO_3.

Silicates.—The silicates of Gr. I. are alone soluble in water; many of the insoluble salts are decomposed by strong acids with the separation of H_4SiO_4. When the acid is liberated from its salts by acids, the greater part generally separates in a gelatinous form, though more or less remains in solution. If such an acid solution is evaporated to dryness, all its Si is left as a hydrate, insoluble in water or acids (except HF). H_4SiO_4 when once formed is insoluble in water or acids (except HF), though soluble in NaOH, and reprecipitated from this solution by H_4NCl. It loses water readily, and on ignition SiO_2 is left insoluble in a bead of microcosmic salt (NaH_4NHPO_4). All silicates are decomposed by fusion with mixed Na_2CO_3, and K_2CO_3. The Ba, Ca, and Ag salts are insoluble, decomposed by HCl.

Sulphates.—The normal salts are all soluble, except $BaSO_4$, $SrSO_4$ and $PbSO_4$, insoluble, and $CaSO_4$ sparingly soluble. The acid has great affinity for water, and dissolves with evolution of heat. When strong it blackens organic water. Sulphates, when heated on charcoal with Na_2CO_3 in the inner blowpipe flame, give Na_2S. $BaSO_4$, white, insoluble in water or acids.

GROUP II. HCl, HBr, HI, HCN, $H_4Fe_2(CN)_6$, $H_6Fe_2(CN)_{12}$, H_2S

Chlorides.—All soluble except AgCl, Hg_2Cl_2 insoluble, and $PbCl_2$ sparingly soluble in water. From its salts H_2SO_4 liberates HCl (with effervescence, if little or no water is present), a gas very soluble in water; H_2SO_4 and MnO_2 evolve Cl_2,[1] a greenish gas, somewhat soluble in water, which bleaches. AgCl insoluble in water, or HNO_3, soluble in H_4NOH.

Bromides.—Salts soluble except AgBr and Hg_2Br_2. From its salts H_2SO_4 liberates HBr, a gas very soluble in water, but mixed with more or less Br_2; H_2SO_4 and MnO_2 liberate Br_2, a red volatile liquid soluble in water, its vapors red. In solutions of the bromides Cl_2 liberates Br_2, which colors the liquid red. The Br_2, thus liberated, can all be collected in a little CS_2, in which it is much more soluble than in water. An excess of Cl_2 bleaches the color.

[1] $2NaCl+3H_2SO_4+MnO_2=$
$2NaHSO_4+MnSO_4+2H_2O_2+Cl_2$.

Iodides.—Soluble except AgI, yellowish white, Hg_2I_2, greenish, HgI_2, red, PbI_2, yellow, and Bi_2I_3, insoluble in water. From its salts H_2SO_4 liberates HI, but it is at once oxidized and I_2 set free. I_2 is almost insoluble in water, readily soluble in CS_2, which it colors violet; soluble, also, in solutions of iodides with a deep brown color. It sublimes with gentle heat, its vapor being violet. Cl_2 liberates I_2 from its salts, an excess of Cl_2 then converts it into colorless ICl_3. I_2 gives with dilute starch paste in a slightly acid solution a deep blue compound of starch and I, bleached by heat or Cl_2. AgI insoluble in water or HNO_3, scarcely soluble in H_4NOH, soluble in solutions of iodides.

Cyanides.—Salts of Grs. I. and II. and $Hg(CN)_2$ soluble, the rest insoluble in water though many are soluble in solutions of cyanides. HCN is a volatile liquid soluble in water. From the soluble salts even dilute acids liberate the acids; strong H_2SO_4 decomposes it, giving CO. The insoluble salts are all decomposed by ignition. Many of the insoluble salts are decomposed by HCl, all by strong H_2SO_4. AgCN, white, insoluble in water or dilute HNO_3, soluble in H_4NOH, or in solutions of cyanides of Grs. I. and II.

Ferrocyanides.—All insoluble in water except the salts of Grs. I. and II. Many of the salts are colored and all the insoluble salts decomposed by NaOH or H_2SO_4. $H_4Fe(CN)_6$ is a white solid readily soluble in water. Cl_2 converts $K_4Fe(CN)_6$ in solution into $K_6Fe_2(CN)_{12}$. $Ag_4Fe(CN)_6$, white, insoluble in water, H_4NOH, or HNO_3. $(Fe_2)_2(Fe(CN)_6)_3$, blue, and $Cu_2Fe(CN)_6$, red brown, insoluble in water, or HCl.

Ferricyanides.—Salts of Grs. I. and II. and Fe_2 soluble in water. Many of the salts are colored, and all insoluble salts decomposed by $NaOH+Aq$ or H_2SO_4. The acid, $H_6Fe_2(CN)_{12}$, is readily soluble in water and converted by reducing agents into $H_4Fe(CN)_6$. $Ag_6Fe_2(CN)_{12}$, orange, insoluble in water, or HNO_3, soluble in H_4NOH. $Fe_3Fe_2(CN)_{12}$ blue, insoluble in water, or HCl. $Fe_2Fe_2(CN)_{12}$ soluble in water, the solution brown.

Sulphides.—The salts of Grs. I. and II. soluble, the rest insoluble in water. The salts of Gr. VI. soluble in NaOH. Most salts attacked by hot HCl, and all by HCl with HNO_3. Solution is effected by HCl with liberation of the acid H_2S, a gas somewhat soluble in water; by HNO_3, or HCl with HNO_3, with separation of S, which by boiling is slowly oxidized to H_2SO_4. Ag_2S, black, insoluble in H_4NOH, soluble in hot HNO_3.

GROUP III. HNO_3, $HClO_3$, $HC_2H_3O_2$

Nitrates.—Normal salts all soluble in water. From its salts H_2SO_4 liberates HNO_3, a fuming liquid, perfectly soluble in water. By the action of HNO_3 upon Cu, NO is formed,[1] a colorless gas, which with the O of the air forms NO_2, orange

[1] $3Cu+(8HNO_3)=$
$$(3Cu(NO_3)_2+4H_2O)+2NO.$$

red. NO is also soluble in a concentrated solution of $FeSO_4$, forming a solution colored black, brown, or reddish, according to its concentration. On heating the solution NO is set free. All the salts deflagrate when heated on charcoal, and all are decomposed by ignition.

Chlorates.—Normal salts all soluble in water. H_2SO_4 added to the chlorates liberates Cl_2O_4, a yellow green gas, smelling like Cl_2 and bleaching, the H_2SO_4 becoming yellow. Heat must be avoided or the decomposition is accompanied by explosion. HCl liberates a gas of similar color and odor, Cl_6O_{13}. $HClO_3$ is liquid, easily decomposed, and readily soluble in water. All the salts deflagrate when heated on charcoal, and are decomposed on ignition into chloride and O_2.

Acetates.—The normal salts are all soluble in water, although many are decomposed by boiling their solutions into insoluble basic salts. The salts are all decomposed by ignition; aceton, C_3H_6O, is almost always one of the products of decomposition, and generally $HC_2H_3O_2$. Salts of Grs. I. and II. give a residue of carbonate, the rest either metal or oxide, generally mixed with C. $Fe_2(C_2H_3O_2)_6$ gives a deep red solution, which on boiling deposits all the Fe_2 as a brown basic salt insoluble in water.

COURSE OF SYSTEMATIC ANALYSIS

Preliminary Examination in the Dry Way

These tests should on no account be slighted. They furnish strong indications and in many cases positive evidence. For suggestions in taking notes see Introduction.

1. *The Physical properties of the substance* are first carefully recorded. Note especially the odor, color, luster, state, crystalline form and structure, and fineness of division.

2. Heat a small quantity of the substance in a *Bulb Tube.*

OBSERVATION	INFERENCE
Water given off	
with fusion	Water of crystallization.
without fusion	Water of constitution.
with decrepitation	Water often mechanically enclosed.
alkaline reaction	NH_4 salts, basic salts, hydrolysis of salts of strong bases.
acid reaction	Volatile acids, acid salts, hydrolysis of salts of weak bases.

Carbonizes or blackens and residue effervesces with acids............Organic matter, such as tartrates (odor like burnt sugar), acetates, etc.

Gas formed (test with glowing splint and moist litmus paper).

Colorless and odorless.	O_2—glowing splint kindles	Chlorates, nitrates, certain dioxides.
	CO_2—renders drop of $Ca(OH)_2$ turbid	Carbonates, certain oxalates and organic compounds.
	CO—burns with blue flame	Oxalates.
With color or odor.	Cl—greenish-yellow	Chlorides, decomposable by heat.
	Br_2—reddish-brown	Bromides.
	I_2—violet	Iodides.
	NO_2—brown	Nitrates or nitrites.

Colorless with odor	H_2S—darkens filter paper moistened with $Pb(C_2H_3O_2)_2$	Sulphides or hyposulphites and sulphites with reducing agents.
	SO_2—clears drop of dilute $KMnO_4$	Sulphites, hyposulphites, and sulphides and S in presence of O_2.
	NH_3—turns red litmus blue	Ammonium compounds, ferro- and ferricyanides, under certain conditions, organic matter containing nitrogen.
	$(CN)_2$—burns with crimson flame	Cyanides.
	Acetone odor	Acetates.

Sublimate formed

yellow, sublimes in red drops on side of tube becoming yellow when cold..........S from certain sulphides and hyposulphites.

yellow when cold, reddish-yellow when hot	As_2S_3.
yellow sublimate, turns yellow when rubbed	HgI_2 (red).
black, vapor violet	Compounds of I_2.
" turns red when rubbed	HgS.
" metallic mirror on cold parts of tube, and garlic-like odor	As.
white, metallic globules	Hg.
" melts before subliming	$HgCl_2$.
" sublimes without melting	HgCl.
white, crystalline	As_2O_3 (glistening), $H_2C_2O_4$ (needles).
" evolves NH_3 with $Ca(OH)_2$	NH_4 compounds.
white, melts and sublimes in needles	Sb_2O_3.

Residue left with change of color

black, characteristic odor and water evolved	Organic matter.
residue effervesces with acids but original substance did not	Acetates, tartrates, or oxalates of Grs. I and II.

black, without characteristic odor	Black oxides from salts of Co, Ni, Mn, and Cu.
black when hot, red when cold.	Salts of Fe.
yellow while hot, white when cold	ZnO.
red-brown while hot, yellow when cold	PbO.
red-brown while hot, pale yellow, when cold	Bi_2O_3.

3. *Heat on Charcoal in inner blow-pipe flame.* This operation is very important and requires practice before best tests can be obtained. For methods of using blow-pipe, see Prescott and Johnson's *Qualitative Chemical Analysis.*

Make a small hopper-shaped depression in a piece of charcoal, and place therein a small quantity of the moistened substance.

OBSERVATION	INFERENCE
Substance gives off garlic-like odor	As.
Substance deflagrates	Nitrates or chlorates.
" decrepitates, due to water held mechanically in crystal	Halogens salts of Gr. I.

Substance melts and runs into charcoal.............Salts of Gr. I. and soluble salts of Gr. II.

Residue white: infusible, but luminous when heated...Gr. II., Zn, Al, or SiO_2.

Residue moistened with a drop of $Co(NO_3)_2$ and heated in outer flame,—
  blue..................Al, silicates, or phosphates.
  blue-green.............Sn.
  green.................Zn.
  pink..................Mg.

Residue, yellow when hot, white when cold...........ZnO.
Residue, yellowish-red when hot, yellow when cold.....PbO.
Residue, reddish-brown when hot, yellow when cold.....................Bi_2O_3.

4. *If residue on charcoal is colored or metallic,* some of the substance should be mixed with Na_2CO_3 and heated in the inner blow-pipe flame on charcoal. The color of the coating around the assay, and the nature of the metallic globule must be noted. If no one large globule can be obtained, the charcoal under the assay must be cut out and

be ground up with water in a mortar. The charcoal can be readily washed away and the metal left, in spangles, if malleable. The presence of As is shown by garlic-like odor. The character of the metallic globules of the reducible metals and the colors of the coating on the charcoal are as follows:

ON CHARCOAL WITH Na_2CO_3

	GLOBULE	COATING	
		Hot	Cold
Bi	Brittle	Dark orange	Lemon yellow
Sb	"	White	White
Ag	Malleable	(Dark red)	
Sn	"	Pale yellow	White
Pb	"	Orange yellow	Yellow
Cu	"		
Zn		Yellow	White
Co		Red brown	Red brown
As			White
Co	Reduced but not fused		
Ni			
Fe			

5. *Examination with Borax.* A small quantity of the substance is melted into a borax bead upon platinum wire. It should first be heated in the outer blow-pipe flame, afterwards in the inner flame, the colors of the bead, both hot and cold, being carefully noted. An excess of substance must be avoided. The colors of the various

beads, both hot and cold, in the inner and outer flames, are as follows:

BORAX BEADS

	OUTER FLAME		INNER FLAME	
	Hot	Cold	Hot	Cold
Cu	Green	Blue	Colorless	Red opaque
Co	Blue	Blue	Blue	Blue
Ni	Violet	Red brown	Gray	Gray
Fe	Red	Yellow	Bottle green	Bottle green
Mn	Violet	Amethyst	Colorless	Colorless
Cr	Green	Green	Green	Green

6. *Flame Colorations.* The coloration given by the substance to the flame of the lamp often gives more or less positive indications. The substance is introduced into the edge of the flame on platinum wire.

Red flames. K, violet; Li, carmine; Sr, crimson; Ca, orange red.

Yellow flames. Na.

Green flames. Cu (most salts), bright green; Ba, yellow green; H_3BO_3, pale green.

Blue flames. $CuCl_2$, bright blue; Pb, As, pale blue.

7. *Warm a small quantity of the substance in a test tube with con.* H_2SO_4. Heat *very* carefully in the beginning; chlorates may be present and explosions occur. Cautiously fan the vapors to the nose. HCN may be evolved from various cyanides.

OBSERVATION	INFERENCE
Volatile acid, fumes in moist air (blow breath across top of test tube), and turns moist blue litmus paper red; sharp odor, colorless	HCl.
Volatile acid, fumes in moist air, violet vapor, odor of H_2S or SO_2, due to the reduction of H_2SO_4 by HI	HI.
Volatile acid, fumes in moist air, sharp odor, and a brown gas visible in the test tube	HBr.
Volatile acid, may fume slightly, if concentrated, brown gas in test tube and suffocating odor	HNO_3 with NO_2
Volatile acid, sulphur odor	SO_2 from sulphur compounds or reducing agents on H_2SO_4.
H_2S odor; darkens filter paper moistened with $Pb(C_2H_3O_2)_2$	Sulphides, or reducing agents on sulphur compounds.
Brisk effervescence, precipitates with drop of $Ca(OH)_2$	CO_2 from carbonates or oxalates.

Yellow gas, explosive, irritating odor	Chlorates.
Gas burns with blue flame	CO from oxalates or cyanides.
HF etches glass, forming a gas, SiF_4, and gives silica bead with drop of water	Fluorides.
Odor of $HC_2H_3O_2$	Acetates.
Substance blackens and may give odor of SO_2 due to reduction of H_2SO_4	Tartrates.

8. Warm a small quantity of the substance in a test tube with *dil.* H_2SO_4.

OBSERVATION	INFERENCE
CO_2 brisk effervescence; renders lime water turbid	Carbonates.
H_2S slight effervescence; observe odor and action on filter paper moistened with $Pb(C_2H_3O_2)_2$	Sulphides.
SO_2 clears drop of $KMnO_4$; observe odor	Sulphites.
SO_2 with separation of free S	Hyposulphites.
HCN, peach-seed odor (caution)	Cyanides.

PREPARATION OF SOLUTION FOR BASIC ANALYSIS

After the preliminaries are completed in the *dry way*, the analysis for the bases in the *wet way* is next in order. The general method of obtaining a solution of a solid substance is as follows:

(1). Reduce the solid to a fine powder and shake thoroughly with about ten times its volume of cold water. If solution is not effected, boil for several minutes. Let settle and either decant off clear liquid or filter as may be necessary. Carefully evaporate one or two drops of the liquid on a watch glass, and observe if any residue is left. If any of the substance has dissolved, set the liquid aside and label (a) *aqueous solution.*

If the substance is entirely soluble in water, dissolve about one gram in 25 c.c. of water and use as stock solution. Test the reaction of this solution with litmus paper. If alkaline, the presence of a base of group I or II is indicated. An acid reaction may be due to free acid, an acid salt, or the hydrolysis of salts of weak bases. Solutions of such substances as $CuSO_4$, $Al_2(SO_4)_3$,$FeCl_3$, or any salt of a strong acid and a weak base forming metal reacts acid.

Wash any residue with small quantities of water. Add the first wash water to the *aqueous solution.*

(2). Boil the insoluble residue with dilute HCl (increase the concentration of acid, if solution is not effected by the use of dilute acid). If a residue is left, filter and wash with a small quantity of dilute HCl and then with water. Evaporate one or two drops of the liquid on a watch glass. If there is a residue, evaporate the entire acid solution nearly to dryness to remove the excess of HCl. Evaporation should be completed on a water bath to avoid the loss of certain volatile substances. See Note 6. Dissolve in water. If a precipitate is formed, add dilute HCl drop by drop until clear. Set aside and label (b) *HCl solution* or *chloride solution I.* If substance is insoluble in water and wholly soluble in HCl, prepare a stock solution.

(3). Repeat process (2) using HNO_3 instead of HCl. Label any solution (c) *HNO_3 solution.* Observe the formation of any brown fumes, indicating that some substance is undergoing oxidation. The HCl solution is in most cases the best. However, it is always advisable to treat a small quantity of the solid with HNO_3. Certain insoluble sulphides, metals, or alloys are not readily attacked by HCl but are easily dissolved or decomposed with HNO_3. Free S separates from sulphides.

(4). Treat any insoluble residue obtained from (1), (2), or (3) with aqua regia. This is best accomplished by adding *con.* HCl, heating and introducing HNO_3 drop by drop. The total quantity of HNO_3 should not exceed one third the volume of HCl. This process should be repeated until no further solution is possible. Evaporate a drop on a water glass. If a residue is found present, filter and save for treatment under (5).

Evaporate solution *almost to dryness* and dissolve in water, adding a few drops of *dil.* HCl if necessary. Set aside and label (d). Since solutions (b) and (d) are chlorides they may be united and labeled (e) *chloride solution II.*

(5). If a residue is found which will not yield to any of the foregoing methods of solution, any of the following substances may be present: S, C, CaF_2, Ag salts of acids of group II, except Ag_2S; sulphates of Ba, Sr,(Ca) and Pb; $PbCl_2$ (soluble in excess of boiling water), fused $PbCrO_4$, ignited or native oxides of Al_2O_3, Fe_2O_3, Cr_2O_3, SnO_2 and SiO_2; all silicates except group I.

NOTES

1. If more than one solution is obtained by the different treatments of water and acids, the substance consists of more than one element or compound and each should be analyzed separately. The basic and acid radicals found in the separate solutions will give in many cases a knowledge of the compounds present in the original substance. However, if two or more compounds are soluble in water, it is difficult to tell by qualitative methods the manner in which the basic

and acid radicals were originally combined. Also, if two or more compounds are soluble in the *acid solution*, it is a difficult task in many cases to report the compounds originally present. Report the separate analyses so far as possible, as water-soluble, acid-soluble, and insoluble.

2. If a substance completely dissolves in HCl and needle-like crystals do not appear on cooling, Ag, Hg(-ous), and large quantities of Pb are absent.

3. Always use the smallest quantity of acids to effect solution. If an excess of an acid is used for any reason, it must be expelled by evaporation, or the subsequent work of analysis will be rendered more difficult, if not impossible.

4. When HCl is used as a solvent, CO_2 (carbonates), SO_2 (sulphites and hyposulphites), H_2S (sulphides) are liberated and should be confirmed by special tests.

5. It sometimes happens that certain mixtures, easily soluble in water and acids separately, are rendered insoluble by treatment of acids alone. Such mixtures as K_2SO_4 and $BaCO_3$; $Pb(NO_3)_2$ and CuS; and $CuSO_4$ and $Sr_3(PO_4)_2$ afford examples. If these mixtures are first carefully treated with water, and the residues dissolved in acids, insoluble substances will less likely be formed.

6. If no residue is left when a few drops of a solution, obtained by any of the above methods, are evaporated to dryness conclusion should not be drawn that no part of the original solution is soluble. Some substances, soluble in water or acids, are volatile and are thus lost on evaporation, especially if the evaporation is conducted rapidly. The most common

substances of this type met with in inorganic analysis are volatile acids, $HgCl_2$, $AsCl_3$, and ammonium salts. If the evaporation be conducted by means of the water bath there is little difficulty in obtaining a solid residue.

7. If a small residue is left when a substance is treated with water, one or two drops of *dil.* HCl usually effect solution.

8. When HCl or HNO_3 are used as solvents special tests must be made for their presence in the original substance.

9. Some substances are insoluble in acids, but freely soluble in water. $Ba(NO_3)_2$ and $Pb(NO_3)_2$ are but slightly soluble in HNO_3 but soluble in water. Also $BaCl_2$ and $PbCl_2$ are insoluble in HCl but soluble in hot water.

If solution is not effected with HCl or HNO_3 and a white insoluble residue is left, it is best to decant the acid solution and test its solubility in water rather than to continue the addition of further quantities of acid. If water does not effect solution, the residue should be saved for the "Treatment of Insoluble Substances."

TREATMENT OF INSOLUBLE SUBSTANCES

S is recognized in the preliminary examination in the dry way by the formation of a yellow sublimate and the odor of SO_2 when heated in a bulb tube.

C is recognized by the black color and its complete combustion when heated in a porcelain crucible. Both *C* and *S* can be removed by strongly heating the substance in a porcelain crucible.

CaF_2, (BaF_2, SrF_2, and MgF_2) when heated with a little SiO_2 and *con.* H_2SO_4 evolves SiF_4, recognized by suspending a drop of water over the mixture in a test tube. An incrustation of silica will cover the surface of the drop. To prove that the base is calcium, heat the mixture strongly in a platinum crucible with *con.* H_2SO_4 until white fumes cease to be evolved. Extract the residue with hot water, filter, render alkaline with NH_4OH, and add $(NH_4)_2C_2O_4$. If Ca is absent the base is probably Ba, Sr, or Mg. Mg may be tested in solution by regular method. Ba and Sr are detected according to methods given for $BaSO_4$ and $SrSO_4$.

AgCl, AgBr, AgI, and AgCN are recognized by any one of the following methods:

(1) Digest for half an hour with Zn and *dil.* H_2SO_4. Reduction to metallic Ag takes place with the formation of the free halogen acids in solution. Remove the Ag after the Zn has entirely dissolved by filtration and dissolve after washing in hot *dil.* HNO_3 and precipitate AgCl with HCl. The filtrate should be neutralized with Na_2CO_3, evaporated to dryness, and tested for the halogens according to special methods given under acids.

(2) Mix with Na_2CO_3 and fuse on charcoal in reducing flame. Ag will be found as a metallic globule and can be confirmed as given under (1).

In the non-metallic residue on the charcoal will be found the sodium salts of the halogens. Remove the residue, treat with water, filter, and evaporate to dryness. Apply the special tests for the halogens.

(3) Ag may be recognized and removed from unknowns, when present, by warming the substance with a solution of KCN. All the silver salts insoluble in acids are dissolved. Filter, if necessary, and test the filtrate with $(NH_4)_2S$. A black precipitate, Ag_2S, soluble in HNO_3 and giving a white precipitate on the addition of HCl, proves the presence of silver.

If silver is found present by either test in (1) or (2), remove with KCN, and thoroughly wash the residue. If silver is absent omit treatment with KCN.

$BaSO_4$, $SrSO_4$, $CaSO_4$, (slightly soluble in water)

and $PbSO_4$ are transformed into their respective carbonates and Na_2SO_4 by prolonged boiling with a concentrated solution of Na_2CO_3. $BaSO_4$ is not completely transformed by one treatment (about 80%. See Finley's *Phase Rule*, pages 337 and 338), but its presence or absence is easily shown. Filter, wash, and dissolve in dilute HNO_3. Test for the metals by the regular methods. The filtrate is acidified with *dil.* HCl and tested for a sulphate with $BaCl_2$.

$PbSO_4$ and $PbCl_2$ may be recognized and separated from an unknown by digesting with a strong solution of $NH_4C_2H_3O_2$. Filter, wash, and divide the filtrate into three parts (a), (b), and (c).

To (a) add $(NH_4)_2S$. A black precipitate, PbS, soluble in hot *dil.* HNO_3 and giving a white precipitate with *dil.* H_2SO_4, which easily settles, shows the presence of Pb.

To (b) add *dil.* HNO_3 and $AgNO_3$. A white precipitate soluble in NH_4OH indicates chlorine.

To (c) add HCl and $BaCl_2$. A white precipitate shows the presence of a sulphate. *If Pb or Ag are present in any form, they must be removed before fusing the substance in a platinum crucible.*

SnO_2, if indicated by blow-pipe on charcoal, should be fused in a porcelain crucible with equal parts of Na_2CO_3 and S until complete solution is effected. Extract the fused mass with hot water and acidify with *dil.* HCl. Yellow SnS_2 is precipitated if Sn is present. Confirm by dissolving in a few c.c. of *con.* HCl and a very small quantity of $KClO_3$. Reduce the $SnCl_4$ with card teeth (Fe) and add $HgCl_2$. A white precipitate, HgCl, often turning gray (free Hg), is obtained.

Chromium compounds can often be detected by fusing on a platinum wire a mixture of the substance and a little $KClO_3$, in a Na_2CO_3 bead. Dissolve the bead in a few drops of water. A yellow solution, which forms a yellow precipitate with $Pb(C_2H_3O_2)_2$ insoluble in acetic acid, proves the presence of chromium.

SiO_2 and complex silicates are recognized by fusing a small quantity of the substance in a microcosmic bead ($NaPO_3$). (See under Silicates.)

Insoluble ferro- and ferricyanides. (See under special tests.) If a substance is difficultly soluble in acids, it is advisable to test a small quantity with hot NaOH. Insoluble ferro- and ferricyanides are decomposed into sodium salts of the acids, and insoluble or soluble hydroxides (of Al, Pb, and Zn). If the entire substance dissolves, it indicates the presence of Al, Pb, or Zn as the base. These must be removed according to methods given under special tests for Insoluble Ferro- and Ferricyanides. The filtrate is acidified and divided into two parts, (a) and (b).

To (a) add $FeSO_4$ (just reduced with Fe and *dil.* H_2SO_4). Result?

To (b) add $FeCl_3$. Result?

If an insoluble residue is left after treatment with NaOH, it may be the insoluble hydroxide of the base originally present with the insoluble ferro- or ferricyanide, together with any substance insoluble in NaOH. This residue should be washed and dissolved in *dil.* HCl and analyzed for bases as usual.

Note.—If an unknown mixture contains several salts, some of which are soluble in acids and others in NaOH, it is generally best to treat with acids first, wash the residue, and complete the solution or decomposition with NaOH. If an insoluble residue is left, set aside for fusion.

However, it may be found best in the course of analysis to treat the substance first with NaOH. If so, wash the residue and dissolve the residue in HCl and analyze as usual.

If an unknown does not yield to any of the foregoing methods of solution the Ag, Pb, S, and C must be removed according to methods already given. The residue is washed, dried, and mixed with about five times its weight of equal parts of Na_2CO_3 and K_2CO_3 with about one gram of KNO_3. The residue is heated to quiet fusion in a platinum crucible, adding more nitrate and carbonate, if found necessary. Cool the crucible and contents, place in a porcelain dish, and almost cover with water. Boil until the contents is dissolved. The acid radicals are found in solution as sodium and potassium salts. Test the solution for sulphates, silicates, chromates, fluorides, and aluminates.

The insoluble residue, consisting of the insoluble carbonates of the bases, is dissolved after washing in *dil.* HCl and tested for bases according to the regular methods.

NOTES

1. Certain substances like alundum do not yield to the above fusion mixture. If such residues are left after ordinary methods of fusion have failed, mix with NaOH and fuse in a nickel crucible. Nickel is not effected by reducing substances, and should always be used when they cannot be removed by other treatments.

Fe_2O_3, Cr_2O_3, and Al_2O_3 can also be reduced to soluble sulphates by fusing in a platinum crucible with $HKSO_4$.

2. If organic matter is found present in the course of analysis, it should be removed before inorganic analysis is undertaken. This may be effected (a) by combustion at red heat. A small quantity of NH_4NO_3 will hasten the operation.

(b) Oxidation with HCl and $KClO_3$ on a water bath. The *dry* residue is dissolved in water and filtered if necessary.

For details and other methods of removal of organic compounds see *Qualitative Chemical Analysis* by Prescott and Johnson.

METALS AND ALLOYS

About one gram or less of the metal or alloy is reduced to shavings, turnings, or clippings in order to facilitate solution or oxidation. Heat with about 10 c.c. of *con.* HNO_3 until brown fumes cease to be evolved, adding more acid from time to time if found necessary.

(a) *If no residue is left* Sb, Sn, and (Au and Pt) are absent. Evaporate to dryness, finishing on a water bath, in order to prevent decomposition of some of the nitrates into oxides or basic salts.

Dissolve the residue in water, adding a few drops of *dil.* HNO_3, if a precipitate appears, which may be due to hydrolysis of certain salts of As, Bi, or Hg. This solution is analyzed for all the bases except Sb and Sn.

If As is known to be absent, the precipitate obtained by adding H_2S does not require digestion with $(NH_4)_2S$, otherwise the analysis is conducted as usual.

(b) *If a white residue is left insoluble in water,* it may be hydrated SnO_2 or Sb_2O_5, or both together with As in the form of tin arsenate. Filter and test the filtrate as in (a). Wash the residue and dissolve in aqua regia. Evaporate on a water bath *nearly* to dryness, dilute with a little water, and analyze for As, Sb, and Sn.

(c) If a metallic residue is left, it should be dissolved in aqua regia, evaporated on a water bath, and tested for Au and Pt. Dissolve in water. To a small portion of the solution add KCl in excess and an equal volume of alcohol. A yellow glistening precipitate, K_2PtCl_6, indicates Pt.

To another portion of the solution add $SnCl_2$. A purple coloration, known as the purple of Cassius, indicates Au.

NOTES

1. If the white residue SnO_2 or Sb_2O_3 does not yield to the treatment with aqua regia, it should be washed, dried, and fused in a porcelain crucible with a mixture consisting of equal parts of Na_2CO_3 and S. Sodium thio-salts are formed. Dissolve the fused mass in water, filter, and slowly add *dil.* HCl to the solution. Sulphides of As, Sb, and Sn are precipitated. Filter and wash thoroughly, first in hot water and lastly in cold water. Treat with cold ammonium carbonate and conduct analysis as usual.

If As is absent dissolve the sulphides of Sb and Sn in a very little *con.* HCl, adding a small quantity of $KClO_3$ if solution is not otherwise effected. Add card teeth and proceed as in (b).

2. Small quantities of C, S, P, and Si are sometimes present in certain alloys of Fe and Steel. Phosphorus and sulphur are oxidized to H_3PO_4 and H_2SO_4 respectively. It is, therefore, advisable to

test small portions of the HNO_3 solution for these acids. Si and C are left as a dark deposit.

3. If a metal or alloy does not readily yield to the HNO_3 treatment, HCl should be added, using dilute at first and increasing the strength as is found necessary. If this treatment fails, add *con.* HCl, heat, and introduce *con.* HNO_3 drop by drop, using in all no more than one third of the total volume of HCl. *In all cases the excess of acid must be removed before beginning the analysis.*

ORDER OF PROCEDURE FOR ANALYSIS OF AN UNKNOWN FOR ACID AND BASIC IONS

1. Tests in the Dry Way.

General appearance.

Heat in bulb tube.

Heat on charcoal with blowpipe in reducing flame.

Mix with Na_2CO_3 and heat on charcoal with blowpipe.

Appearance of borax bead.

Appearance of flame and spectrum tests.

Warm with con. H_2SO_4 in a test tube.

Warm with dil HCl in a test tube.

2. Tests in the Wet Way.

(a) For Bases.

Select a suitable solvent and prepare a stock solution for basic analysis. Test small portions of the stock solution with each of the group reagents, HCl, H_2S, NH_4Cl, and NH_4OH, $(NH_4)_2S$, $(NH_4)_2CO_3$, and HNa_2PO_4. If no precipitate is obtained with any particular group reagent, time is often gained by taking a fresh portion of the stock solution and testing with the next group reagent. If As and Sb are absent, $(NH_4)_2CO_3$ may be used at once on a portion of the solution. If *no precipitate* appears, only Mg or bases of Group I are present. If a precipitate is obtained, HCl should be added and the base "run down."

(b) For Acids.

The tests in the Dry Way usually give strong indications and in some cases positive evidence of the presence or absence of certain acid radicals and metals.

The tests in the Wet Way have determined what bases are present, also the following acid radicals: chromates, arsenites, sulphites, and hyposulphites of Gr. I, sub. 1; CO_2 of Gr. I, sub. 2; and H_2S of Gr. II.

It is advisable at this stage of the analysis to make a study of the solubility of the compounds of the bases found present. (See "Properties of the Bases and their Salts," pages 9–22 and "The Tables of Solubilities," page 189.)

If a substance is soluble in water and no bases except Group I are present, any of the acid radicals may be present, and it is best to look for all.

If a substance is soluble in water, no acid can be present which forms insoluble salts with any of the bases found in solution. For example, if Cu and Ca have been found, no acid radical which forms insoluble compounds with these bases can be present. Look up the solubilities of the salts of these metals and find what acids are necessarily absent. What acids are absent when the substance is soluble in water and the base is Pb? Ba? Ag?

If substances are soluble in acids only, the number of acid radicals forming soluble salts with the bases present is usually small, and it is advisable to look for all.

If substances are insoluble in water and acids, a knowledge of the bases found present will usually render the number of acids to be tested for very small. (See under "Substances Insoluble in Acids.")

PREPARATION OF SOLUTION FOR ANALYSIS OF ACID IONS

If the substance is soluble in water, the bases will not generally interfere with the detection of those acids which can be present, although in testing for $HC_2H_3O_2$ and $H_2C_4H_4O_6$, bases of Grs. III–VI must be removed.

If the substance is soluble in acids alone, the removal of bases of Grs. III–VI always facilitates the detection of the acids, and is often essential.

All the bases are removed except As and Sb by boiling for several minutes with a strong solution of Na_2CO_3, the acids remaining in solution as soluble sodium salts. The solution should be neutralized with dil. HNO_3, boiled to remove CO_2, and concentrated to 15–20 c.c. Filter, if necessary, and label (S) Stock Solution for Acid Analysis.

The Na_2CO_3 residue contains hydroxides, carbonates, and basic carbonates of the metals except As and Sb. It may contain phosphates, fluorides, and silicates, which may not have been rendered soluble by boiling with Na_2CO_3. Save the residue and if these acids are not found by the special tests, divide it into two parts (a) and (b).

To (a) add dil. NHO_3 and evaporate to dryness on a water bath, extract with a little water and dil. HNO_3 and filter. Test residue for silica with microcosmic bead, and the filtrate for a phosphate with $(NH_4)_2MoO_4$.

Test (b) for fluorides.

Note.—If As and Sb are present, remove by passing H_2S into the warm acid solution for twenty minutes (arsenates react very slowly with H_2S, especially when oxidizing substances are present).

Method of Acid Analysis.—The acids are not separated from one another after precipitation with the group reagents, as was done in the analysis of the bases. The group reagent only establishes the presence or absence of certain acids, otherwise special tests for each acid radical must be made independently by taking small portions of the stock solution for each test.

The acids are divided into three groups. *$BaCl_2$ in neutral or alkaline solution precipitates* all the members of Group I, but does not precipitate any of the acids of Groups II and III.

$AgNO_3$ in dil. HNO_3 solution precipitates only the members of Group II, but in neutral solution almost all of the members of Group I.

Group III has no group reagent, since its members are soluble in water.

GROUP I. (1) M_2CrO_4, M_3AsO_3, M_3AsO_4, M_2SO_3, and $M_2S_2O_3$

These acids will have been discovered, if present, by the examination in the *dry way*, or in the course of analysis for the bases.

Chromates in acid solution become green on reduction with H_2S to basic chromium, and can be confirmed by methods of analysis for basic chromium.

Arsenites and arsenates in acid solution give with H_2S a yellow precipitate of As_2S_3 or As_2S_5.

Sulphites and hyposulphites evolve SO_2. The latter with separation of free S, when dil. HCl is added in beginning the analysis of the bases.

To confirm the presence or absence of these acids, the following special tests are made.

SPECIAL TESTS FOR ACID RADICAL OF GROUP I

GROUP I. (1) M_2CrO_4, $M_2Cr_2O_7$, M_3AsO_3, H_3AsO_4, M_2SO_3, and $M_2S_2O_3$

In making tests use a very small amount of the substance.

Chromates.—To 1 c.c. of $K_2Cr_2O_7$ or K_2CrO_4 diluted with water, add a few c.c. of $Pb(C_2H_3O_2)_2$. To 1 c.c. of a strictly neutral soluble chromate add a few drops of $AgNO_3$, a purplish precipitate, $AgCrO_4$, should appear. Test solubility of a small portion of the precipitate in dilute HNO_3. Test solubility of another small portion in NH_4OH. Do not mistake reddish brown $AgCrO_4$ for an arsenate. Chromates as a rule should be removed in testing for certain acids, especially those in which the color of the precipitate is the determining factor.

To 5 c.c. of $K_2Cr_2O_7$ add a few c.c. of dilute HCl, heat and pass H_2S into the solution for several minutes (10 minutes will do no harm). The solution becomes green due to the reduction of the acid to basic chromium. Boil off the H_2S

and add NH_4OH which precipitates $Cr(OH)_3$. Confirm according to the direction given under basic chromium. Chromium will always be found by this treatment in the basic analysis. Chromates may be readily reduced by adding a small amount of Na_2SO_3, and dilute HCl. When the reduction is complete boil off the excess of SO_2 and proceed as under basic chromium. By this method NaCl is introduced into the solution, the presence or absence of Na and Cl, therefore, should be determined in the original substance.

Arsenites.—Arsenites will be found in the analysis for bases. Warm a few c.c. of Na_3AsO_3 solution acidified with dilute HCl and pass H_2S into the solution. An immediate bright yellow precipitate, As_2S_3, is obtained. Wash this precipitate into the tip of the filter paper, dry, and burn with a very little of the filter paper. The carbon of the filter paper reduces the compound to metallic arsenic, which sublimes, giving the characteristic garlic odor. To a few c.c. of a strictly neutral solution of Na_3AsO_3 add $AgNO_3$. Result? Do not mistake this yellow precipitate for a phosphate.

Make a little hopper-shaped cavity in a piece of charcoal, place a small quantity Na_3AsO_3 therein and heat in the inner blowpipe flame. Note odor.

Arsenates.—(a) Pass H_2S into a warm solution of Na_2AsO_4 acidified with dil. HCl until a light yellow precipitate is obtained. Observe that the

precipitate appears only after some time. Arsenates should not be considered absent until H_2S has been passed into the solution for at least fifteen minutes. The H_2S first reduces the arsenate to arsenite then precipitates the As_2S_3 with free S. An arsenate may be quickly removed from a solution by adding a small quantity of solid Na_2SO_3 and dilute HCl solution. SO_2 is generated, which reduces the arsenate to the arsenite from which H_2S precipitates As_2S_3 immediately. Since we have introduced NaCl into the solution by this treatment, the presence or absence of these must be determined in the original substance. Arsenates are easily mistaken for phosphates, especially the precipitate $MgNH_4AsO_4$, obtained by adding NH_4Cl, NH_4OH, and $MgSO_4$ to a solution of Na_3AsO_4. This precipitate, like $MgNH_4PO_4$, is crystalline in appearance.

(b) An HNO_3 solution of an arsenate gives with $(NH_4)_2MoO_4$ a finely divided yellow precipitate only on heating strongly or boiling. Phosphates give the same appearance on gently warming (not above 40°). Arsenites are not precipitated by either the magnesium mixture of the ammonium molybdate. With solutions of Na_2HPO_4 and Na_3AsO_4 in separate test tubes apply test in (b).

Sulphites and Hyposulphites.—Sulphides if present should be removed by adding $ZnSO_4$ solution and filtering off the ZnS before applying the tests for sulphites.

To a small quantity of Na_2SO_3 in a test tube add dilute HCl and warm gently. Observe effervescence and odor of SO_2. Repeat the test, using dilute H_2SO_4 instead of the HCl. If no reducing agent is present the sulphuric acid is the best since it is non-volatile. Arrange a short generating tube so as to pass a small quantity of the SO_2 into a very dilute solution of $KMnO_4$ acidified with dilute H_2SO_4. The solution becomes clear. Since SO_2 is a rather heavy gas, it can with care often be decanted directly from a test tube into the dilute solution of $KMnO_4$. Prepare the solution of $KMnO_4$ so that the red color is just visible. When H_2S is passed into a solution of a sulphite or hyposulphite acidified with dil. HCl, sulphur is precipitated and must not be mistaken for sulphides of Gr. VI (As and Sb). To a solution of Na_2SO_3 in a test tube add a few pieces of Zn and dil. HCl, hold a filter paper moistened with $Pb(C_2H_3O_2)_2$ in the escaping gas. Observe any blackening caused by reduction of SO_2 to H_2S.

Heat a small quantity of $Na_2S_2O_35H_2O$ in a bulb tube. Notice if sulphur distills on the side of the tube. Dissolve a crystal about the size of a small pea in about five c.c. of water and add a few c.c. of dil. HCl. Warm and carefully observe result, especially the odor of the SO_2. What separates? How does a hyposulphite differ from a sulphite?

Hyposulphites heated in a bulb with organic matter (tartrates and acetates) often liberate

Notes

H_2S. To a hyposulphite solution add a few c.c. of $Pb(C_2H_3O_2)$. Result? Boil. Result? Repeat using $AgNO_3$ instead of $Pb(C_2H_3O_2)_2$ and record result. If sulphides are present they must be removed as stated under sulphites.

GROUP I. (2). H_3PO_4, H_3BO_3, $H_2C_2O_4$, HF, M_2CO_3, H_2SiO_3, $H_2C_4H_4O_6$, and H_2SO_4

If carbonates or silicates are present, they have already been found in the tests made in the *dry way*, or in the course of analysis for the bases. If present, they must be removed by dil. HCl or HNO_3, the solution concentrated and filtered before applying the group test.

To a solution free from acids of Gr. I (1), and H_2CO_3 and H_2SiO_3, add NH_4OH until slightly alkaline, then $BaCl_2$. The precipitate may contain the Ba salts of H_3PO_4, H_3BO_3 (if solution is sufficiently concentrated), $H_2C_2O_4$, HF, $H_2C_4H_4O_6$, and H_2SO_4. Add dil. HCl in excess. All the Ba salts dissolve except $BaSO_4$. A slight turbidity indicates only traces of sulphate, often found in the reagents. Filter, if a sulphate is present, and add NH_4OH in excess to the filtrate. $Ba_3(PO_4)_2$ and BaC_2O_4 are precipitated, if present; the other Ba salts, more or less soluble in NH_4Cl, will probably not be precipitated, if present. If therefore NH_4OH causes a precipitate in the HCl solution, special tests must be made for all the acids except H_2SO_4, whose presence or absence is already estab-

lished; if NH_4OH gives no precipitate, H_3PO_4 and $H_2C_2O_4$ are absent, and for the rest special tests must be made.

It is advisable to add $CaCl_2$ to a fresh portion of the solution made slightly alkaline with NH_4OH. The Ca salts of H_3PO_4, H_3BO_3, $H_2C_2O_4$, HF, and $H_2C_4H_4O_6$ are thus precipitated; $CaSO_4$ is not thrown down, if the solution is moderately dilute. Of these Ca salts CaC_2O_4 and CaF_2 alone are insoluble in $HC_2H_3O_2$; if the precipitate is soluble in acetic acid, $H_2C_2O_4$ and HF are absent; if insoluble, all may be present.

GROUP I. (2). H_3PO_4, H_3BO_3, $H_2C_2O_4$, HF, M_2CO_3, H_4SiO_4, $H_2C_4H_4O_6$, H_2SO_4

Phosphates. — (a) To a dilute solution of HNa_2PO_4 add a few c.c. of NH_4Cl, NH_4OH until odor is pronounced, then $MgSO_4$ solution. Warm, agitate, and scratch the side of the test tube with stirring rod, if precipitate does not appear after standing a few minutes. A white crystalline precipitate $MgNH_4PO_4$ should appear. If the precipitate is too abundant to observe well, pour off a part and add water until it can be viewed by means of transmitted light. Notice the little particles of the precipitate tending to climb up the sides of the test tube. Test solubility of the precipitate in acetic acid. Result? Do not mistake arsenates for phosphates. They give a similar precipitate with above reagents and therefore must be removed before testing for a phosphate.

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(b) Phosphates insoluble in water should be dissolved in HNO_3 (or HCl if arsenates are present). $(NH_4)_2MoO_4$ is added a little at a time with gentle warming (not above 40°) until about ten c.c. are added, if results are not obtained with a smaller quantity. Let stand and observe the formation of a canary-yellow precipitate usually finely divided and tending to creep up the sides of the test tube. If arsenates are present, remove by passing H_2S into the hot acid solution for fifteen minutes. Boil to remove the H_2S, add a few drops of con. HNO_3 and boil again in order to oxidize any substance reduced by the H_2S which might interfere with the $(NH_4)_2$ MoO_4 test. (See **Arsenates.**) If phosphates are found present in substances soluble in acid only, see special method necessary for detection of bases of Groups IV, III, and II.

With a small quantity of $Ca_3(PO_4)_2$ in a test tube apply method (b).

Oxalates.—These should be found in making tests in the dry way with bulb tube and with con. H_2SO_4.

(a) To 2 c.c. of $(NH_4)_2C_2O_4$ diluted with an equal volume of water, add a few c.c. of $CaSO_4$ solution, warm and observe the formation of a white precipitate, CaC_2O_4. (If this precipitate is not crystalline but gelatinous, a fluoride may be present.) Divide into two parts (1) and (2). To (1) add dil. HCl. Result? To (2) add $HC_2H_3O_2$. Result?

(b) Mix a small quantity of a solid oxalate with about one half gram of MnO_2 in a test tube. Add dil. H_2SO_4, heat and pass the gas (CO_2) into another test tube containing a few c.c. of lime water. Result? Carbonates must be removed before applying the above test as follows: (1) Add acetic acid to the solution in a test tube and boil off all of the CO_2. How told? Filter if necessary and add $CaSO_4$. Result? Or (2) add dilute HCl and evaporate almost to dryness in a water bath and test with MnO_2 and dilute H_2SO_4 as above.

Oxalates may be further distinguished from phosphates by giving no precipitate with $MgSO_4$ in presence of NH_4OH, NH_4Cl.

Oxalates of the bases in IV, III, II insoluble in water give, when boiled with concentrated solution of Na_2CO_3, carbonates of Grs. II and IV, with hydroxides of Gr. III (Fe, Al, Cr) insoluble in water. The oxalate is found in solution as $Na_2Cr_2O_4$ and may be tested for as in (a).

If oxalates are found present in a substance, soluble only in acids, like phosphates, special methods must be used for detection of metals of Grs. IV, III, II.

Borates.—(a) *Turmeric paper test.* Acidify a borate solution ($Na_2B_4O_7$) with dil. HCl. Moisten a strip of turmeric paper with this solution and wrap around the top of a clean test tube containing a few c.c. of water. Boil the water (100°) in the test tube and observe the color of the turmeric

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paper as the drying proceeds. The color is a claret red and changes to a greenish black when moistened with a drop of Na_2CO_3.

The turmeric test is not reliable in the presence of certain oxidizing substances such as iodides, chlorates, chromates, also ferro- and ferricyanides, because they react with the coloring matter in the paper. As a rule it is best to remove the bases of Grs. VI–II and the above oxidizing agents by appropriate methods. Ask instructor. After removing the bases and the above oxidizing agents, if present, neutralize the solution with Na_2CO_3 and concentrate the solution and apply test (a).

(b) *The flame test* in absence of barium and copper. The Cu and Ba may be removed, however, by H_2S and dilute H_2SO_4. Place a small quantity of a borate in an evaporating dish, acidify with a few c.c. of dil. HCl. Add a little alcohol. Stir and ignite the mixture. Observe that the borders of the flame are green, due to the ignition of the volatile compound $(C_2H_5)_3BO_3$—best observed by darkening the room. (c) For *spectrum test,* see Stieglitz's *Qualitative Analysis* part II, p. 79.

Fluorides.—In the *dry tests* with con. H_2SO_4HF, a gas is liberated from most fluorides and if present in sufficient amount, will etch the sides of the test tube.

(a) Mix a small quantity of some fluoride with a little dry sand. Place mixture in a dry test tube and carefully add a few drops of con. H_2SO_4.

Warm gently and suspend directly over the mixture a small drop of water on a stirring rod or in the loop of a platinum wire. Observe that the water bead is coated with gelatinous silicic acid. Do not mistake fluorides for oxalates. $CaCl_2$ precipitates fluorides and oxalates, the former gelatinous and the latter crystalline, both soluble in dil. HCl. On addition of NH_4OH the oxalate alone is reprecipitated.

(b) Fluorides not decomposed with H_2SO_4 must be fused with an equal mixture of Na_2CO_3 and K_2CO_3. A very little sand will assist in rendering the reaction more complete. Extract with water and filter. The filtrate is a solution of NaF and Na_2SiO_3. Evaporate to dryness on water bath, add a little more sand and con. H_2SO_4 and test as in (a).

Tartrates.—(a) Heat a small quantity of any tartrate in a bulb tube, observe the charring and changes in color due to the different degrees of carbonization. Also note odor resembling burnt sugar. Add a few drops of HCl to the residue and note result. The residue of a tartrate of the alkali metals will effervesce with dil. HCl and evolve CO_2. The residues of the heavy metals give the oxide of the metal itself.

(b) Heat a small quantity of some tartrate with a few drops of con. H_2SO_4 and note color and odor of SO_2. Observe carefully, the SO_2 may be scant if small amount of the tartrate is present.

(c) To distinguish a tartrate from other organic compounds apply the following test. If heavy metals are present, remove by dissolving in water and a very small quantity of dil. HCl. Treat successively with H_2S and Na_2CO_3 and filter after each reagent is added. Neutralize the sodium carbonate with dil. HCl and concentrate to about ten c.c. Make sure that the solution is not acid; filter, if necessary. Add an excess of $CaCl_2$. Shake vigorously, and scratch sides of test tube with stirring rod to start crystallization. Let stand for some time. Crystalline $CaC_4H_4O_6$ (together with CaC_2O_4 and $Ca_3(PO_4)_2$ if present) are precipitated. Filter and wash out adhering $CaCl_2$. Puncture bottom of filter paper and add cold, moderately strong NaOH, allowing the precipitate to be washed into a test tube. Shake thoroughly and filter out dissolved $CaC_4H_4O_6$ (oxalates and phosphates are insoluble in NaOH). Heat and observe the formation of a gelatinous precipitate which redissolves on cooling—(distinction from citrates)—and soluble in acetic acid.

(d) Tartrates act as a reducing agent in presence of certain substances such as chromates (turning green) and permanganates (becoming brown).

With a small quantity of $PbC_4H_4O_6$ carry out test (c).

With a small quantity of $NaKC_4H_4O_6$ carry out test (d).

Carbonates.—(a) To a small quantity of some carbonate in a test tube add a small quantity of dil. H_2SO_4 or HCl. Warm gently and watch for effervescence. Carefully decant gas into another test tube containing a few c.c. of lime water. Gently rock test tube and then shake. Result? If only a small amount of carbonate is present as indicated by slight effervescence, it is well to suspend a small drop of lime water on a stirring rod directly over the substance in the test tube and observe the formation of any precipitate as a film on the surface of the water. If too much heat is applied, HCl, if used, may be volatilized with the CO_2 and thus dissolve any $CaCO_3$ that might be formed. This can be obviated however by adding one or two drops of a NaOH solution to the $Ca(OH)_2$ solution.

Sulphites, hyposulphites, and fluorides, if present, are often mistaken for carbonates, not only because they effervesce with acids, but by rendering $Ca(OH)_2$ turbid. If they are found present it is best to treat the substance with a strong solution of $K_2Cr_2O_7$ containing a very little dil. H_2SO_4. The CO_2 will be liberated but the SO_2 and H_2S are oxidized to H_2SO_4. With a small quantity of Na_2SO_3 in a test tube apply the carbonate test in (a). Does the lime water become turbid? Repeat using test under (b). Result? Now dissolve a mixture of Na_2SO_3 and Na_2CO_3 in a little water and again repeat test (b). Do you get the carbonate test?

Silicates.—*Alkaline silicates soluble in water.* (a) To a solution of Na_2SiO_3 (water glass) add dil. HCl. A gelatinous white precipitate of H_2SiO_3 may appear if the solution is not too dilute, in which case silicic acid remains in solution in the form of a hydrosol. If a precipitate appears, test the solubility of a small portion in a few drops of con. HCl; another portion in NaOH. Evaporate the remaining solution, together with any precipitated H_2SiO_3 present, to dryness on a water bath. The H_2SiO_3 is dehydrated and is thus rendered insoluble in HCl. The more complete the dehydration the more insoluble the residue becomes. Note the grit by feeling the residue. Place a small portion between the teeth and note the grit. On a platinum wire make a bead of microcosmic salt, $NaNH_4HPO_4$, thus forming $NaPO_3$. Place a small quantity of the powder on the bead and heat. Observe the whirling motion of the insoluble silica skeleton, while the fusion is taking place. This is sometimes used to distinguish SiO_2 from Al_2O_3 which dissolves. The microcosmic bead test may be applied to the original substance with success.

Insoluble Silicates. (b) In a lead dish mix a little sand (SiO_2), pure CaF_2 and con. H_2SO_4. Suspend a drop of water from a stirring rod or in the loop of a platinum wire above the mixture and observe the coating of silica. This test may be applied to the residue of the original substances for silicates which do not yield further to other solvents.

(c) Mix insoluble silicates of insoluble residues from original substances free from S, C, P, Ag, and Pb (see section on treatment of substances insoluble in water or acids) with equal parts of K_2CO_3 and Na_2CO_3 and KNO_3 and heat to a quiet fusion in a platinum crucible. If the substance is in a very finely divided form it should require about a half an hour. Place the crucible and contents in a beaker and cover with water. Boil until contents are removed, and filter. The bases are left as insoluble carbonates (except Al found in solution as sodium or potassium aluminate and Cr as chromate) and, after thorough washing, are dissolved in dil. HCl and analyzed as usual. Add dil. HCl to the filtrate and treat as in case of soluble silicates.

If members of Gr. I are to be looked for in natural silicates, fuse for half an hour either with four parts of $Ba(OH)_2$ or six parts of $CaCO_3$, and one part of NH_4Cl to one of the substance. On extracting with water the alkali metals are found in solution and may be tested for as usual.

Sulphates.—Sulphates soluble in water. (a) To 2 or 3 c.c. of a very dilute solution of any soluble sulphate add a few c.c. of $BaCl_2$, and dil. HCl in excess. Result? This is a sufficient test for a sulphate, because all other barium salts of this group of acids are soluble in dil. HCl.

(b) Sulphates insoluble in water ($BaSO_4$, $SrSO_4$, $PbSO_4$, and $CaSO_4$, sparingly soluble), ignited on charcoal with Na_2CO_3 in a reducing flame, form

Na_2S, which when moistened with water stains a silver coin black. With a small quantity of $BaSO_4$ apply test (b).

GROUP II. HCl, HBr, HI, HCN, H_2S, $H_4Fe(CN)_6$, $H_6Fe_2(CN)_{12}$

The presence of H_2S will have been already established, and probably that of HCl, HBr, HI, and HCN. H_2S, if present, must be expelled. As the Ag salts of all the acids of Gr. I except AgF are insoluble in water and soluble in HNO_3, *acidify the solution with* HNO_3 *and add* $AgNO_3$. The precipitate may contain Ag salts of all the members of the group. They are soluble in H_4NOH, except AgI and $Ag_4Fe(CN)_6$. Further than this special tests must be made.

Iodides.—(a) Fuse in a test tube a small crystal of KI with a small amount of solid $K_2Cr_2O_7$. Result? (b) To a dilute solution of KI add a few drops of a freshly made starch solution and a few c.c. of chlorine water. Result?

Bromides.—Repeat (a) under iodides, using a small crystal of KBr instead of KI. How do bromides differ from iodides in this treatment? Add to the fused mass dil. H_2SO_4 and heat. Carefully note odor and color. Decant the bromine fumes into a test tube containing a few c.c. of NH_4OH. Observe that the NH_4OH remains colorless.

Chlorides.—Repeat (a) under iodide, using a

pinch of NaCl instead of KI. How do chlorides differ from iodides? Compare with bromides by this treatment. Divide the fused mass into two parts (a) and (b). To (a) add dil. H_2SO_4 and carefully heat. Observe that no colored fumes are given off. To (b) add con. H_2SO_4, heat and pass deep red fumes (CrO_2Cl_2) into a solution of NH_4OH. Note yellow color. In applying these tests use an excess of $K_2Cr_2O_7$, especially if bases forming insoluble chromates are present. Make sure that the NH_4OH is not colored accidentally by the potassium dichromate on the fingers or on the test tube.

Test for Chlorine, Bromine, and Iodine when all are Present

Test for the presence of iodine with starch and chlorine water, if present mix substance in a small porcelain crucible with dry $K_2Cr_2O_7$ and fuse until iodine is expelled. If iodine is absent, fusion is unnecessary; simple mixing is sufficient. Divide the mass into two parts (a) and (b). To (a) add *dilute* H_2SO_4, heat and look for bromine, recognized by reddish-brown color and odor. To (b) add *con.* H_2SO_4, heat and pass fumes into a solution of NH_4OH. The solution becomes yellow, due to the formation of $(NH_4)_2CrO_4$ if Cl is present. Mix one small crystal each of KI and KBr with a pinch of NaCl and apply the above test.

Notes

The insoluble halogen salts of silver should be treated with Zn and dil. H_2SO_4. The salts are reduced by the nascent hydrogen to metallic Ag, and HCl and HBr and HI are found in the solution. The Ag is filtered off, the solution is neutralized with sodium carbonate and evaporated to dryness on the water bath. The resulting solid, which may consist of NaCl, NaBr, and NaI, is tested as before. HgCl may be recognized by blackening with NH_4OH.

To solutions of NaCl, KBr, and KI in separate test tubes add a few c.c. of $AgNO_3$. Record colors. Test the solubility of a few c.c. of each in NH_4OH.

Cyanides.—Because of the dangerous effects of cyanides, none will be given to a student without due warning.

(a) To a solution of a cyanide add some $FeSO_4$, $FeCl_3$, and NaOH, all of which are in solution. This should give a greenish precipitate, being a mixture of ferrous-ferric hydroxide and Prussian blue, $Fe_4[Fe(CN)_6]_3$. Warm and add dil. HCl which dissolves the mixed hydroxides, leaving the Prussian blue.

(b) To a drop of a soluble cyanide add a little $(NH_4)_2S$ and evaporate to dryness on a water bath, acidify with dil. HCl and add $FeCl_3$ when blood-red $Fe(SCN)_3$ is formed.

(c) To detect HCN in insoluble cyanides, place a drop of $(NH_4)_2S_x$ on the top of the lid of a platinum crucible and carefully invert over top of test

tube containing the cyanide just treated with hot dil. H_2SO_4. After a few minutes carefully remove the lid and evaporate to dryness on water bath and proceed as in (b).

Ferrocyanides.—(a) To five c.c. of water containing a few drops of some soluble ferrocyanide add $FeCl_3$. Observe the deep blue precipitate of ferric-ferrocyanide or Prussian blue.

(b) Insoluble cyanides must be boiled with NaOH and filtered. The solution containing the soluble sodium salt is acidified and treated as in (a). The residue on the filter paper is the hydroxide of the bases, unless the hydroxide is soluble in an excess of NaOH as Zn, Pb, and Al. Zn and Al are precipitated from the ferrocyanide by passing a stream of CO_2 into the solution—Zn as basic carbonate and Al as the hydroxide. They may be separated and tested according to methods given under the bases. Pb may be separated by means of H_2S. Test a small quantity of $Pb_4[Fe(CN)_6]_3$ according to method (b). Test a small quantity of $Fe_4[Fe(CN)_6]_3$ according to method (b).

Ferricyanides.—(a) Repeat as in (a) under ferrocyanides, adding a freshly reduced $FeSO_4$ solution instead of $FeCl_3$. Observe the deep blue ferro-ferricyanide or Turnbull's blue.

Note.—The $FeSO_4$ is best made by dissolving a few crystals of $FeSO_4$ in half a test tube of water and adding dil. H_2SO_4 and card teeth. Let stand for

some time before using. This method of preparation prevents the formation of any ferric salts. It is also used in testing for nitrates.

(b) Insoluble salts are tested as in (b) under ferrocyanides and the solution tested with $FeSO_4$.

Note.—Ferrocyanides and ferricyanides are completely decomposed by hot con. H_2SO_4, forming the sulphates of the metals and evolving CO. If the acid is dilute, HCN is liberated. Care must be exercised in the preliminary testing of the unknowns. The odor should always be observed very cautiously.

In the presence of reducing agents such as H_2S ferricyanides are reduced to ferrocyanides.

Sulphides.—(a) Cover a small piece of FeS in a test tube with water. Add con. HCl, and hold at the mouth of the test tube a filter paper moistened with $Pb(C_2H_3O_2)_2$. Observe the color. If only a small amount of the sulphide is present, watch for any effervescence on addition of HCl. Gentle heat drives the H_2S out of the test tube on the moistened filter paper.

(b) Some sulphides like PbS, CuS, HgS, As_2S_3, Sb_2S_3, CoS, and NiS, scarcely attacked by dil. HCl or dil. HNO_3, should be treated with some oxidizing agent or solvent such as con. HNO_3, aqua regia, or con. HCl and $KClO_3$. Sulphur is liberated, often spongy, and floats on the top of the solution. This should be collected, dried, and burned to SO_2 and odor noted. The solution will

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contain a sulphate or free H_2SO_4 which can be looked for as usual.

(c) Sulphides behaving like those under (b) may be successfully treated with Zn and dil. HCl thus liberating H_2S.

(d) Heat a small amount of CuS in the angle of a bent tube open at both ends. Observe the odor of SO_2. This method is often used in testing minerals for sulphides. Place a small amount of CuS in separate test tubes and apply tests (b), (c), (d).

GROUP III. HNO_3, $HClO_3$, and $HC_2H_3O_2$

All normal salts of this group are soluble in water and therefore have no group reagent. Separate tests must be made to determine their presence or absence. Certain basic nitrates and acetates are insoluble in water, but their presence should be indicated in the examination in the *dry way*.

Nitrates.—(a) Nitrates are easily detected in the dry tests: (1) By heating in a bulb tube, or (2) with the blowpipe on charcoal and (3), heating with H_2SO_4 in a test tube. Make tests with a small quantity of nitrate in (1), (2), and (3), and record results. Are your results in accord with what should have happened? See under course of examination in *dry way*.

(b) To a very small amount of some nitrate add a piece of copper and a little con. H_2SO_4.

Heat and carefully observe the color of the gas bubbles. Place the test tube on a piece of white paper and view it from above, thus giving a greater depth to view the intensity of the color.

(c) To about 2 c.c. of a very dilute solution of a nitrate add twice the volume of a strong solution of $FeSO_4$ and carefully add an equal volume of con. H_2SO_4, allowing it to run down the side of the test tube so as not to mix with the solution. Gently rock the test tube and note the reddish-brown ring forming at the zone of contact. The intensity and color of the ring will largely depend upon the amount of nitrate present. If a large amount of nitrate is present the ring will be dark. HNO_3 is first formed then reduced by the $FeSO_4$ to NO, which combines with the excess of $FeSO_4$, forming the reddish-brown ring.

Note.—Tartrates, bromides, iodides, chlorates, chromates, ferrocyanides, and ferricyanides interfere with test (c) and should be removed before applying the test.

Chlorates.—Carefully heat a very little $KClO_3$ with a few drops of con. H_2SO_4 in a test tube. ClO_2, a greenish yellow gas, is liberated and violently explodes on slight heat. Because of some danger attending this test, it is best (in making a preliminary test with con. H_2SO_4) to heat the acid in a test tube and introduce a very small amount of the substance. If a chlorate does not appear

to be present, add a little more of the substance and apply heat very gradually, always keeping the mouth of the test tube pointing in a safe direction. Chlorates are powerful oxidizing agents and in the presence of reducing agents are changed to chlorides.

Acetates.—(a) Heat a small amount of $NaC_2H_3O_2$ in a bulb tube. Does it char? Note odor of acetone. After cooling add a few drops of dil. HCl. Is there any evidence of effervescence? If so, test gas with lime water. (b) Heat a small amount of $NaC_2H_3O_2$ with con. H_2SO_4. Observe odor. (c) To a dilute solution of an acetate add a few c.c. of $FeCl_3$ and note red color of $Fe(C_2H_3O_2)_3$. Compare color of the solution obtained with that of the reagent. Boil. Result? Bases from Grs. VI to II should be removed in testing for acetates in unknowns and the solutions made strictly neutral. Why? Rely more on the red coloration than upon the subsequent precipitation on boiling. Tartrates are often mistaken for acetates. Ferricyanides and ferrocyanides, iodides, bromides, chromates, sulphites and hyposulphites interfere with this test. Ferrocyanides and ferricyanides may be removed with $CuSO_4$; I, Br, and chromates are treated with $AgNO_3$ and filtered. The Cu and Ag should be removed with Na_2CO_3 and the filtrate concentrated, neutralized, and tested as before. (d) Add a few c.c. of an acetate to a cooled mixture composed of equal volumes (about 3 c.c.) of

alcohol and con. H_2SO_4. Note the ethereal or fruity odor.

Note.—Pour the H_2SO_4 into the alcohol drop by drop and cool with tap water after each addition. When this method is used in testing for acetates in the original substance, it is best to compare the unknown with the odor of ethyl acetate as produced by taking a known acetate. One inexperienced often confuses the odor of the acetic acid and alcohol with that of ethyl acetate.

Note.—Removal, of tartrates, bromides, iodides, chlorates, chromates ferro- and ferri-cyanides before testing for nitrates.

Tartrates, bromides, and iodides are partially oxidized by con. H_2SO_4 with the liberation of C, Br, and I, which color the solution and thus interfere with the test. These acid radicals should be removed with Ag_2SO_4 (free from nitrates) or $Pb(C_2H_3O_2)_2$. The Pb or Ag is removed from the filtrate with H_2S. Filter, boil, and proceed with test.

Chlorates give ClO_2 (greenish-yellow) with con. H_2SO_4 and mask the nitrate test. Chromates are reduced by $FeSO_4$ and give green $Cr_2(SO_4)_3$ which renders the "nitrate ring" difficult to detect.

Chlorates and chromates are removed by boiling the solution with Na_2SO_3 and dil. H_2SO_4. The chlorate is reduced to chloride, which will do no harm; and the chromate to basic chromium, which can be removed by adding an excess of Na_2CO_3 to the hot solution. Filter and acidify with dil. H_2SO_4 and proceed as before.

Ferro- and ferri-cyanide give blue precipitates with $FeSO_4$ and therefore must be removed by adding $CuSO_4$, which forms insoluble salts with these acid radicals. The Cu should be removed with H_2S and the solution boiled and tested as before. Ferro- and ferri-cyanides may also be removed by means of Ag_2SO_4, or $Pb(C_2H_3O_2)_2$. The metals are removed with H_2S, the solution boiled, and tested for a nitrate.

ANALYSIS OF METALS OF GROUPS II, III, AND IV IN PRESENCE OF ORGANIC MATTER, OXALATES, AND PHOSPHATES

Oxalates and phosphates of Grs. IV, III, and II of the bases are soluble in HCl or HNO_3, but are reprecipitated when NH_4OH is added in the separation of the metals in Gr. III. For example, the phosphates and oxalates of Fe, Al, Cr, Co, Ni, Mn, Zn, Ba, Sr, Ca, and Mg are all soluble in HCl, but when NH_4Cl and NH_4OH are added to precipitate Fe, Al, and Cr as hydroxides, the phosphates and oxalates are also precipitated. The presence of phosphates and oxalates do not interfere with tests in Grs. V and IV, since the solution is acid. Therefore, it is necessary to test for oxalates and phosphates before beginning the analysis of Grs. III and IV. Boil the filtrate from Grs. V and VI until the H_2S is expelled.

Oxalate Test.—Boil about 2 c.c. of the H_2S filtrate with an excess of a strong solution of Na_2CO_3 for about one minute. Filter, acidify with $HC_2H_3O_2$, and boil to expel CO_2. Add a few c.c. of $CaSO_4$, warm, a white precipitate, CaC_2O_4 indicates the presence of an oxalate. Explain the reaction.

Notes

Oxalates and organic matter should be removed by evaporating the filtrate from Grs. V and VI to dryness and gently igniting with solid NH_4NO_3 and a few drops of con. HNO_3. Dissolve the residue in dil. HCl and proceed with analysis according to the regular method.

Phosphate Test.—Boil 2 c.c. of the H_2S filtrate with 1 c.c. of con. HNO_3 almost to dryness, dilute with a little water and add 5 c.c. of $(NH_4)_2MoO_4$. A yellow precipitate $(NH_4)_3PO_4 \cdot 12MoO_3$ indicates a phosphate.

If a phosphate is present, boil remainder of the H_2S filtrate (or HNO_3 or HCl solution not containing Grs. V and VI) with a few c.c. of Br_2 water, if Fe was found in the original solution. To the solution add 2 c.c. NH_4Cl, and NH_4OH until precipitation is complete. Fe, Al, and Cr are precipitated as hydroxides, if present, together with the phosphates. Filter and label filtrate (A). This may contain Co, Ni, Mn, Zn, Ba, Sr, Ca, or Mg, except such as were precipitated entirely or in part as phosphates with Fe, Cr, and Al. Analyze the filtrate (A) according to the regular method. Dissolve precipitate (Fe, Al, and Cr and phosphates) in a small quantity of dil. HCl. Nearly neutralize with Na_2CO_3. If a precipitate appears, add a drop of dil. HCl and add 3 or 4 grams of $NaC_2H_3O_2$ and a few c.c. of $HC_2H_3O_2$. If a precipitate appears, Fe, Al, and Cr are present. Boil and filter. Label this precipitate P. If no precipitate is formed, Fe, Cr, and Al are absent.

Notes

To the filtrate or solution containing $NaC_2H_3O_2$ and $HC_2H_3O_2$ add $FeCl_3$ drop by drop, shaking after each addition until precipitation is complete. At this point it begins to assume a red color due to the formation of $Fe(C_2H_3O_2)_3$ and indicates that all of the phosphate has been precipitated as $FePO_4$. Neutralize with NH_4OH (a slight excess will do no harm) and boil. This converts all of the iron in solution as $Fe(C_2H_3O_2)_3$ into an insoluble basic acetate. Filter and analyze filtrate for Co, Ni, Mn, Zn, Ba, Sr, Ca, and Mg by the usual methods. The only bases found in the filtrate will be those which were precipitated as phosphates with NH_4OH in the beginning.

The precipitate P (phosphates of Fe, Cr, and Al) is dissolved in 2 c.c. of warm con. HNO_3. Add $KClO_3$ and boil to 1 c.c., dilute to about 5 c.c., a yellow solution indicates Cr. Add NaOH, Fe is precipitated as $Fe(OH)_3$ and $FePO_4$, reddish-brown in color.

Al and Cr go into solution as Na_3AlO_3 and Na_2CrO_4 respectively. Divide the solution into two parts (a) and (b). To (a) add $HC_2H_3O_2$ until acid, then $Pb(C_2H_3O_2)_2$. A yellow precipitate, $PbCrO_4$, proves the presence of Cr. Acidify (b) with dil. HNO_3 and add NH_4OH. A white, gelatinous precipitate indicates Al.

GENERAL QUESTIONS

1. Why is it necessary to wash precipitates? Why do we usually employ hot water to effect the washing? Why do we sometimes add a small quantity of the reagent to the wash water? What is the theory of washing precipitates?

2. Explain how small grains change into large grains when precipitates are allowed to stand. Why are the large grains more desirable?

3. Explain the phenomena of adsorption and absorption.

4. What are colloidal solutions? Where do we meet such conditions in qualitative analysis? How may we deal with such conditions? How may their formation be prevented?

5. What effect has heat on the velocity of chemical reactions? Explain.

6. Explain the law of mass action. Develop mathematically. What is the law of Berthollet?

7. Why should we always use a slight excess of the reagent when a precipitate is obtained?

8. What is meant by the solubility product? Show how it is derived. What is the effect of an excess of a common ion on the solubility of precipitates?

9. What is hydrolysis? Under what conditions does it take place? How may it be controlled?

10. What is meant by the law of successive reactions? Explain.

11. What is the electrolytic ionization theory? How may we illustrate the conductivity of different acids, bases, and salts by observing the intensity of glow in the incandescent lamp?

12. Fully explain in terms of the ionization theory and solubility product:

(a) $ZnSO_4 + H_2S = ?$
$ZnSO_4 + HCl + H_2S = ?$
$ZnSO_4 + HCl + NaC_2H_3O_2 + H_2S = ?$
(b) $MgSO_4 + NH_4OH = ?$
$MgSO_4 + NH_4Cl + NH_4OH = ?$

QUERIES—GROUPS V AND VI

If original solution is cloudy, what does it indicate? Why is it not necessary to clear the solution with HCl before treating with H_2S? Why is it necessary to test the reaction of the solution with litmus paper? How may we prove that the acid reaction is due to HCl? Why should the solution be cold when HCl is added? If Ag and Hg′ are absent, why should we avoid an excess of HCl? Explain how HCl prevents the precipitation of Groups III and IV with H_2S? What can be said of the solubility product of the sulphides of the metals of Groups V and VI compared with those of Groups IV and III? Why does Pb, if present, always come down with H_2SO_4 in the HCl filtrate?

H_2S acts both as a weak acid and reducing agent. Explain these two functions of H_2S in the treatment of Groups V and VI.

How may we know when a sufficient quantity of H_2S has been added in precipitating members of Groups V and VI?

Why is it necessary to thoroughly wash the H_2S precipitate?

Why should the filtrate be at once boiled to remove the H_2S? If a rather large quantity of free HNO_3 is present [which is necessary when $Hg(NO_3)_2$ and $Bi(NO_3)_3$ are present to prevent hydrolysis] and the solution is kept hot during the passage of H_2S, what metals may be lost? Why?

How are As, Sb, and Sn separated from the other members of Group V? Describe how they are separated from each other? What two purposes do the card teeth serve? What is the final precipitate in testing for Sn? How are small quantities of As found?

How is Hg″ separated from Pb, Bi, Cu, and Cd?

How is Pb separated from Bi, Cu, and Cd?

How is Bi separated from Cu and Cd?

How is Cu separated from Cd?

What is the confirmation test for Hg″, Pb, Bi, and Cu? Explain the principle involved in each of the above separations.

Why must a solution be alkaline when KCN is used as a reagent?

Write out a list of fifty reactions for Groups V and VI.

What metals of this group have an acid tendency? What can be said of the action of their salts with water?

QUERIES—GROUPS III AND IV

Why should oxalates and phosphates be looked for at the beginning of the analysis of Group III? How is an oxalate detected and removed? How test for a phosphate? Why is it best to test for Fe in the original solution? Explain the necessity of boiling the H_2S filtrate with Br_2 water before testing for Fe. What elements are precipitated by NH_4OH? Why add NH_4Cl before adding NH_4OH? When may NH_4Cl be omitted?

Under what conditions may Mn be partially precipitated when NH_4OH is added? What provisions are made for its detection?

Why thoroughly dry the NH_4OH precipitate before dissolving in con. HNO_3? What is the function of $KClO_3$ in this connection? How is Fe separated from Cr and Al? What office does the NaOH perform besides removing the Fe? How test for Cr and Al? Why is Al so frequently reported when absent?

Why is $FeCl_3$ used to remove phosphates? What is the purpose of the $NaC_2H_3O_2$ in removing phosphates? How find the base that was originally combined with the phosphate?

Should we use yellow $(NH_4)_2S$ to precipitate Co, Ni, Mn, and Zn? Why? If the filtrate from the $(NH_4)_2S$ is brown, explain the significance and method of treatment. Why should the sulphides of this group be kept covered with water? How is Co and Ni separated from Mn and Zn? How separated from each other? What office does the KCN perform? Why is an excess of Br_2 water necessary? Explain the principle of the borax bead.

How are Mn and Zn separated? Explain the Na_2CO_3 and KNO_3 bead in testing for Mn. In precipitating Zn with Na_2CO_3, it is not necessary to wash the precipitate. Explain. If a yellow precipitate appears in the final test for Zn, what does it signify? How may Zn be detected under those conditions? Write thirty reactions which occur in the course of analysis of Groups III and IV. Make a list of the soluble and insoluble salts of this group.

QUERIES—GROUP II

Why is it often necessary to boil the filtrate from Groups III and IV to dryness before beginning the analysis of Group II? If $(NH_4)_2CO_3$ gives no precipitate, how may traces of this group be found? Explain the appearance of the Mg test. Why dissolve the $(NH_4)_2CO_3$ precipitate in acetic acid?

How test for Ba in the presence of Sr and Ca? How separated? Why is it necessary to add NH_4OH and $(NH_4)_2CO_3$ a second time? How test for Sr if Ca is present? Why use $CaSO_4$ as a reagent in this group? How is Ca detected in the presence of Sr? In the absence of Sr? Is it completely separated from Sr? Why?

Write six reactions which occur in the course of analysis of this group.

GROUP I

What can be said of the solubility of the salts of Group I? Discuss the principle of the spectroscope and its use in the detection of the bases of this group. How may Mg be removed if the quantities of Na, K, and Li are required? Why expel all ammonium salts? Why test for ammonia in the original solution?

REAGENTS AND SOLUTIONS

Acids.

Con. HCl, sp. gr. 1.2, 39% HCl by weight.
Dil. HCl, 1 part con. HCl to 4 parts water.
Con. HNO_3, sp. gr. 1.42, 68% HNO_3 by weight.
Dil. HNO_3, 1 part con. HNO_3 to 4 parts water.
Con. H_2SO_4, sp. gr. 1.84, 98% H_2SO_4 by weight.
Dil. H_2SO_4, 1 part con. acid to 4 parts water.
Glacial acetic acid, sp. gr. 1.04, 99½% by weight.
Dil. $HC_2H_3O_2$, 1 part of con. acid to 4 parts water.

Bases.

Con. ammonia, sp. gr. .90, 28% NH_3.
Dil. ammonia (reagent), 1 part con. ammonia to 4 parts water.
Sodium hydroxide, $NaOH$, 142.5 gms. per liter.
Potassium hydroxide, KOH, 200 gms. per liter.
Barium hydroxide, $Ba(OH)_2$, saturated solution.
Calcium hydroxide, $Ca(OH)_2$, saturated solution.

Salt Solutions.

Aluminum sulphate, $Al_2(SO_4)_3.18H_2O$, 100 gms.; water 300 c.c. Dilute 4–100.[1]

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[1] 4–100 means four parts of the con. stock solution to 100 parts of water by volume.

Ammonium acetate, $NH_4C_2H_3O_2$, 25% solution.

Ammonium carbonate, $(NH_4)_2CO_3$, 1675 c.c. water, 200 c.c. con. ammonia, and 375 gms. of $(NH_4)_2CO_3$.

Ammonium chloride, NH_4Cl, 10% solution.

Ammonium molybdate, $(NH_4)_2MoO_4$. To a mixture of cold distilled water and 144 c.c. of con. ammonia (sp. gr. .90), slowly add with constant stirring 100 gms. of powdered MoO_3; slowly add this solution with stirring to a mixture of 489 c.c. con. HNO_3 (sp. gr. 1.42) and 1148 c.c. of water. Let stand in a warm place for a few days until a portion heated to 40° deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any deposit and preserve.

Ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$. Saturated solution.

Ammonium sulphide, $(NH_4)_2S$. Pass H_2S into con. ammonia until a small portion diluted with water gives no precipitate with $MgSO_4$ solution. Dilute 1 part of strong solution to 3 parts of water.

Ammonium sulphide (yellow), $(NH_4)_2S_x$. Add about 5 gms. of flowers sulphur to 1 liter of con. $(NH_4)_2S$. Dilute as before.

Ammonium sulphate, $(NH_4)_2SO_4$, 10% solution.

Barium chloride, $BaCl_2.2H_2O$, 10% solution.

Barium nitrate, $Ba(NO_3)_2.2H_2O$, 10% solution.

Bromine water, saturated solution.

Calcium chloride, $CaCl_2.6H_2O$. $CaCO_3$, 100 gms.; water and con. HCl q. s. (quantum satis) 300 c.c. Dilute for solutions 2–100.

Calcium sulphate, $CaSO_4.2H_2O$, saturated solution.

Calcium nitrate, $Ca(NO_3)_2$. See stock solutions.

Chrome alum, $K_2Cr_2(SO_4)_4.24H_2O$, 67 gms; water 200 c.c. Dilute 4–100.

Cobalt chloride, $CoCl_2.6H_2O$, 10% solution.

Cobalt nitrate, $Co(NO_3)_2.6H_2O$. See stock solutions.

Cobalt nitrate (for confirmation of Al and Zn), .5 gm. of crystallized salt to 1 liter of water.

Copper nitrate. See stock solutions.

Copper sulphate, $CuSO_4.5H_2O$, 300 gms.; water 900 c.c. Dilute 2–100.

Ferric chloride, $FeCl_3.6H_2O$, 625 gms.; water 1000 c.c. Dilute 1–1.5 (for solutions). Dilute 1–6 for reagent (test for acetate etc.).

Ferric nitrate. See stock solutions.

Ferrous sulphate, $Fe (SO_4).7H_2O$. Dissolve a few grams of the solid salt in 10 c.c. dil. H_2SO_4 and keep in contact with card teeth or two or three bright iron nails. (Solution to be prepared by the student.)

Hydrochlorplatinic acid, $H_2PtCl_6.6H_2O$, 10% solution.

Lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$, 10% solution.

Lead nitrate. See stock solution.

Magnesium sulphate, $MgSO_4.7H_2O$, 333 gms.; water 1000 c.c. Dilute 2–100.

Manganese sulphate, $MnSO_4.7H_2O$, 280 gms.; water 1000 c.c. Dilute 2–100.

Mercuric chloride, $HgCl_2$, saturated solution.

Phenolphthalein, 1% sol. in 50% C_2H_5OH.

Potassium bromide, KBr, 10% solution.

Potassium chromate, K_2CrO_4, 10% solution.

Potassium di-chromate, $K_2Cr_2O_7$, 10% solution.

Potassium ferrocyanide, $K_4Fe(CN)_6$, 10% solution.

Potassium ferricyanide, $K_3Fe(CN)_6$, 5% solution.

Potassium iodide, KI, 2% solution.

Potassium permanganate, $KMnO_4$, 1% solution.

Potassium sulphocyanide (thiocyanate), 5% solution.

Silver nitrate, $AgNO_3$, 34 gms. per liter.

Silver sulphate, Ag_2SO_4, saturated solution.

Sodium arsenite. See stock solutions.

Sodium arsenate, $Na_3AsO_4.12H_2O$, 70 gms.; water 250 c.c. Dilute 6–100.

Sodium carbonate, Na_2CO_3 (dry), 10% solution.

Sodium phosphate, $Na_2HPO_4.12H_2O$, 10% solution.

Stannous chloride. See stock solutions.

Zinc sulphate, $ZnSO_4.7H_2O$, 500 gms.; water 500 c.c. Dilute 1–100.

PREPARATION OF STOCK SOLUTIONS FOR UNKNOWN TESTS

In most cases nitrates are employed in the preparation of the unknowns. Since the nitrates of certain metals (As, Sb, and Sn) are not easily prepared and preserved, the chlorides may be used, care being taken that salts of certain other metals are absent.

Concentrated stock solutions are prepared as given below. Solutions of proper concentrations to be given out for analysis are prepared from these concentrated stock solutions and preserved in separate bottles for immediate use. About 10 c.c. of each dilute stock solution is drawn off and the mixture given to the student for analysis. For example, if it is desirable to give a student a solution containing Ag, Hg′, Cu, Cd, Fe, Ni, Zn, Sr, and Mg, it will be necessary to draw off 10 c.c. of each dilute stock solution, thus making 100 c.c. in all. About one-third of this solution is used for analysis, the remainder being saved for subsequent analyses in case of error.

Ag. $AgNO_3$, 30 gms.; water 1000 c.c. Proper dilution for use.

Hg′.$HgNO_3$, saturated. Crystals boiled in contact with Hg until filtered from precipitate with dil. HCl give no precipitate with H_2S.

Pb.$Pb(NO_3)_2$, 300 gms.; water 1000 c.c. Dilute 4–100.

Hg″.$Hg(NO_3)_2$, 1080 gms. or Hg 666.6 gms.; water and con. HNO_3 q. s. 1000 c.c. Dilute 2–100.

Bi.$Bi(NO_3)_3.5H_2O$, 490 gms.; con. HNO_3 c.p. 150 c.c., water q.s. 900 c.c. Dilute 2–100 and add 5 c.c., of HNO_3.

Cu.$Cu(NO_3)_2.3H_2O$, 250 gms.; water 250 c.c. Dilute 1–100.

Cd.Cd (metallic sticks c.p.), 125 gms.; water and con. HNO_3 to dissolve. Water q. s. 750 c.c. Dilute 2–100.

As.As_2O_3, 100 gms.; Na_2CO_3 c.p. (dry) 150 gms; water 300 c.c. Dilute 1–100.

Sb.$KSbOC_4H_4O_6$. ½H_2O, 230 gms.; water 500 c.c. Con. HCl until clear. Dilute 2–100.

Sn.$SnCl_2.2H_2O$, 128 gms.; con. HCl 125 c.c. and water q.s. 200 c.c. Dilute 2–100.

Fe.Fe (metal c.p.), 50 gms.; water 200 c.c. con. HNO_3 c.p. 200 c.c. Dilute 1–100.

Cr.$Cr(NO_3)_3$ 40% solution, 500 gms. Dilute 1–150.

Al.$Al(NO_3)_3.9H_2O$, 210 gms.; water 100 c.c. Dilute 2–100.

Co.$Co(NO_3)_2.6H_2O$, 150 gms.; water 300 c.c. Dilute 3–100.

Ni.$Ni(NO_3)_2.6H_2O$, 150 gms.; con. HNO_3 2 c.c. water 300 c.c. Dilute 3–100.

Mn.$Mn(NO_3)_2.6H_2O$, 450 gms.; water 1000 c.c. Dilute 2–100.

Zn.ZnO, 145 gms.; water and con. HNO_3 q.s. to dissolve. Concentrate to 500 c.c. Dilute 1–100.

Ba.$Ba(NO_3)_2$, saturated. Dilute 4–100.

Sr.$Sr(NO_3)_2$, 170 gms.; water 1000 c.c. Dilute 6–100.

Ca.$CaCO_3$, 450 gms. added gradually to 440 c.c. con. HNO_3 diluted with water q.s. 1000 c.c. Dilute 2–100.

Mg.$MgCO_3$, 300 gms. added gradually to 450 c.c. con. HNO_3 diluted with water q.s. 1000 c.c. Dilute 2–100.

Na.$NaNO_3$, 60 gms.; water 100 c.c. Dilute 2–100.

K.KNO_3, saturated. Dilute 1–50.

Li.Li_2CO_3, 50 gms.; water and con. HNO_3 q.s. 250 c.c. Dilute 4–100.

NH_4.NH_4NO_3, 90 gms.; water 250 c.c. Dilute 2–100.

Table Showing the Solubility in Water and Acids of the More Common Salts

	O.	H_2S.	HCl.	HBr.	HI.	HCN.	H_2CrO_4.	H_3AsO_3.	H_3AsO_4.	H_2SO_4.	H_3PO_4.	H_3BO_3.	$H_2C_2O_4$.	HFl.	H_2CO_3.	H_4SiO_4.*	$H_2C_4H_4O_6$.	$H_4Fe(CN)_6$.	$H_6Fe_2(CN)_{12}$.	HNO_3.	$HClO_3$.	$HC_2H_3O_2$.
K	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Na	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
H_4N	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	..	1	1	1	1	1	1
Ba	1	1	1	1	1	1–2	2	2	2	3	2	2	2	2–3	2	2	2	1–2	.	1	1	1
Sr	1	1	1	1	1	1	1–2	2	2	3	2	2	2	2–3	2	2	2	1	..	1	1	1
Ca	1–2	1	1	1	1	1	1–2	2	2	1–3	2	2	2	2–3	2	2	2	1	1	1	1	1
Mg	2	2	2	1	1	1	1	2	2	1	2	1–2	2	2–3	2	2	1–2	1	1	1	1	1
Al_2	2 & 3	2	2	1	1	..	..	.	2	1	2	2	2	1	.	2–3	1		..	1	1	1
•Cr_2	2 & 3	2 & 3	1 & 3	1 & 3	1	2	2	.	2	1 & 2	2	2	1–2	1	.	2	1		..	1	1	1
Fe_2	2	2	1	1	1	..	1	2	2	1	2	2	2	1	.	2	1	3	1	1	1	1
Fe	2	2	1	1	1	2–3	..	2	2	1	2	2	2	1–2	2	2	1–2	3	3	1	1	1
Zn	2	2	1	1	1	2	1	.	2	1	2	2	2	1–2	2	2	2	2–3	2	1	1	1
Mn	2	2	1	1	1	2	1	2	2	1	2	2	1–2	2	2	2	1–2	2	3	1	1	1
Ni	2	2	1	1	1	2–3	2	2	2	1	2	2	2	1–2	2	2	2	3	3	1	1	1
Co	2	2	1	1	1	2–3	2	2	2	1	2	2	2	1–2	2	2	1	3	3	1	1	1
Ag	2	2	3	3	3	3	2	2	2	1–2	2	2	2	1	2	.	2	3	3	1	1	1
Pb	2	2	1–3	1–3	1–2	2	2–3	2	2	2–3	2	2	2	2	2	2	2	2	1–2	1	1	1
Hg_2	2	2	2–3	2–3	2	..	2	2	2	1–2	2	..	2	..	2	.	1–2	..	..	1	1	1–2
Hg	2	2	1	1	2	1	1–2	2	2	1	2		2	1–2	2		2		..	1	1	1
Bi	2	2	1–2	1–2	2	..	2	.	2	1	2	2	2	1	2	.	2	.	..	1	1	1
Cu	2	2	1	1	1	2	1	2	2	1	2	2	2	2	2	2	1	3	..	1	1	1
Cd	2	2	1	1	1	2	2	.		1	2	1–2	2	1–2	2	2	1–2	..	.	1	1	1
Sn	2	2	1	..	1		2	.	.	1	2	2	2	1	..	..	2	3	3	..	1	1
Sn^{iv}	2 & 3	2	1	..	1		.	.	2	..	2	.	1	1	.	..	..	3	..	..	..	1
Sb	2	2	1–2	1–2	1–2	..	2	2	2	2	1–2	..	2	1	..	..	2	..	..	.	.	..

1 = soluble in water; 2 = soluble in acids only; 3 = insoluble in water or acids; 1–2 = sparingly soluble in water, readily in acids; 1–3 = sparingly soluble in water and acids; 2–3 = sparingly soluble in acids only.

* The solubility of the silicates marked (2) refer to the precipitated silicates and not to the mineral silicates which are all insoluble in water or acids except Group I.