TABLE OF COMPOUNDS.

The table below gives the compounds of each metal which are formed in the course of an analysis. It may be followed as a guide in analysis by any one who is familiar with the details involved. It may also be of service to the beginner in gaining a clear conception of the analytical processes.

Gr. I.	$PbCl_2$	$PbCrO_4$							
	Hg_2Cl_2	$(NH_2HgCl+Hg)$							
	$AgCl$	$Ag(NH_3)_2Cl$	$AgCl$						
	HgS	HgS	HgS	$HgCl_2$	Hg_2Cl_2	Hg			
	PbS	PbS	$Pb(NO_3)_2$	$PbSO_4$	$Pb(C_2H_3O_2)_2$	$PbCrO_4$			
	Bi_2S_3	Bi_2S_3	$Bi(NO_3)_3$	$Bi_2(SO_4)_3$	$BiOOH$	$BiCl_3$	$BiOCl$	Bi	
	CuS	CuS	$Cu(NO_3)_2$	$CuSO_4$	$Cu(NH_3)_4SO_4$	$CuSO_4$	Cu		
		CdS	$Cd(NO_3)_2$	$CdSO_4$	$Cd(NH_3)_4SO_4$	$CdSO_4$	$CdSO_4$	CdS	
	$_3$	$(NH_4)_3AsS_4$	As_2S_5	As_2S_5	H_3AsO_4	$(NH_4)_3AsO_4$	$MgNH_4AsO_4$	(As_2S_3+S)	
	$_3$	$(NH_4)_3SbS_4$	Sb_2S_5	$SbCl_3$	Sb_2S_3	$SbCl_3$	Sb		
	SnS_2	$(NH_4)_2SnS_3$	SnS_2	$SnCl_4$	$SnCl_4$	Sn	$SnCl_2$	$SnCl_4[Hg_2Cl_2]$.	
	H)$_3$	$AlCl_3$	$NaAlO_2$	$Al(NO_3)_3$	$Al(OH)_3$				
	H)$_3$	$CrCl_3$	Na_2CrO_4	$Na_2Cr_2O_7$	Na_2CrO_4	$Na_2Cr_2O_7$	$BaCrO_4$		
		$ZnCl_2$	Na_2ZnO_2	$Zn(NO_3)_2$	$[Zn(NH_3)_4](NO_3)_2$	$Zn(C_2H_3O_2)_2$	$Zn(C_2H_3O_2)_2$	ZnS	
		$MnCl_2$	$MnO(OH)_2$	$Mn(NO_3)_2$	$MnO(OH)_2$	$HMnO_4$			
		$FeCl_2$	$Fe(OH)_3$	$Fe(NO_3)_3$	$Fe(NO_3)_3$	$Fe(OH)_3$			
		$CoCl_2$	$Co(OH)_3$	$Co(NO_3)_2$	$Co(NO_3)_2$	$[Co(NH_3)_6](NO_3)_2$	CoS	$CoCl_2$	$K_3Co(NO_2)_6$
		$NiCl_2$	$Ni(OH)_{2-3}$	$Ni(NO_3)_2$	$Ni(NO_3)_2$	$[Ni(NH_3)_6](NO_3)_2$	NiS	$NiCl_2$	$Ni(OH)_3$
	CO_3	$Ba(C_2H_3O_2)_2$	$BaCrO_4$						
	CO_3	$Sr(C_2H_3O_2)_2$	$Sr(C_2H_3O_2)_2$	$SrCO_3$	$Sr(C_2H_3O_2)_2$	$SrSO_4$			
	$CaCO_3$	$Ca(C_2H_3O_2)_2$	$Ca(C_2H_3O_2)_2$	$CaCO_3$	$Ca(C_2H_3O_2)_2$	$Ca(C_2H_3O_2)_2$	$CaSO_4$	CaC_2O_4	
	MgX_2	$MgNH_4PO_4$							
	NH_4X								
Gr. V.	KX	$KClO_4$	KX—violet flame	Spectroscopic examination.					
	NaX		NaX—yellow flame						
	LiX		LiX—red flame						

SOLUBILITY OF SOME "INSOLUBLE" SALTS IN WATER.

	Cl	Br	I	CNS	F	S	OH	CO_3	SO_4	CrO_4	C_2O_4
Ag	1.53	0.084	0.003	0.13		0.10	27	17	5500	25	35
Pb	9610	8340	613		700	0.86	75	1	43	0.2	1.5
Hg^{I}	0.5	0.04	0.0002								
Hg^{II}			60	696		0.013	51				
Bi						0.18					
Cu^{II}						0.34					
Cd						1.30					
As^{III}						0.52					
Sb^{III}						1.75					
Zn					5.1	6.88	5				6
Mn						6.23	5.5				
Fe^{II}						6.16	7				
Co						3.79					
Ni						3.62					
Ba					1600		37000	23	2.3	3.8	86
Sr					120		7700	11	110	1200	46
Ca					16		1700	13	2000	4000	5.6
Mg					76		15	800			300

The table gives the number of milligrams of the anhydrous salt that are held in solution by 1 liter (*i. e.*, 1,000,000 mg.) of water at 18–20°.

G.W.C. Vaughan
Brown 1918

THE ELEMENTS
OF
QUALITATIVE ANALYSIS

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SIXTH EDITION
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PREFACE TO THE FIRST EDITION.

Two reasons have led to the writing of this book. One has been the desire to give to my classes a scheme for qualitative analysis in which points where a beginner is liable to make mistakes are especially guarded by careful and explicit directions for procedure. In this respect the book is the result of considerable experience with classes in the laboratory, where especial pains have been taken to discover the reasons for errors on the part of ordinary students. Qualitative analysis is of no value unless it leads to *certain* results, and the beginner needs to have it impressed upon his mind that certainty can only be attained by performing each operation in exactly the right way. In the author's opinion it is better to teach the student the right way at first, rather than to give only an outline and expect him to fill in the details of manipulation for himself. Every one who has had experience in the matter knows, however, that no amount of careful direction in a text-book can supply the place of constant watchfulness on the part of the instructor.

The second reason for the book has been the desire to connect the reactions given by way of a study of the elements before actual analysis more closely with the course of analysis itself. With this end in view, the reactions given for the student to try before taking up the actual analysis are chosen and arranged in each case with reference to their immediate use in the separation and detection of the elements under consideration. As a result, the preliminary reactions given are fewer in number than is usually the case. These reactions are supplemented, however, by the tables given at the close of Part I. For the idea embodied in these tables and, indeed, for most of the matter which they contain I must acknowledge my indebtedness to Biedermann's "Chemiker-Kalender" for 1887.

The plan to be followed in using this book is largely implied in the text. In the first part of the work it is my custom to have the student perform the preliminary experiments with the metals of a group, writing the equations representing the reactions involved and keeping a careful record of his work. A mixture containing all of the metals of the group is then given and he is required to analyze it, keeping in some systematic form a record of each reagent used and of the results obtained. When the analysis is complete he is required to explain his record and give the reason for each operation. Then mixtures containing part of the metals of the group are given. After completing the study of the metals in this way, simple salts containing one metal and one acid are given for analysis and then general mixtures of various kinds.

The author will be very glad of any corrections or suggestions for improvement which may occur to anyone who uses the book.

W. A. N.

PREFACE TO THE SIXTH EDITION.

Owing to a desire to bring the book up to date, especially in consequence of the researches of A. A. Noyes and his co-workers, and to the further desire to incorporate in the text the subject-matter for which the students in qualitative analysis at this university are held responsible, the book has been very largely rewritten. The chief alterations made necessary by the work of A. A. Noyes were the introduction of the provisions for the proper conditions of acid concentration in the precipitation of the Hydrogen Sulphide Group, and also in the separation of arsenic, antimony and tin; the rewriting of the entire procedure for the analysis of the Ammonium Sulphide Group, which, owing to the above-mentioned researches, has been very greatly simplified; and the introduction of a systematic procedure for the preparation of the solution to be analyzed for the metallic elements. The procedure for the detection of acids has also been largely rewritten. The general plan of the book, however, has remained unaltered.

After having performed the preliminary experiments with the metals of a group, the beginner is required to analyze a solution known to contain all the metals of the group *in given quantities.* Then solutions containing certain metals of the group (and sometimes of preceding groups as well) are given. Finally, solutions which may contain members of all five groups are given for analysis. Following this work, the reactions of the anions are studied, after which general mixtures of solids are given for analysis. The latter are made more and more difficult as the analyst's experience increases.

URBANA, ILL., W. A. N.
January, 1911. G. McP. S.

QUALITATIVE ANALYSIS

INTRODUCTION.

Under analytical methods are understood all the operations which are made use of in order to detect in, or obtain from, chemical compounds or mixtures of chemical substances the separate parts of which they are composed. The branch of chemistry under which these methods are treated is called analytical chemistry. Analytical chemistry itself is subdivided into two general parts:

(1.) Qualitative Analysis.
(2.) Quantitative Analysis.

Qualitative analysis, with which we are here concerned, deals with the qualitative composition of bodies; *i.e.*, with the separation (either free or in the form of characteristic compounds) and identification of the various elements present in them.

In the course of a qualitative analysis it is usually necessary to transform an element into a number of different compounds, successively, either because the compound first formed is so similar to some compound of another element that it cannot be identified with certainty, or because it is necessary to separate the element from others with which it is mixed or combined. The substances of known behavior by means of which such transformations are brought about are called **reagents.**

A qualitative analysis to be successful must prove with *certainty* that the elements sought are present or that they are absent. The latter is in many cases more important than the former. *Furthermore, some idea should be formed as to the relative quantities in which the elements found are present.* Success can only be attained by the exercise of care in all operations and by the most scrupulous cleanliness.

One who attempts to analyze a substance by following mechanically a scheme which is laid down may sometimes succeed in finding the substances which he seeks, but he is sure to fail in many cases. In order to avoid frequent mistakes the analyst must understand thoroughly the object of every operation and the effect of the operation upon every substance present in the mixture with which he is working. For this reason it is best to perform the operations of analytical chemistry, at first, with substances of known composition, studying carefully the effect upon these of the operations which are afterward to be used in the analysis of unknown substances. *It should also be an invariable rule, when in doubt about a test, to apply the same test to some suitable compound of the substance sought, and to compare the two results.*

Furthermore, it should be borne in mind that the substances tested for may be present in the reagents as impurities. In any case where this seems possible the reagent should be directly tested. The neglect of such blank tests with reagents may give rise to serious errors.

Precipitation is more often used than any other means for the separation and detection of substances. In carrying out this operation, the reagent should always be added gradually, with stirring, and only as long as the precipitate continues to form. This can be determined by allowing the precipitate to settle, or by filtering a little of the liquid, and then adding a drop more of the reagent to the clear solution. In many cases it can be determined by simply noting the odor or color of the solution (*e.g.*, in the precipitation of Group II. with H_2S, or of barium with $K_2Cr_2O_7$), since the reagent is present in excess if its characteristic properties are shown by the solution. By adding the reagent in this way, *an undue excess is avoided,* and at the same time the precipitation is proved to be complete. The latter result is essential for the success of an analysis.

A precipitate is **washed** for the purpose of removing the liquid which is mechanically held within its mass. Washing may be performed by decantation or by repeatedly pouring water upon the precipitate as it lies on the filter; unless the precipitate is heavy and settles rapidly, washing upon the filter is usually most effective. It is frequently advisable to remove the first filtrate before beginning to wash a precipitate, as the washings sometimes pass through turbid even when the first filtrate is clear. *Too much emphasis cannot be laid upon the fact that the success of an analysis depends very greatly upon complete precipitations, and upon the proper washing of the precipitates.* The object of precipitation is to separate one or more substances from others in solution, and it is obvious that a complete separation is not attained unless the precipitation is complete and the precipitate is entirely freed from the liquid in which it was produced. The analyst should always assure himself that the precipitate is thoroughly washed by testing the last portions of the filtrate. (If the solution contains acid or alkali, for example, the precipitate should be washed as long as the filtrate reacts with litmus paper.)

The precipitate sometimes assumes the **colloidal state** to a certain extent; in this state it is under certain conditions insoluble and under others soluble. The insoluble form is called the **hydrogel,** and the soluble the **hydrosol.** When in the hydrosol condition substances enter the solvent in suspension in the form of minute particles, and, on filtration, these pass through the filter. Some precipitates assume the hydrosol condition when brought in contact with pure water, *e. g.*, when being washed upon the filter. When this happens, the filtrate becomes turbid, and the pores of the filter are apt to become clogged, thus rendering further washing almost impossible. Heat, agitation, or the addition of certain salts or acids will often cause the precipitation of colloidal substances.

IONIZATION IN SOLUTION.

Since in the following we shall have to deal very extensively with reversible ionic reactions, it will not be out of place at this point to review the evidence that the molecules of acids, bases, and salts are dissociated into parts by the aqueous solvent.

All acids, bases, and salts are made up of two radicals, and the reversible double decompositions into which they enter with other acids, bases, and salts consist in exchanges of these radicals. All acids, for example, act as if composed of hydrogen and another radical, and their sour taste and their effect on litmus seem to be properties of this easily separable hydrogen. Similarly, the peculiar properties of bases seem to be due to the easily separable hydroxyl, which they all contain.

It is, however, chiefly in aqueous solution that the special properties of acids, bases, and salts become apparent. Their behavior is often quite different in the absence of this solvent. If, for example, potassium chlorate and acid sodium tartrate, each in the form of a powder, are gently mixed together, there is no evidence of a chemical change. But if we apply heat to the mixture, a violent interaction takes place, accompanied by the evolution of heat and light. If, on the other hand, the two substances are dissolved in water before being brought in contact, the difference is very great. A white, crystalline precipitate separates, which on examination is found to be cream of tartar, and the liquid contains mainly sodium chlorate in solution. The two actions may be represented by the respective equations:

$$6NaHC_4H_4O_6 + 10KClO_3 \rightarrow 3Na_2CO_3 + 10KCl + 21CO_2 + 15H_2O,$$

$$\text{and } NaHC_4H_4O_6 + KClO_3 \rightleftarrows KHC_4H_4O_6 + NaClO_3.$$

In the interaction between the dry substances the molecules are completely disintegrated, and the change is not reversible. In the action in water no heating is required, and certain atomic groupings, called radicals, are transferred as wholes, in a very quiet manner, from one state of combination to another; and in this case the action is reversible.

Again, as an example of the different behavior of an acid in the practical absence of water, and in its presence, we may cite the evolution by zinc of sulphur dioxide from concentrated sulphuric acid, on heating, and the evolution by the same metal of hydrogen from the dilute acid, with or without the application of heat.

In the cases of acids, bases, and salts in aqueous solution, each compound usually splits in the same way. Thus, potassium chlorate gives double decompositions involving K and ClO_3—it gives no precipitate with silver nitrate, for example, because silver chloride is not produced by the interaction of the two salts, and the silver chlorate which is formed is not insoluble. Similarly, acids always offer hydrogen in exchange, and bases hydroxyl, so that nitric acid behaves as if composed of H and NO_3, and potassium hydroxide as if composed of K and OH. The result is that we can make a list of the radicals, such as K, Ag, H, OH, Cl, NO_3, ClO_3, etc., exchanged by acids, bases, and salts in their interactions. The molecule of each acid, base, or salt contains at least two of these radicals.

The question naturally presents itself whether solution in water simply produces in the molecules of these substances a sort of "*plane of cleavage*" and thus leads to a uniform kind of chemical change, or whether it *actually divides* the molecules into separate parts, and leaves subsequent chemical actions to occur by cross-combination of the fragments. The question is not answered by the chemical evidence alone; it can, however, be answered by a study of the physical properties of solutions.

Laws of Freezing-Point Depression.—If a substance such as sugar is dissolved in water, and the resulting solution is sufficiently cooled, a separation of pure ice takes place, and it is found that the temperature at which equilibrium exists between the very small quantity of ice and the solution is lower than the freezing-point of pure water. Furthermore, the lowering of the freezing-point of the solvent is directly proportional to the weight of sugar dissolved in a given amount of the solvent. But if equal weights of different substances, such as sugar, glucose, alcohol, etc., are dissolved in equal portions of the same solvent, different freezing-point depressions are produced. If, however, *equal numbers of molecules* of different solutes are dissolved in equal quantities of the same solvent, then the same lowering of the freezing-point is observed in every case. Thus, solutions containing 342 grams of sugar ($C_{12}H_{22}O_{11}$), or 180 grams of glucose ($C_6H_{12}O_6$), or 74 grams of methyl acetate ($CH_3.C_2H_3O_2$) or 46 grams of alcohol (C_2H_5OH)—*i.e.*, 1 gram molecule in each case—in 10,000 grams of water, all show a freezing-point lowering of 0.185°.

It is important to emphasize that the freezing-point lowering depends solely upon the concentration of the solute particles; what these particles themselves may be makes no difference. One-fourth mol each of the four substances dissolved together in 10 liters of water would give the same depression as 1 mol of any one of the substances in the same quantity of water, since in both cases the actual number of particles is the same.[1]

The substances which present the most conspicuous exceptions to the above laws are acids, bases, and salts, in aqueous solution; the freezing-point is generally lower than we should expect from the concentration of the solution. Thus, a solution containing 58.5 grams of sodium chloride in 10 liters of water is found to freeze at –0.350°. If sodium chloride were present only in the form of NaCl-molecules in the solution, the freezing-point would be –0.185°, as with the other substances named. That the acutal lowering is 0.350°, or $\frac{0.350}{0.185} = 1.89$ times as great as that which would result if sodium chloride behaved in the same manner as sugar, etc., shows that the solu-

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[1] These laws describe the facts most exactly when the solutions are dilute. They hold only when there is no chemical interaction between solute and solvent, and when pure ice separates from the freezing solution.

tion contains a larger number of particles than the number of chemical molecules (NaCl). The explanation would be simple if, for example, out of 100 of the original NaCl- molecules 89 should, when dissolved, dissociate into the smaller particles Na and Cl, while 11 remained united in the chemical molecules NaCl. The total number of particles would then be 1.89 times the number of the original chemical molecules. Likewise, of 100 molecules of such a substance as barium chloride, $BaCl_2$, 75 molecules might dissociate into 75 particles of Ba and 150 of Cl, while there remained 25 of the original $BaCl_2$ molecules, thus giving 250 particles in solution. This supposition is in accord with the actual freezing-point (–0.469°) of a 0.1 molal barium chloride solution, which indicates the presence of $\frac{0.469}{0.185} = 2.5$ times as many particles as the original number of chemical molecules ($BaCl_2$).

The same conclusion, that the molecules of acids, bases, and salts are dissociated in aqueous solution, follows also from the study of the boiling-points and of the osmotic pressures of solutions.

The Ionic Theory.—It is seen then that a solution of hydrogen chloride, or sodium nitrate, or potassium hydroxide, etc., contains, besides undivided molecules of the solute, at least two other kinds of particles, H, Na, K, Cl, NO_3, OH, etc., which result from the dissociation of the molecules. These subdivisions of the original molecules have distinct physical and chemical properties of their own; the particles of Na and Cl, for example, are apparently as different from free molecular sodium and chlorine as is red phosphorus from yellow, or graphite from diamond. The explanation of the difference between these particles and ordinary molecules is best arrived at through a study of the electrical behavior of such solutions.

If the platinum terminals of a battery are dipped into a vessel filled with pure water, no passage of electricity will take place through the water; and if the same experiment is tried with anhydrous, liquid hydrogen chloride, the latter is also found to be a non-conductor. But if the two liquids are mixed, or if gaseous hydrogen chloride is dissolved in water, and the solution is tested in the same manner, it is found that electricity readily passes through the liquid. At the same time, equivalent quantities of hydrogen and chlorine are separated at the negative and positive pole, respectively. We have already seen that upon solution in water a fraction of the molecules of hydrogen chloride are broken up into peculiar particles of hydrogen and of chlorine; but, even if the hydrogen and chlorine particles were composed of conducting material, distributed throughout the non-conducting solvent as independent particles, they could not furnish a continuous medium for the passage of electricity. This will be clear when we recall the fact that although liquid mercury is an excellent conductor, mercury vapor, composed as it is of conducting particles, is not a conductor. Why then should the hydrogen and chlorine particles be attracted by electrically charged plates lowered into the solution?

The answer to this question is obvious. The only bodies which are found to be conspicuously attracted by electrically charged objects are bodies which are already provided with electric charges of their own. We are thus led to assume that molecules which undergo dissociation in solution divide themselves into a special kind of electrically charged sub-molecules. Since the solution itself has no charge, equal quantities of positive and negative electricity must be produced. Moreover, since like kinds of electricity repel one another, while unlike kinds attract each other, and since hydrogen and the metals are separated at the negative pole, while chlorine and other similar radicals go to the positive pole, we conclude that, upon solution in water, hydrogen chloride undergoes the change represented by the equation:

$$HCl \rightleftarrows H^+ + Cl^-.$$

In a similar manner, in aqueous solution,

$$AgNO_3 \rightleftarrows Ag^+ + NO_3^-,$$
$$NaOH \rightleftarrows Na^+ + OH^-,$$
$$K_2SO_4 \rightleftarrows 2K^+ + SO_4^{--}.$$

The negatively charged plate attracts all the positively charged particles, and, although these particles are in continuous and irregular motion, they nevertheless begin to move toward the plate in question; their motion in this direction is further encouraged by the fact that they are at the same time repelled by the positively charged plate. For similar reasons, the negatively charged particles travel in the opposite direction. Upon coming in contact with the plates, the particles lose their electric charges and change into the ordinary free forms of matter of which they are composed. If these are hydrogen and chlorine, the atoms of each unite in pairs to form molecules of ordinary gaseous hydrogen and chlorine. If however the particles are sodium and CO_3, for example, we find that equivalent amounts of hydrogen and oxygen are evolved at the cathode and anode, respectively; but if, instead of being made of platinum, the cathode consists of mercury, and the anode of silver, then the discharged sodium particles are taken up by the mercury, with which they form $NaHg_5$, and the CO_3-particles by the silver, with which they form insoluble Ag_2CO_3.

By rapidly whirling a tube filled with a solution of hydrogen, lithium, sodium, or potassium iodide in a powerful centrifugal machine it has been shown that the solution at the peripheral end of the tube acquires a negative electrical charge, while that at the central end acquires a positive charge. This behavior is readily explained by the ionic theory: The heavy iodide ions are driven outward by the centrifugal force so that they are present in excess at the outer end of the tube, while the lighter positive ions are left in excess in the central end. Upon ceasing to rotate the tube, the distribution of the positive and negative ions in the solution instantly reassumes its original condition.

Nomenclature.—The electrically charged radicals which result from the dissociation of the molecules of acids, bases, and salts upon solution in water, are called *ions.* The dissociation of molecules into ions is called *ionization,* and substances which are *ionized* are called *ionogens.* The positive ions, which separate at the negative pole, are called *cations* and the negative ions are called *anions.* Upon the ions formed from one molecule, the number of positive and negative charges is always equal; the number of charges upon any ion is the same as its valence as a radical.

Degree of Ionization.—In solutions made from salts, the greater, and by far the most active, part of the contents is almost invariably ionic. In the case of acids and bases there is a wider range, and a larger proportion of these are less highly ionized; but even then the ions are nearly always much more active than the undissociated molecules. The acids and bases that are commonly called "*strong*" are highly ionized, *i.e.*, their solutions are especially active because they contain high H^+- and OH^--ion concentrations. The degree of ionization of the commoner ionogens in normal and 0.1 normal solution is given in the following table:

1. ACIDS.

	Per cent. ionized.	
	Normal.	0.1 Normal.
H^+Cl^-, H^+Br^-, H^+I^-,	78.4	90
$H^+NO_3^-$,	82.0	90
$H^+HSO_4^-$,	51.0	60
$H^+HC_2O_4^-$,	....	34
$H^+C_2H_3O_2^-$,	0.4	1.3
$H^+HCO_3^-$,	....	0.12
H^+HS^-	....	0.05
H^+CN^-	....	0.01

2. BASES.

K^+OH^-	77	86
Na^+OH^-	73	86
Ammonia,	0.4	1.5

3. SALTS.[1]

Type M^+A^- (*e.g.*, $AgNO_3$, KCl, etc.),	75	86
Type $M^{++}A_2^-$ (*e.g.*, $Ba(NO_3)_2$, $SrCl_2$, etc.),	53	72
Type $M_2^+ A^{--}$ (*e.g.*, K_2SO_4, etc),	53	72
Type $M^{++} A^{--}$ (*e.g.*, $MgSO_4$, etc.),	....	45

THE LAW OF MASS-ACTION.

Ionic Equilibrium.—When acetic acid is dissolved in water, it ionizes as follows:

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-.$$

The quantity of the molecular acid that is ionized per second in a given quantity of the solution is proportional to the concentration of the un-ionized molecules (C_1), while the amount of the ions that unite to form molecules depends upon the frequency of the encounters of the two kinds of ions, which in turn is proportional to the product of their concentrations ($C_2 \times C_3$).

The speed of the respective actions will therefore be

$$S_1 = C_1 \times F_1 \text{ and } S_2 = C_2 \times C_3 \times F_2,$$

where F_1 is the intrinsic tendency of $HC_2H_3O_2$ to ionize, and F_2 is that of H^+ and $C_2H_3O_2^-$ to combine.

When equal amounts of material are being transformed each way, *i.e.*, at equilibrium, we have $S_1 = S_2$, whence

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[1] Notable exceptions are $CdCl_2$ and $HgCl_2$, which in 0.1 normal solution are 47 per cent. and 0.01 per cent. ionized, respectively, and $Pb(C_2H_3O_2)_2$, which gives a very low concentration of Pb^{++} ions.

$$C_1 \times F_1 = C_2 \times C_3 \times F_2,$$

or

$$\frac{C_2 \times C_3}{C_1} = \frac{F_1}{F_2} = K \qquad (1.)$$

$\frac{F_1}{F_2}$, being the ratio of two constants, is constant (=K). This ratio of the affinities driving the opposed actions is called the *affinity constant* of the reversible reaction. At any given temperature, the numerical value of K remains the same no matter what the total concentration of the solution may be. For example, the data, obtained from conductivity determinations, in regard to acetic acid, at 18°, are as follows:

Total molal concentration of acid	Proportion ionized	Molal concentration of H+,(C_2); and of $C_2H_3O_2^-$,(C_3).	Molal concentration of $HC_2H_3O_2$, (C_1).
1.	0.0041	0.0041	1. −0.0041
0.1	0.0130	0.0013	0.1 −0.0013
0.01	0.0407	0.000407	0.01−0.000407

Substituting these data in equation (1) above, we get:

$$\frac{(0.0041)^2}{0.9959} = 0.0000169; \quad \frac{(0.0013)^2}{0.0987} = 0.0000171;$$

$$\text{and } \frac{(0.000407)^2}{0.009593} = 0.0000172.$$

It is seen that, although the third solution is a hundred times more dilute than the first, and the degree of ionization has increased ten times, the values of **K** are practically identical in both cases.[1]

The Common-ion Effect.—When, through the presence of

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[1] When data like the above are applied in this way to the cases of highly ionized substances, the values of K are far from constant. The cause of this is not yet known. However, the general conclusions arrived at through the application of such data are as a rule not invalidated by this fact.

two substances with a common ion, C_2 is not equal to C_3, the law of mass action (formula 1) still holds. For example, if a single liter of solution contains 1 mol each of acetic acid and sodium acetate, the solution is uni-molal in respect to the acid and to the salt as well, and all the $C_2H_3O_2^-$ ions are available for uniting with either H^+- or Na^+-ions. C_3 in formula (1) is, therefore, abnormally large, and the ionization of the acid is repressed. In uni-molal sodium acetate, 0.53 of the salt is ionized, and, initially in the mixture of acid and salt, C_3 will be $0.53+0.004=0.534$, or nearly 134 times as large as in the acid alone. Since the fraction $\frac{C_2 \times C_3}{C_1}$ remains constant, and since C_1 is not appreciably increased by the small additional amount of molecular acid formed, the product $C_2 \times C_3$ must recover a value much nearer the old one; *i.e.*, C_2 must be diminished to about 1/134 of its former magnitude. The ionization of the salt is, of course, reduced also, but the $C_2H_3O_2^-$ ions furnished by the acid are relatively so few (0.004:0.53) that their effect upon the ionization of the salt is imperceptible. The H^+ and $C_2H_3O_2^-$ ions disappear in equivalent quantities, for they unite; but there are so few of the former that practically none of them remain, while *there are so many of the latter that the loss of a very few is not noticed.*

The student should especially note that the concentration of a given ion can be lowered in this way to almost nothing *only when that ion unites with an ion added to form a very slightly ionized substance, such as acetic acid, ammonium hydroxide,* etc. The addition of sodium chloride to sodium hydroxide solution, for example, produces no very marked effect, but the addition of ammonium chloride to ammonium hydroxide solution greatly reduces the hydroxide-ion concentration; similarly, the addition of sodium acetate to hydrochloric-acid solution greatly lowers the hydrogen-ion concentration, owing to the formation of the slightly ionized acetic acid.

The Theory of Precipitation.—One of the commonest and most interesting applications of the above conceptions is met with in connection with saturated solutions, especially those of relatively insoluble substances.

When a substance, like salt or sugar, is placed in contact with a liquid, such as water, there is a tendency for molecules to leave the solid and enter the liquid; after having done this the molecules move in every direction, and consequently some of them return to the solid and attach themselves to it. This occurs the more frequently, the greater the concentration of the molecules in the liquid becomes, until, finally, a stage is reached at which the number of molecules leaving the solid has become the same as the number of those deposited upon it in a given time. If the entire liquid is equally charged with dissolved molecules, the liquid immediately surrounding the solid will lose none by diffusion, and a condition of equilibrium will have been established. The quantity of undissolved solute remains thereafter unchanged, no matter how long the materials are left in contact. It is at this point that the solution is said to be saturated with respect to the substance dissolving.

In the case of silver bromate, for example, we have the following scheme of equilibria:

$$AgBrO_3(\text{solid}) \rightleftarrows AgBrO_3(\text{dissolved}) \rightleftarrows Ag^+ + BrO_3^-.$$

The solid $AgBrO_3$ molecules tend to enter the solution, while at the same time dissolved $AgBrO_3$ molecules tend to come out of solution, and the solution is saturated when these tendencies produce equal effects. The ions and any foreign material present do not deposit themselves upon the solid; they take, therefore, no *direct* part in the equilibrium which controls solubility. That is, *in solutions saturated at a given temperature by a given solute, the concentration of the dissolved molecules considered by themselves will be constant no matter what other substances may be present, provided their quantity is not great enough to change the nature of the solvent.*

The total solubility of an ionogen, as we ordinarily use the term, is made up of a molecular and an ionic part. The latter is not constant when a foreign substance giving a common ion is already in the liquid. In a saturated solution of silver bromate, for example, we have the mathematical relation (formula 1):

$$\frac{[Ag^+]\times[BrO_3^-]}{[AgBrO_3]}=\mathbf{K}, \text{ or } [Ag^+]\times[BrO_3^-]=\mathbf{K}\times[AgBrO_3].$$

But since, in a saturated solution, the concentration of the molecular salt $[AgBrO_3]$ is constant, its product into **K** is also constant. That is, *in a saturated solution of a given ionogen the product of the molal concentrations of the ions* (*e.g.*, $[Ag^+]\times[BrO_3^-]$) *is constant.* This product is called the **solubility product,** because the two values jointly determine the magnitude of the total solubility of the ionogen. The solubility of the molecules cannot be diminished, but the ionic part of the solute may become vanishingly small if the concentration of the common ion is made relatively great as compared with that of the other ion of the solute.

The theory of the precipitation and solution of *slightly soluble* ionogens may be summed up as follows:[1]

If the product of the molal concentrations of any pair of ions in a solution becomes greater than the solubility product for the saturated solution of the ionogen formed by their union, the latter will be precipitated until the ion-concentration product has been reduced to the value of the solubility product. And conversely, *if the product of the concentrations of any pair of ions in a solution is less than the solubility product for the saturated solution of the ionogen formed by their union, the latter, if present in sufficient excess, will*

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[1] That is, of ionogens formed by the union of one cation and one anion only. In other cases the solubility product should contain ion-concentrations raised to the second, third, etc., powers; but in reality the relations are not so simple. Thus, in the case of $PbCl_2$, if a soluble salt giving chloride ions (*e. g.* NaCl) is added to the saturated solution, some $PbCl_2$ will be precipitated in accordance with the theory; but the addition of a salt giving the common bivalent ion (*e. g.*, $Pb(NO_3)_2$), for some reason not yet known, fails to produce a precipitate.

continue to dissolve until the ion-concentration product has been increased to the value of the solubility product.

As an illustration of the effect of adding a salt with a common ion to the saturated solution of another salt, the following table is offered:

Solubility of $AgBrO_3$ in Mols per Liter.

Amount added per liter, in mols., of $KBrO_3$ or of $AgNO_3$	Solubility		
	$AgNO_3$ added	$KBrO_3$ added	Calculated
0	0.00810	0.00810	....
0.00850	0.00510	0.00519	0.00504
0.0346	0.00216	0.00227	0.00206

It is seen that a small excess of either salt reduces the solubility to one-fourth the value for pure water.

PART I.

A. DETECTION OF THE METALS.

GROUPS OF THE METALS.

For the purpose of qualitative analysis the metallic ions are divided into five groups in accordance with their deportment toward various reagents.

Group I.—Metals whose chlorides are insoluble in water and dilute acids: **Lead** (chloride slightly soluble), **silver, mercurous mercury.**

Group II.—Metals whose chlorides are soluble, but whose sulphides are precipitated from dilute acid solutions: **Mercuric mercury, lead, bismuth, copper, cadmium, arsenic, antimony, tin.**

Group III.—Metals whose sulphides are not precipitated from dilute acid solutions, but whose hydroxides or sulphides are precipitated by ammonia and ammonium sulphide, in the presence of ammonium salts: **Aluminium, chromium, zinc, manganese, iron, cobalt, nickel.**

Group IV.—Metals whose hydroxides and sulphides are soluble in the presence of ammonium salts, but whose carbonates are precipitated in the presence of ammonium salts: **Barium, strontium, calcium.**

Group V.—Metals whose chlorides, hydroxides, sulphides and carbonates are soluble in the presence of ammonium salts: **Magnesium, potassium, sodium, lithium, ammonium.**

GROUP I.

HYDROCHLORIC ACID GROUP.

To this group belong **lead, silver, and mercury in mercurous salts.** It is often called the silver group.

The chlorides of the metals of this group are insoluble in water and dil. HCl, with the exception of lead chloride, which is very sparingly soluble. If present in sufficiently small amount, lead may not be found at all in the first group; it should, however, if present, always be detected and removed in Group II., whether it was found in Group I. or not.

From an alkaline solution HCl may also precipitate many other substances; *e.g.*, As_2S_5 from an ammonium sulphide solution, metallic hydroxides from solution in caustic alkalies, etc. *If, therefore, the original solution is alkaline, do not add HCl, but see Part II.*

The sulphides of the metals of this group, like those of mercuric mercury, bismuth, copper and cadmium, are insoluble in cold, dilute acids and in ammonium sulphide.

PRELIMINARY EXPERIMENTS.

In performing the experiments with each metal the student should keep a concise record of his work, and afterward in analyzing a solution containing the metals of the group, he should refer to his record and *be sure that he understands thoroughly the effect of every reagent which he uses, and the object of every operation which he performs.* See Appendix for a form of record.

Lead.—Take 2 c.c. of a solution of a lead salt (*e.g.*, the nitrate) in a test-tube, add a little dil. HCl, shake vigorously and allow the white precipitate of $PbCl_2$ to settle. Decant the liquid. Boil the precipitate with water, pour off the solution, boil again with water and repeat until the lead chloride is completely dissolved. Test different portions of the solution with H_2S, dil. H_2SO_4 and $K_2Cr_2O_7$ solution. The precipitates are PbS, $PbSO_4$ and $PbCrO_4$.
black white yellow

Silver.—Take 2 c.c. of a solution containing silver. Add dilute HCl, with shaking, as long as white, curdy AgCl continues to form. Allow the AgCl to settle, decant, boil the precipitate with water, decant through a filter and test the filtrate for Ag^+ with H_2S. Add to the AgCl remaining in the test-tube NH_4OH and shake. To the solution, which contains the silver as ammonio-silver chloride, $[Ag(NH_3)_2]Cl$, add dil. HNO_3. The precipitate is $AgCl$. (yellow white)

$AgCl$, though very slightly soluble in water, dissolves readily in ammonia, owing to the union of the Ag^+-ions in the saturated solution with NH_3-molecules to form the complex cation $Ag(NH_3)_2{}^+$. This cation, however, is very slightly dissociated according to the equation: $Ag(NH_3)_2{}^+ \rightleftarrows Ag^+ + 2NH_3$. Upon the addition of HNO_3, OH^--ions in the solution unite with H^+-ions of the acid to form water, and in consequence the entire equilibrium, $NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4{}^+ + OH^-$, is displaced toward the right; the removal of the NH_3- molecules enables the complex cation to further dissociate, with the result that the $AgCl$ is reprecipitated, since the solubility product for its saturated solution is very soon exceeded.

Mercury in Mercurous Salts.—Take 2 c.c. of a solution of mercurous nitrate, $Hg_2(NO_3)_2$, add dil. HCl, shake, decant, boil the Hg_2Cl_2 three times with about 10 c.c. of water, decanting each time, to remove mercuric salts, then boil a fourth time, decant through a filter and test the filtrate for $Hg_2{}^{++}$ with H_2S. Add NH_4OH to the Hg_2Cl_2 remaining in the test-tube. The mercurous chloride is changed to a black mixture of ammonobasic mercuric chloride and mercury, $NH_2.Hg.Cl + Hg$.

ANALYSIS.

I. Hydrochloric Acid Group.

(1.) Precipitation.—Add to the neutral or slightly acid solution in a small beaker 4 c.c. of dil. HCl (sp. gr. 1.12), and dilute the mixture to 40 c.c. The precipitation of group I. is carried out in this way in order that the acid concentration of the filtrate may be suitable for the precipitation of Group II. by H_2S. *If the solution is at the start strongly acid with an unknown quantity of* H_2SO_4, *or if it contains free* HNO_3, *dil. HCl may be added here drop by drop as long as a precipitate continues to form and the mixture filtered without previous dilution.*

If the dilute solution already contains HCl, Group **I.** is of course absent.

a. *No precipitate is formed.* Silver and mercurous mercury are absent. Pass on to (**5.**).

b. *A precipitate may contain* $PbCl_2$, AgCl, Hg_2Cl_2. Shake the mixture, allow it to stand 2–3 minutes, filter, and wash the precipitate twice with small portions of cold water, rejecting the washings. Treat the filtrate by (**5.**).

(**2.**) **Lead.**—Pour a 5–10 c.c. portion of boiling water repeatedly over the precipitate on the filter. Divide the filtrate in two portions: to one add dil. H_2SO_4. A white pulverulent precipitate is $PbSO_4$. To the other portion add $K_2Cr_2O_7$ solution. A yellow precipitate is $PbCrO_4$.

(**3.**) **Silver.**—If lead has been found, wash the precipitate with hot water until the wash water no longer gives a precipitate with dil. H_2SO_4. Then pour a few c.c. of NH_4OH repeatedly through the filter, and acidify the filtrate with HNO_3. (*In every case like this, test the solution with litmus paper,* **after having thoroughly mixed the liquids.**)

If the $PbCl_2$ is not washed out, it is changed by the NH_4OH to a white basic salt, which runs through the filter and gives a turbid filtrate, but which is soluble in the HNO_3. If much mercury is present and silver is not found here, it is best to test the black mercury residue for silver as follows: Punch a hole in the filter and rinse the residue into a test-tube; allow to settle, and decant the liquid. Boil the solid with a little dilute *aqua regia*,[1] dilute the solution with an equal quantity of water, filter, and if a residue (AgCl) remains test it with NH_4OH and HNO_3.

(**4.**) **Mercurous Mercury.**—If the precipitate on the filter blackens on treatment with NH_4OH, (**3.**), the presence of mercurous mercury is shown.

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[1] *Aqua regia* should always be freshly prepared before use. In this case, cover the solid with 2–3 c.c. dil. HCl, add 2–3 drops conc. HNO_3 and boil.

GROUP II.

HYDROGEN SULPHIDE GROUP.

The chlorides of the metals of this group are soluble, but the sulphides are insoluble in cold dilute acids. The group is divided into two sub-groups.

A. The Copper Group.—To this belong **mercury in mercuric salts, lead, bismuth, copper** and **cadmium.** The sulphides of the metals of this sub-group are insoluble in yellow ammonium sulphide.

B. The Tin Group.—To this belong **arsenic, antimony** and **tin.** The sulphides of the metals of this sub-group are all soluble in yellow ammonium sulphide, with which they give the soluble sulpho-salts $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$. On adding dil. HCl to the solution the sulpho-salts are decomposed; H_2S is evolved, and a precipitate of As_2S_5, Sb_2S_5 and SnS_2 is obtained.

A. The Copper Group.

PRELIMINARY EXPERIMENTS.

Mercury in Mercuric Salts.—Take 1 c.c. of mercuric chloride, add a few drops of dil. HCl, dilute to 10 c.c., pass H_2S slowly as long as a change is observed in the color of the precipitate, warm, allow to settle and wash three or four times by decantation. Add 1 or 2 c.c. of dil. HNO_3, boil for a short time; then add 1–2 c.c. dil. HCl, and boil again. Cool the solution, dilute, filter, if necessary, and add to the liquid a small quantity of $SnCl_2$ solution, at first drop by drop, and then add several cubic centimeters. At first, white Hg_2Cl_2 precipitates; the excess of $SnCl_2$ reduces the white precipitate to gray, finely divided mercury.

Lead.—Take 10 c.c. of a solution of $PbCl_2$, add a little HCl, warm, pass H_2S, allow the PbS to settle, decant, wash, boil the precipitate with 1 c.c. of dil. HNO_3. To the solution containing lead nitrate, add 2–3 c.c. dil. H_2SO_4, and evaporate in a porcelain dish until dense white fumes of H_2SO_4 begin to come off. Cool and pour into 10–15 c.c. of cold water, rinsing out the dish with the same solution. Cool, shake, and filter. Pour repeatedly over the $PbSO_4$ on the filter a 10–20 c.c. portion of 10 per cent. $NH_4C_2H_3O_2$ solution, and to the filtrate add a few drops of $K_2Cr_2O_7$ solution and 2–3 c.c. $H.C_2H_3O_2$. The precipitate is $PbCrO_4$, "chrome yellow." The $PbSO_4$ dissolves in $NH_4C_2H_3O_2$ solution owing to the fact that $Pb(C_2H_3O_2)_2$ furnishes only a very low concentration of Pb^{++} ions.

Bismuth.—Take 2 c.c. of a solution of $BiCl_3$. Dilute to 10 c.c. This may cause the precipitation of BiOCl. Whether it does or not, warm, pass H_2S, allow the Bi_2S_3 to settle, decant, wash, boil the precipitate with 1 c.c. of dil. HNO_3. To the solution of $Bi(NO_3)_3$ add 2–3 c.c. conc. H_2SO_4, and evaporate in a porcelain dish until dense white fumes of H_2SO_4 begin to come off. Cool and pour into 10–15 c.c. cold water, rinsing out the dish with the same solution. To the clear, cold solution add NH_4OH slowly until its odor persists strongly after shaking. Shake, filter, and wash the precipitate. Dissolve the precipitate by pouring a very little dil. HCl through the filter, evaporate the filtrate until the residue is barely moist with acid, add 1–2 c.c. water, pour the solution into 100 c.c. warm water and allow the mixture to stand a couple of minutes. The precipitate is BiOCl. Filter, wash once, and pour through the filter a little freshly prepared sodium stannite solution.[1] The black residue is metallic bismuth.

The BiOCl formed upon the addition of $BiCl_3$ to water is produced according to the equation: $BiCl_3 + H_2O \leftrightarrows BiOCl + 2HCl$. If HCl is present in the solution, the reaction will not be complete, and some bismuth will remain in solution. The

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[1] Made by adding to 2–3 c.c. $SnCl_2$ solution, in a test-tube, a solution of NaOH until the precipitate at first formed redissolves on shaking. The solution must react alkaline with litmus paper.

quantity of this increases rapidly with the acid concentration in accordance with the law of mass-action. It is for this reason that the HCl must be so completely removed by evaporation, and that the solution must be added to so large a volume of water.

The formation of BiOCl according to the above equation is an example of **hydrolysis.** Two simpler examples will be considered here. When pure KCN is dissolved in water, the solution has a strongly alkaline reaction—*i.e.*, it exhibits the reactions of OH^--ions; but when pure $FeCl_3$ is dissolved in water, the solution shows the reactions of H^+-ions. In order to explain these phenomena it is necessary to take into account the fact that water itself is very slightly ionized into H^+- and OH^--ions. The extent of this ionization is so slight that it may ordinarily be neglected (in 1 liter of pure water there is present but 1/10,000,000 of a mol of H^+- or OH^--ions), but in the case of compounds which, while more highly ionized than water, are nevertheless themselves very slightly ionized (*e.g.*, HCN), the ionization of water becomes of the greatest importance. In such cases hydrolysis may take place. Thus, in a solution of KCN the H^+-ions of the water combine with the CN^--ions of the salt to form a small quantity of undissociated acid:

$$K^+,CN^- + H^+,OH^- \rightleftarrows K^+ + HCN + OH^-.$$

This removal of hydrogen ions must cause the dissociation of a further quantity of water and an increase in the number of hydroxyl ions, which will give to the solution an alkaline reaction. At the same time the odor of hydrocyanic acid will be apparent. Similar phenomena take place with carbonates and borates. With salts of weak bases hydrogen ions accumulate in the solution, which thus acquires an acid reaction.

$$Fe^{+++},3Cl^- + 3H^+,3OH^- \rightleftarrows 3H^+ + 3Cl^- + Fe(OH)_3.$$

In the case of $BiCl_3$, unstable $Bi(OH)_2Cl$ is probably the product formed by hydrolysis; it at once decomposing into BiOCl and H_2O. Or, on the other hand, it may be that BiOCl is directly formed, owing to the presence of O^{--} ions, from the secondary ionization $OH^- \rightleftarrows H^+ + O^{--}$.

Copper.—Take 2 c.c. of a copper salt solution, add a few drops of dil. HCl, dilute to 10 c.c., warm, pass H_2S, allow the CuS to settle, decant, wash, dissolve in 1 c.c. dil. HNO_3 by boiling, add 1–2 c.c. dil. H_2SO_4 to the nitrate solution and then NH_4OH until its odor persists strongly after shaking. The blue color is due to the complex ion $Cu(NH_3)_4^{++}$ (see under Cadmium). Acidify a portion of the solution with $HC_2H_3O_2$ and add 1–2 drops $K_4Fe(CN)_6$ solution. The red precipitate is $Cu_2Fe(CN)_6$. To the remainder of the solution add dil. H_2SO_4 till the deep blue color just disappears, then some iron filings and boil for a short time. Filter, acidify with dil. H_2SO_4, unless the solution is still acid, dilute and pass H_2S into the liquid.

Cadmium.—To 5 c.c. of a cadmium salt solution add 4 c.c. HCl (sp. gr. 1.12), and dilute to 40 c.c. Heat the solution nearly to boiling, and pass H_2S into the hot liquid for 2–3 minutes. Does a precipitate form? If so, filter. Now cool the liquid, add to it 60 c.c. water, and saturate the resulting solution in the cold with H_2S. Filter, wash the precipitate, and boil it in a test-tube with 2–3 c.c. dil. HNO_3. Add to the solution 1–2 c.c. dil. H_2SO_4, and then NH_4OH until its odor persists strongly after shaking. Acidify a portion of the solution with $HC_2H_3O_2$ and add 1–2 drops $K_4Fe(CN)_6$ solution. The white precipitate is $Cd_2Fe(CN)_6$. To the remainder add dil. H_2SO_4 to acid reaction, then some iron filings and boil for a short time. Filter, acidify with dil. H_2SO_4, unless the solution is still acid, and pass H_2S into the liquid. The yellow precipitate is CdS.

The $Cu(OH)_2$ and $Cd(OH)_2$, though very slightly soluble in water, dissolve readily in ammonia, owing to the union of the Cu^{++} and Cd^{++} ions in the saturated solutions with NH_3 molecules to form the complex ions $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$. These complex cations have an extremely slight tendency to dissociation, and the simple ion concentration (Cu^{++} or Cd^{++}) in the solution is exceedingly low. Ammonium salts, however, owing to the common ion effect, greatly reduce the OH^--ion concentration in the solution, and thus permit the Cu^{++} or Cd^{++} ion concentration, and therefore also the corresponding complex cation concentration, to attain a much higher value than in the saturated solutions of $Cu(OH)_2$ or $Cd(OH)_2$ in ammonia alone. In other words, the solubility of $Cu(OH)_2$ or $Cd(OH)_2$ in ammonia is greatly increased by the presence of ammonium salts. It should be noted that (in the case of cadmium, for example) the following distinct sets of equilibria are involved:

$$(1.)\ \underset{\text{(Solid)}}{Cd\,(OH)_2} \rightleftarrows \underset{\text{(Dissolved)}}{Cd(OH)_2} \rightleftarrows Cd^{++} + 2OH^-;$$

$$(2.)\ Cd^{++} + 4NH_3 \leftrightarrows Cd(NH_3)_4{}^{++};$$

$$(3.)\ NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4{}^+ + OH^-.$$

ANALYSIS.

II. Hydrogen Sulphide Group.

(5.) Precipitation.—Heat the solution, which should contain 4 c.c. HCl (sp. gr. 1.12), and which should have a volume of 40 c.c.,[1] in a small conical flask nearly to boiling, and saturate it hot with H_2S. Then, keeping the temperature at 70–90°, pass in H_2S for 15 minutes longer. Cool, add without filtering 60 c.c. cold water, completely saturate the mixture in the cold with H_2S, cork the flask, shake it, and allow it to stand for a short time.

a. *No precipitate forms.*—Group II. is absent. Treat the solution according to **(16.)**.

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[1] If the solution contains HNO_3, or an unknown quantity of HCl or H_2SO_4, and is free from silica and organic matter, add to a quantity of it sufficient to give about 1 gram of residue 5 c.c. conc. HNO_3, and evaporate the mixture in a porcelain dish under a hood until it is barely moist, *taking care not to ignite the residue,* since in that case As and Hg will be lost by volatilization, and tin will be rendered insoluble in HCl. Disintegrate the residue with the blunt end of a glass rod, add to it 2–3 c.c. conc. HCl, and evaporate until the residue is barely moist. Add to the residue 4 c.c. HCl (sp. gr. 1.12) from a small graduate, and about 20 c.c. water; boil gently for a few minutes. Pour the solution into a graduate and dilute the volume to 40 c.c. Treat this solution by (5.).

If a solid substance was originally started with, treat separately the various acid solutions obtained (each of which should contain 4 c.c. HCl, sp. gr. 1.12, or 1.5 c.c. H_2SO_4, sp. gr. 1.84, and have a volume of 40 c.c.) by (5.). See *Part II.*

b. *A fine white precipitate is formed.*—If the solution has changed in color from reddish-yellow to green, the presence of a chromate is indicated; if it has changed from purple to almost colorless the presence of a permanganate is indicated. Group II. is absent. Filter and treat the filtrate according to **(16.)**.

When oxidizing substances, like ferric salts, are present, H_2S is largely oxidized to sulphur and also to some extent to H_2SO_4. Barium, if present, is thereby precipitated as $BaSO_4$, and this may therefore also be contained in the precipitate. Hence, although barium does not belong to Group II., provision must be made for its detection here, since if present in small quantity all of it may have been removed from the solution at this point. The fine white precipitate is therefore filtered off and boiled (together with the filter) with strong Na_2CO_3 solution, which changes the $BaSO_4$ to $BaCO_3$. This is filtered off, washed, dissolved by pouring a little dil. HCl through the filter, the solution is heated to boiling, and then 1–2 c.c. dil. H_2SO_4 are added, and the mixture is allowed to stand. A white precipitate is $BaSO_4$.

c. *A colored precipitate is formed.*—This may contain HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, SnS, SnS_2, and also it may contain sulphur and a very little $BaSO_4$. Filter, and wash the precipitate thoroughly with hot water, rejecting the washings. Treat the filtrate according to **(16.)**. Treat the precipitate as described in **(6.)** unless it is known that the copper group alone is present, in which case treat the sulphides at once according to **(7.)**.

The precipitation of the sulphides by H_2S takes place as the result of reversible ionic chemical reactions, and the effect of acid upon the precipitation is explained as follows: When a dilute solution is saturated at a definite temperature and under a definite pressure with H_2S, the molecular H_2S always has a certain definite concentration, which corresponds to its solubility at that temperature and pressure. Now the H_2S itself is a very weak acid; it ionizes to a very slight extent into H^+ and HS^- ions, and still less into $2H^+$ and S^{--} ions. Only the latter form of ionization needs to be considered here (since the HS^- ions are not directly concerned in the action, and since the H^+-ion concentration derived from the H_2S is negligibly small). Now between the H_2S and its ions is maintained the equilibrium expressed by the equation $\frac{[H^+]^2 \times [S^{--}]}{[H_2S]} = \text{const.}$;[1] or, since in this case $[H_2S] = \text{const.}$, also $[H^+]^2 \times [S^{--}] = \text{const.}$ It is therefore evident that when $[H^+]$ is increased by the addition of acid to the solution, $[S^{--}]$ must be decreased in proportion; thus, if $[H^+]$ is doubled, $[S^{--}]$ is decreased to one-fourth. But in order that a sulphide (*e.g.*, CdS) may precipitate, the ion-concentration product $[Cd^{++}] \times [S^{--}]$ must exceed the value of the solubility product. The solubility product varies, however, with the nature of the sulphide and with the temperature; and therefore the acid (*i.e.*, H^+-ion) concentration that barely permits of precipitation when the metallic ion has a definite concentration is different for different sulphides and for the same sulphide at different temperatures.[2] Thus if the metallic ions are arranged in the order in which they are precipitated from cold HCl solutions of decreasing acid concen-

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[1] H_2S ionizes according to the scheme

$$\begin{tikzcd} & H^+ + HS^- \arrow[dl, shift left] \arrow[d, shift left] \\ H_2S \arrow[ur, shift left] \arrow[dr, shift left] & \\ & 2H^+ + S^{--} \arrow[ul, shift left] \arrow[u, shift left] \end{tikzcd}$$

In the equilibrium $H_2S \rightleftarrows H^+ + HS^-$, we have the relation $\frac{[H^+] \times [HS^-]}{[H_2S]} = \text{const.}$, and in the equilibrium $HS^- \rightleftarrows H^+ + S^{--}$, we have $\frac{[H^+] \times [S^{--}]}{[HS^-]} = \text{const.}$ Multiplying the two together, we get the expression $\frac{[H^+]^2 \times [S^{--}]}{[H_2S]} = \text{const.}$, which is the equilibrium condition for the reaction $H_2S \rightleftarrows 2H^+ + S^{--}$. This expression may be derived directly from the reaction, as follows (cf. previous development of the law of mass action): The speed of the forward action, $S_1 = [H_2S] \times F_1$, while that of the opposing action, $S_2 = [H^+]^2 \times [S^{--}] \times F_2$, where F_1 represents the tendency of the H_2S to ionize into $2H^+ + S^{--}$, and S_2 that of $2H^+$ and S^{--} to unite to form molecular H_2S. At equilibrium the two speeds are equal, whence $[H_2S] \times F_1 = [H^+]^2 \times [S^{--}] \times F_2$, or $\frac{[H^+]^2 \times [S^{--}]}{[H_2S]} = \frac{F_1}{F_2} = \text{const.}$

[2] Concerning the solubility of the sulphides in water, see the table of solubilities on the front cover sheet.

tration, the series is approximately as follows: As^{v} and As^{+++}, Hg^{++}, Cu^{++}, Sb^{v} and Sb^{+++}, Bi^{+++} and Sn^{++++}, Cd^{++}, Pb^{++} and Sn^{++}, Zn^{++}, Fe^{++}, Ni^{++} and Co^{++}, Mn^{++}.

As an example of the effect of dilution, consider a solution of $CdCl_2$, which has been somewhat strongly acidified with HCl, saturated in the cold with H_2S, and filtered from the precipitated CdS. The filtrate gives no more precipitate with H_2S, and in it exist the relations:

$$\frac{[H^+]^2 \times [S^{--}]}{[H_2S]} = \text{const.}, \quad \text{and} \quad \frac{[Cd^{++}] \times [S^{--}]}{[CdS]} = \text{const.}$$

Dividing the first equation by the second, we obtain the condition of equilibrium

$$\frac{[H^+]^2 \times [CdS]}{[Cd^{++}] \times [H_2S]} = \text{const.} = \mathbf{K}. \qquad (2.)$$

In cases such as this, in which the solution is saturated with CdS and with H_2S at a definite temperature and pressure, [CdS] and $[H_2S]$ have constant values. It follows therefore that in such cases $\frac{[H^+]^2}{[Cd^{++}]} = \text{const.}$, from which it is obvious that the less acid the solution, the more complete will be the precipitation of the cadmium upon saturation with H_2S.

Certain metals, especially pentavalent arsenic, are best precipitated by H_2S from hot, strongly acid solutions, while others, like cadmium, are not precipitated under these conditions. If too little acid is present, zinc may be precipitated, out of place, in Group II. It is therefore of the greatest importance to so regulate the acid concentration that it shall finally be sufficiently low to permit of the complete removal of the metals of Group II. by H_2S, and at the same time sufficiently high to prevent the precipitation of any zinc. *The beginner should be careful to follow the directions for the precipitation with H_2S as exactly as possible, since it is here of all places that he is most likely to fall into error.*

Owing to the volatility of $AsCl_3$ and $HgCl_2$, HNO_3 is added to the solution of unknown acid concentration before evaporation, in order to prevent the loss of any As or Hg that may be present (see note under **5.**).

(6.) Separation of the Copper and Tin Groups.—By means of a glass spatula[1] transfer the precipitate to a small procelain dish, add 5–10 c.c. $(NH_4)_2S_x$, cover the dish with a watch-glass, and warm very gently for ten minutes with frequent stirring (**do not boil**). Dilute with an equal volume of water, filter, and if there is a residue, wash it once with hot water. In order to ascertain whether the tin group has been completely removed, warm a small portion of the residue in a test-tube with 1 c.c. water and 5–10 drops $(NH_4)_2S_x$ solution, dilute with 1–2 c.c. water, filter, and make distinctly acid with dil. HCl. If the precipitate is finely divided and nearly white, the separation is known to be sufficiently complete; if, however, the precipitate is colored,[2] warm the main residue again with 5–10 c.c. $(NH_4)_2S_x$, as above, and filter, but keep this filtrate separate from the first one.

a. *The colored precipitate dissolves completely in* $(NH_4)_2S_x$. The copper group is absent. Treat the solution according to (**12.**). If there should be left a very minute quantity of a very light colored residue, insoluble in $(NH_4)_2S_x$, it should be at once examined for barium according to (**5.**) b.

b. *A colored residue is left.* The copper group is present. Treat the residue according to (**7.**); treat the $(NH_4)_2S_x$ filtrate according to (**12.**).

(7.) Mercuric Mercury.—Wash the $(NH_4)_2S_x$ residue thoroughly with hot water, to which, if the solid tends to run

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[1] Easily made by softening half an inch of glass tubing in the flame and pinching it with forceps. It should then be held in the flame again and annealed.

[2] A pronounced yellow color indicates arsenic or tin, and an orange-red color indicates antimony. Darker colored precipitates sometimes consist of mixtures of the sulphides of this sub-group, though their color may be due to traces of CuS (or of HgS), which are very slightly soluble in $(NH_4)_2Sx$, and which are reprecipitated, along with sulphur, upon acidifying the solution.

through the filter, add 2–3 grams of solid NH_4NO_3. Transfer the residue, which may contain HgS, PbS, Bi_2S_3, CuS, CdS, ($BaSO_4$ and SnS), to a small beaker, add 10–20 c.c. of a mixture of one volume HNO_3 (sp. gr. 1.20) and two volumes water, cover the beaker with a watch glass and boil gently for 2–3 minutes. Filter and wash. Treat the filtrate by (8.). Boiling HNO_3 of this concentration dissolves the sulphides of lead, bismuth, copper, and cadmium very quickly. Hardly any HgS is dissolved, unless the boiling is long continued, in which case the acid becomes more concentrated, black HgS is dissolved in part, and the remainder is converted into a heavy white compound, $Hg(NO_3)_2.2HgS$. Any SnS not extracted by the $(NH_4)_2S_x$ solution, is converted by the HNO_3 into meta-stannic acid, most of which remains undissolved (if much cadmium is present and tin is in the stannous state, as much as 15 mg. of the latter may be wholly left in the $(NH_4)_2S_x$ residue).[1]

Transfer the HNO_3 residue, with the filter if necessary, to a test-tube, add 2–3 c.c. conc. HCl and 4–5 drops conc. HNO_3, and boil, adding more HNO_3 if necessary. Dilute to 10–15 c.c., filter, add to the filtrate *clear* $SnCl_2$ solution, at first drop by drop, and finally 2–3 c.c. A white or gray precipitate shows the presence of mercury.

(8.) **Lead.**—To the filtrate containing Pb, Bi, Cu, Cd (and Ba) as nitrates, add 3–4 c.c. conc. H_2SO_4, and evaporate in a porcelain dish until dense white fumes of H_2SO_4 just begin to come off. Cool and pour cautiously into a small beaker containing 15 c.c. cold water, rinsing out the dish with the same solution. Shake, cool again, and allow to stand 4–5 minutes.

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[1] If it is necessary to recover any tin which may be present in the HNO_3 residue, transfer the latter to a porcelain dish, add 20–40 c.c. saturated bromine water, cover the dish, and warm gently under a hood for 5–10 minutes, with frequent stirring. Boil to expel the bromine, filter, cool the solution, and add to it a few drops of dil. HCl. Test the solution for mercury with $SnCl_2$ solution as described above. Bromine water dissolves HgS, but leaves in the residue any meta-stannic acid. (If the residue is still dark colored, extract it with a fresh portion of bromine water to remove the rest of the HgS, filter, and reject the filtrate.) Warm the residue gently with 2 c.c. $(NH_4)_2Sx$ solution, dilute with 2 c.c. of water, filter, and add the solution to the main $(NH_4)_2Sx$ extract obtained in (6.).

on Filter stand

Filter, wash the precipitate with dil. H_2SO_4 and then with a little water. Treat the filtrate by (**9.**). $PbSO_4$ is fairly soluble in dil. HNO_3[1] (or HCl) and therefore, to insure complete precipitation of lead, the HNO_3 must be entirely removed by evaporation. A finely divided, white precipitate indicates the presence of lead or of barium; but a coarsely crystalline precipitate may be due to bismuth—$(BiO)_2SO_4$. (If such a precipitate has separated with the $PbSO_4$, filter, treat the filtrate by (**9.**), and dissolve the precipitate by pouring repeatedly through the filter a 10 c.c. portion of HCl (sp. gr. 1.12), and treat the resulting solution by (**8.**).

Pour repeatedly over the $PbSO_4$ precipitate on the filter a 10-20 c.c. portion of 10 per cent. $NH_4C_2H_3O_2$ solution. To the filtrate add a little $K_2Cr_2O_7$ solution and 3-4 c.c. $HC_2H_3O_2$. A yellow precipitate is $PbCrO_4$. $(BiO)_2SO_4$ dissolves in $NH_4C_2H_3O_2$ solution and gives a yellow precipitate with $K_2Cr_2O_7$; but this precipitate, unlike $PbCrO_4$, is soluble in $HC_2H_3O_2$. If a white residue, insoluble in $NH_4C_2H_3O_2$, remains, it should be tested for barium according to (**5.**) **b**.

have this one already to test

(**9.**) **Bismuth.**—To the solution, containing Bi, Cu and Cd as sulphates, add NH_4OH until its odor persists strongly after shaking. Shake to coagulate the precipitate (BiOOH), filter, and wash. Treat the filtrate by (**10.**). Dissolve the precipitate by pouring 1-2 c.c. dil. HCl through the filter, evaporate *until the residue is barely moist* with acid, add 2 c.c. water, pour the solution into a flask containing 100 c.c. water heated until it can just be held in the hand, and allow to stand 2-3 minutes. A white precipitate is BiOCl. Filter, wash once, and pour over the precipitate a little freshly prepared Na_2SnO_2 solution. A black residue is metallic bismuth. This test is extremely delicate; if the BiOCl from just enough bismuth to produce a hardly visible turbidity is collected on a white filter and tested with Na_2SnO_2, the black color is very apparent.

(**10.**) **Copper.**—If the filtrate from (**9.**) is blue, copper is

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[1] 10 grams of pure 11 per cent. HNO_3 dissolve 33 mg. $PbSO_4$.

present. Acidify one-fourth of the solution with $HC_2H_3O_2$, add 2–3 drops $K_4Fe(CN)_6$ solution, and allow to stand five minutes. A red precipitate (or coloration) is $Cu_2Fe(CN)_6$. Treat the remainder of the solution by (**11.**). Cadmium is precipitated by $K_4Fe(CN)_6$ as white $Cd_2Fe(CN)_6$, but this does not hide the pink color of the $Cu_2Fe(CN)_6$, provided very little $K_4Fe(CN)_6$ is added; the copper salt is less soluble, and hence it precipitates first.

(11.) Cadmium.—If copper is absent, add dil. H_2SO_4 just to acid reaction, and pass H_2S through the solution. A yellow precipitate is CdS. If copper is present, add dil. H_2SO_4 till the deep blue color disappears, then some iron filings, boil for a short time, filter from the iron filings, and, unless the solution is still acid, just acidify it with dilute H_2SO_4, and pass into it H_2S. A yellow precipitate is CdS.

If, owing to previous errors in the analysis, a black precipitate (containing HgS, CuS, FeS, etc.) is obtained at this point, filter it off, wash it, and boil it with a mixture of 3 c.c. dil. H_2SO_4 and 10 c.c. water; filter, dilute the filtrate, and test it with H_2S. The diluted H_2SO_4 is without action upon HgS or CuS, it changes PbS to insoluble $PbSO_4$, and it dissolves CdS (and FeS).

When fragments of iron are immersed in a copper salt solution, the iron at once becomes coated with copper, and a quantitative examination of the solution shows that an atom of iron is dissolved for each atom of copper that is removed from the solution. This action will continue until the iron has completely dissolved, leaving in its place a spongy mass of metallic copper; or, if the iron is in excess, the process will continue until all of the copper is removed from the solution. Metallic silver, however, will not remove copper from such a solution; nor will iron remove cadmium from a cadmium salt solution. These facts are explained by the ionic theory as follows: Metallic iron and copper are made up of electrically neutral atoms, while copper and iron sulphate solution, for example, consist essentially of Cu^{++}- and SO_4^{--}-ions, and of Fe^{++}- and SO_4^{--}-ions, respectively. The real change, then, is $Fe + Cu^{++} \rightarrow Cu + Fe^{++}$; *i.e.*, the iron atoms assume the positive charges of the copper ions, the former entering the solution in the ionic condition while the latter are deposited as electrically neutral copper atoms. It has been found that every metal has a definite tendency to pass from the atomic to the ionic condition, as iron does in the above illustration. The impelling force here is called the *electrolytic solution tension* of the metal in question. Arranged in the decreasing order of magnitude of their solution tensions, the metals fall into the following series, known as the *electromotive series of the metals;* Na, Ca, Mg, Al, Zn, Cd, Fe, Ni, Sn, Pb, H, Bi, Sb, As, Cu, Hg, Ag, Pt, Au. In general, any metal when immersed in a solution containing ions of a metal of lower solution tension, will tend to displace that metal from solution.

B. The Tin Group.

PRELIMINARY EXPERIMENTS.

Arsenic in Arsenious Compounds.—Use a solution of As_2O_3 in HCl. (Such a solution contains, besides arsenious acid, a small quantity of unhydrolyzed $AsCl_3$, which ionizes according to the equation $AsCl_3 \rightleftarrows As^{+++} + 3Cl^-$.) Precipitate with H_2S, warming the solution. Filter, put the precipitate into a test-tube by means of a spatula, add a little $(NH_4)_2S_x$ and warm gently. The As_2S_3 dissolves as ammonium sulpo-arsenate, $(NH_4)_3AsS_4$. (Compare with the formula of ammonium arsenate.) Add dil. HCl to acid reaction, filter, wash and boil the As_2S_5 obtained with 1 or 2 c.c. of conc. HCl. Then add a fragment of $KClO_3$ and boil again. This time the arsenic will dissolve as arsenic acid, H_3AsO_4. Add NH_4OH to alkaline reaction, filter, if necessary, then add NH_4Cl and $MgCl_2$, and shake vigorously. The precipitate is $MgNH_4AsO_4$.

Arsenic in Arsenic Compounds.—Use a solution of sodium arsenate, Na_2HAsO_4. Pass H_2S into the cold solution and note carefully what happens. Now heat a fresh portion of the solution nearly to boiling, add 2–3 c.c. conc. HCl, and pass H_2S into the hot solution. The arsenic is precipitated in this case as a mixture containing As_2S_5 and (As_2S_3+2S) in varying proportions, according to the conditions. It often requires considerable time and trouble to completely remove the arsenic from such a solution.

Antimony.—Use a solution of $SbCl_3$. Warm, precipitate with H_2S, filter, dissolve the Sb_2S_3 in $(NH_4)_2S_x$, and acidify the solution with dil. HCl. Filter, boil the Sb_2S_5 with 10 c.c. HCl (sp. gr. 1.20) until the H_2S is completely expelled (the solution contains $SbCl_3$), filter if necessary, dilute to 50 c.c., heat, and pass in H_2S. Filter, dissolve the precipitate in strong HCl in a porcelain dish, lay in the dish a piece of platinum foil[1] and place upon it a piece of pure tin. The black deposit on the platinum is metallic antimony.

Tin in Stannous Compounds.—Use a solution of $SnCl_2$. Warm, precipitate with H_2S, filter, wash, dissolve the SnS in $(NH_4)_2S_x$ and add dil. HCl to the solution. The precipitate is now SnS_2. Filter, boil the precipitate with 10 c.c. HCl (sp. gr. 1.20) until the H_2S is completely expelled, dilute to 50 c.c., heat, and pass in H_2S. Cool the solution, dilute it with 30 c.c. water, and pass in H_2S. The yellow precipitate is SnS_2. Evaporate the mixture without filtering to 5–10 c.c., add about 1 gram of granulated zinc, and allow the action to continue for some time, but not until all the zinc is dissolved. The gray, spongy precipitate is metallic tin. Decant the solution, and heat the residue with 5 c.c. HCl (sp. gr. 1.20) until everything is dissolved. Dilute the solution with one-half its volume of water, and pour it at once into 5 c.c. $HgCl_2$ solution. The white precipitate is Hg_2Cl_2; this, of course, shows the presence of tin.

Tin in Stannic Compounds.—If $SnCl_4$ solution is used instead

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[1] Platinum is more valuable than gold and should be carefully preserved.

of $SnCl_2$ in the above experiments, the results are the same, except that the first precipitate in this case is SnS_2; SnS and SnS_2 both dissolve in $(NH_4)_2S_x$ to form $(NH_4)_2SnS_3$.[1]

ANALYSIS.

(12.) Dilute in a small flask the first portion of the $(NH_4)_2S_x$ solution with 20 c.c. of water, add to it dil. HCl until it reacts acid after shaking, and warm it slightly for five minutes with shaking to coagulate the precipitate.

a. *A finely divided* (not flocculent) *white or pale yellow precipitate is obtained.* The tin group is absent. Ammonium polysulphide gives such a precipitate of finely divided sulphur upon the addition of HCl, according to the equation: $(NH_4)_2S_x + 2HCl \rightarrow 2NH_4Cl + H_2S + (x-1)S$.

b. *A flocculent yellow or orange precipitate is obtained.* The tin group is present. (Treat the second portion of the $(NH_4)_2S_x$ solution in the same way, and unite the precipitate, if the sulphides of the tin group are present in it, with the first one.) Filter, and wash the precipitate, using suction; and finally suck it as dry as possible.[2] Reject the filtrate; treat the precipitate by **(13.)**.

c. *A buff-colored, brown, or dark gray precipitate is obtained.* A buff color indicates the presence of copper, a dark gray indicates that of mercury, both of whose sulphides are slightly soluble in $(NH_4)_2S_x$. The tin group may or may not be present. When the HCl precipitate is fairly small and is dark brown or gray or black, or of unpronounced yellow or orange color, so as to render it doubtful whether the tin group is present, the precipitate should be treated as follows: Heat it with 20 c.c.

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[1] SnS is insoluble in ammonium monosulphide, $(NH_4)_2S$; by ammonium polysulphide it is converted into SnS_2, which then reacts with the excess of the reagent to form $(NH_4)_2SnS_3$.

[2] In case a suction pump is not at hand, the precipitate may be freed from excess of moisture by pressing the filter containing it between several thicknesses of clean filter paper.

NH_4OH almost to boiling for five minutes and filter; test the residue for copper by **(7.)**, **(9.)**, and **(10.)**, unless copper has already been found present; pass into the filtrate H_2S for 15–20 seconds, filter if necessary, heat to boiling, acidify with dil. HCl, shake, filter off the precipitate and treat it by **(13.)**. In this way 1 or 2 mg. of copper, which might otherwise have been overlooked, may be detected. Moreover, the character of the HCl precipitate thus obtained will clearly indicate the presence or absence of the tin group, since the NH_4OH dissolves everything in the first HCl precipitate except CuS and sulphur, the H_2S precipitates any mercury present, and the final HCl precipitate can contain only sulphides of the sub-group and a little sulphur. Much time is saved if the tin group is thus found to be absent.

(13.) Arsenic.—Introduce the precipitate, which may contain As_2S_5, Sb_2S_5, and SnS_2, into a wide test-tube, add exactly 10 c.c. conc. HCl (sp. gr. 1.20), and heat for ten minutes, on a steam bath, with frequent stirring. Add 5 c.c. water from a portion of 40 c.c. contained in a graduate, filter, wash once with about 5 c.c. water from the graduate, collecting the washings with the filtrate; remove the filtrate, and add to it the rest of the 40 c.c. of water. Treat this solution by **(14.)**. *The directions in regard to the quantities of HCl and water used must be followed very closely, since the separation of antimony and tin (by* 14*) depends upon a proper concentration of the acid.*

Wash the residue of As_2S_5 with dil. HCl (sp. gr. 1.12), and then warm it in a test-tube with 5–10 c.c. dil. HCl (sp. gr. 1.12), adding solid $KClO_3$ one crystal at a time until the arsenic is dissolved; filter off the sulphur, and evaporate the solution to about 2 c.c. Add NH_4OH very slowly until its odor persists after shaking, cool, filter, and reject any precipitate. Add to the filtrate about one-third its volume of NH_4OH (sp. gr. 0.90) and at most 0.5 c.c. of magnesium ammonium chloride reagent "*magnesia mixture*," and shake vigorously for some time. If no precipitate forms, rub the walls of the test-tube with the end of a glass rod, and allow to stand for some time. A white crystalline precipitate is $MgNH_4AsO_4$. Dissolve it, after filtering, by pouring a little dil. HCl through the filter, heat the filtrate nearly to boiling, and pass H_2S for at least five minutes into the hot solution. A white precipitate turning yellow shows the presence of arsenic.

The main reaction between $KClO_3$ and conc. HCl is the formation of Cl_2; the yellow color is due to the formation of relatively little ClO_2. As_2S_5, though almost insoluble in HCl alone, is dissolved rapidly by it in the presence of Cl_2, because, owing to the destruction of the H_2S by oxidation, the equilibrium $As_2S_5 + 10HCl \rightleftarrows 2\ (AsCl_5) + 5H_2S$ is displaced from left to right. It dissolves to give H_3AsO_4; $AsCl_5$ has not been shown to exist, it is probably at once hydrolized to give H_3AsO_4. $MgNH_4AsO_4$ is somewhat soluble in water, hence the solution should be fairly concentrated. Owing to hydrolysis into NH_4OH and $Mg^{++} + HAsO_4^{--}$, the precipitate is much more soluble in water than in a conc. NH_4OH solution; therefore a large quantity of the latter should be added. Furthermore, the salt tends to form a supersaturated solution; hence the agitation. The NH_4Cl in the $MgCl_2$–NH_4Cl reagent prevents the precipitation of $Mg(OH)_2$ by NH_4OH, the common-ion (NH_4^+) reducing the OH^--ion concentration in accordance with the law of mass action.

(14.) Antimony.—Heat the solution from **(13.)**, which should contain 10 c.c. HCl (sp. gr. 1.20) in a total volume of 50 c.c., to about 90°, and pass into it H_2S for about five minutes, keeping the temperature at about 90°. If no precipitate is formed, add 5 c.c. water, and again saturate with H_2S at 90°. An orange-red precipitate is Sb_2S_3. Filter while hot, add 5 c.c. water, heat the filtrate nearly to boiling, saturate with H_2S to completely precipitate any antimony, and filter if a precipitate forms. Treat the solution by **(15.)**. If the HCl solution is too dilute, or if it is not kept hot, some SnS_2 may precipitate, and this when mixed with a little Sb_2S_3 gives a brown precipitate. Also, if mercury or copper were originally present, HgS or CuS may be precipitated at this point as a gray or black precipitate. Therefore, unless the H_2S precipitate is distinctly orange red in color, dissolve it in a little conc. HCl in a porcelain dish and evaporate the solution to about 1 c.c. Put beneath the solution a piece of platinum foil and place upon it a piece of pure granulated tin. After several minutes wash carefully with water. A jet black deposit on the platinum[1] is metallic antimony.

(**15.**) **Tin.**—Cool the filtrate from (**14.**), which may contain $SnCl_4$, dilute it with 20 c.c. of water, and pass in H_2S for ten minutes. A yellow precipitate is SnS_2. If there is a precipitate, evaporate without filtering to 5–10 c.c., add 1 gram granulated zinc, and allow the action to continue for at least 3 minutes, but not until all the zinc is dissolved (since the tin might then also dissolve). A gray, spongy precipitate is metallic tin. Decant the solution into a test-tube, allow any suspended particles to settle, decant again, and unite the two residues. Heat the residues of zinc and tin with 4–5 c.c. dil. HCl until everything (except any *black* particles of carbon) is dissolved. Dilute the solution with 2 c.c. of water, and filter it at once into a test-tube containing 5 c.c. $HgCl_2$ solution. A white precipitate of Hg_2Cl_2 shows the presence of tin.

OXIDATION AND REDUCTION.

When iron is heated in air, forming iron oxide, there is a direct addition of oxygen, and the process is called oxidation. If the oxide is heated in a current of hydrogen, its oxygen is removed, and it is said to be reduced. Instead of oxygen, other electro-negative elements, such as sulphur or chlorine, can be made to unite with iron to form compounds, in which, by suitable means, the iron may again be freed from the negative element in question. The meanings of the terms oxidation and reduction have been extended to include cases such as the

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[1] This deposit can be readily removed by covering the platinum with tartaric acid solution and then adding a drop or two of conc. HNO_3.

latter, in which other negative elements than oxygen are added or removed.

Iron dissolves in hydrochloric acid according to the equation, $Fe+2H^+ \rightarrow H_2+Fe^{++}$. If the resulting solution is evaporated, Fe^{++} and $2Cl^-$ unite, and solid $FeCl_2$ is obtained. The important change here really occurs when the iron atoms acquire positive charges; the oxidation of the iron upon solution consists in the acquisition by it of positive charges, and the hydrogen ions through the agency of which it receives these charges, are correspondingly reduced. If before evaporation, chlorine gas is passed into the solution of $FeCl_2$, and the solution is then evaporated, solid $FeCl_3$ is obtained. Here the essential change consists in the acquisition of a third positive charge by the iron atom, whereby it changes from a ferrous to a ferric ion, the properties of which are very different ($2Fe^{++}+4Cl^-+Cl_2 \rightarrow 2Fe^{+++}+6Cl^-$). At the same time, a chlorine atom has received a negative charge, thus becoming a chlorine ion; the chlorine has been reduced.

The oxidation of any substance may consist in the addition of atoms of a negative element to its molecules ($4FeO+O_2 \rightarrow 2Fe_2O_3$), *atoms* ($2Fe+3Cl_2 \rightarrow 2FeCl_3$), *or ions* ($SO_3^{--}+O \rightarrow SO_4^{--}$), *or in the withdrawal of atoms of a positive element; or it may consist in the addition of positive charges of electricity, or in the withdrawal of negative charges.*

Reduction is the reverse of this, namely, the addition of the atoms of positive elements or of negative electrical charges, or the withdrawal of the atoms of negative elements, or of positive electrical charges.

The oxidation of one substance always involves the simultaneous reduction of some other substance, and vice versa.

The changes in the state of oxidation which the elements may undergo are very characteristic of them, and therefore they are of great importance in analytical chemistry.

In the following examples the substance oxidized is placed first:

1. $2FeCl_2 + Cl_2 = 2FeCl_3$.
2. $2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl$.
3. $H_3AsO_3 + Cl_2 + H_2O = H_3AsO_4 + 2HCl$.
4. $3PbS + (\text{dil.})8HNO_3 = 3Pb(NO_3)_2 + 3S + 2NO + 4H_2O$.
5. $3PbS + (\text{conc.})8HNO_3 = 3PbSO_4 + 8NO + 4H_2O$.

Generally, in inorganic chemistry, the valence of some element is increased upon oxidation. In the fourth example, however, it is seen that this is not necessarily the case.

The substitution of one radical for another should not be confused with oxidation, *e.g.*, the equation,

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O,$$

does not represent an oxidation, but a simple double decomposition; the two NO_3-groups are not added, but simply take the place of one bivalent oxygen atom. But in the reaction,

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

the lead is oxidized, and one-fourth of the HNO_3 is reduced to NO. In the reaction,

$$K_2Cr_2O_7 + 8HCl + 3H_2S = 2KCl + 2CrCl_3 + 7H_2O + 3S,$$

the chromate is reduced, but the reaction,

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + H_2O + 2KCl,$$

does not represent an oxidation or a reduction. Why?

Several methods have been suggested for writing equations for reactions of oxidation and reduction. The one which seems to be most readily acquired by the beginner is given below.

In writing equations of oxidation and reduction, consider, on the one hand, the number of oxygen atoms the oxidizing agent furnishes, and, on the other hand, the number required for the substance to be oxidized, thus obtaining the relative numbers of molecules that enter into the reaction. For example, in the oxidation of $FeSO_4$ with HNO_3 in the presence of H_2SO_4, the $FeSO_4$ is known to be oxidized to $Fe_2(SO_4)_3$, and the HNO_3 to be reduced to NO.

Nitric acid here acts as an oxidizing agent according to the equation.

$$2HNO_3 = 2NO + H_2O + 3O. \qquad (1.)$$

The oxygen furnished by the nitric acid may be regarded as combining with the H of the sulphuric acid and liberating the acid radical, which then combines with the $FeSO_4$, as follows:

$$3H_2SO_4+3O=3H_2O+3(SO_4) \qquad (2.)$$

$$\text{and } 6FeSO_4+3(SO_4)=3Fe_2(SO_4)_3. \qquad (3.)$$

Adding (1.), (2.) and (3.), and cancelling the intermediate products assumed to have been formed, and which appear on both sides, we obtain the final equation:

$$6FeSO_4+2HNO_3+3H_2SO_4=3Fe_2(SO_4)_3+2NO+4H_2O.$$

Similarly, if, instead of sulphuric acid, hydrochloric, nitric, or acetic acid is present in the solution, we obtain the equations (the oxidizing agent is underlined):

$$6FeSO_4+\underline{2HNO_3}+6HCl=2Fe_2(SO_4)_3+2FeCl_3+2NO+4H_2O;$$

$$6FeSO_4+\underline{2HNO_3}+6HNO_3=2Fe_2(SO_4)_3+2Fe(NO_3)_3+2NO+4H_2O;$$

$$6FeSO_4+\underline{2HNO_3}+6HC_2H_3O_2=2Fe_2(SO_4)_3+2Fe(C_2H_3O_2)_3+2NO+4H_2O.$$

All four equations may be translated into the common ionic expression, $6Fe^{++}+6H^{+}+(3O)\rightarrow 6Fe^{+++}+3H_2O$.

Oxidizing agents.—Among the more important oxidizing agents are:

(1.) The halogens (Cl_2, Br_2), and oxygen.
(2.) Nitric acid, nitrates and nitrites.
(3.) *Aqua regia.*
(4.) Potassium chlorate.
(5.) Hydrogen and sodium peroxides.
(6.) Potassium dichromate.
(7.) Potassium permanganate.
(8.) Lead peroxide.

(1.) The halogens sometimes act directly:

$$2FeCl_2+Cl_2\rightarrow 2FeCl_3.$$

$$2K_4Fe(CN)_6+Br_2\rightarrow 2K_3Fe(CN)_6+2KBr.$$

Sometimes they act indirectly, as follows:

$$H_2O+Cl_2 \leftrightarrows HCl+HClO; \quad \text{and } HClO \rightarrow HCl+O;$$

e.g., $H_3AsO_3+H_2O+Cl_2 \rightarrow H_3AsO_4+2HCl$,

and $2NaCrO_2+8NaOH+3Br_2 \rightarrow 2Na_2CrO_4+6NaBr+4H_2O$.

(2.) As an oxidizing agent, HNO_3 is ordinarily reduced to NO. Its action has been illustrated above.

(3.) *Aqua regia* is prepared by mixing 1 volume (or less) HNO_3 with 3 volumes of HCl. Its action is practically the same as that of chlorine, which it furnishes according to the reaction:

$$3HCl+HNO_3 \rightarrow NO+2H_2O+3Cl.$$

In the absence of an oxidizable substance, however, the reaction is,

$$3HCl+HNO_3 \rightarrow NOCl+2H_2O+Cl_2.$$

(4.) When $KClO_3$ is used as an oxidizing agent in the presence of conc. HCl, the effect is similar to that of *aqua regia* and of chlorine, as is indicated in the following equations:

$$2KClO_3+2HCl \rightarrow 2HClO_3+2KCl;$$
$$2HClO_3+2HCl \rightarrow 2ClO_2+2H_2O+Cl_2.$$

i.e., $2KClO_3+4HCl \rightarrow 2KCl+2ClO_2+2H_2O+Cl_2$.

The main reaction is, however,

$$KClO_3+6HCl \rightarrow KCl+3H_2O+3Cl_2,$$

ClO_2 being formed in relatively small amount.

(5.) Hydrogen peroxide gives water and oxygen; *e.g.*, in the oxidation of $Cr(OH)_3$ in alkaline solution,

$$2Cr(OH)_3+3H_2O_2 \rightarrow 2H_2CrO_4+4H_2O;$$
$$2H_2CrO_4+4NaOH \rightarrow 2Na_2CrO_4+4H_2O.$$

i.e., $2Cr(OH)_3+3H_2O_2+4NaOH \rightarrow 2Na_2CrO_4+8H_2O$.

(6.) $K_2Cr_2O_7$, in acid solution, may be considered to act as follows in the presence of oxidizable substances:

$$K_2Cr_2O_7+8HCl=2KCl+2CrCl_3+4H_2O+3O$$

or $K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O$.

Thus: $6FeSO_4+K_2Cr_2O_7+8H_2SO_4 \rightarrow 3Fe_2(SO_4)_3+2KHSO_4+Cr_2(SO_4)_3+7H_2O$.

(7.) $KMnO_4$, in acid solution, acts as follows:

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$.

Thus: $10FeSO_4 + 2KMnO_4 + 9H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 +$
$2MnSO_4 + 2KHSO_4 + 8H_2O$.

(8.) PbO_2, in the presence of certain oxidizable substances, gives PbO and O, the PbO dissolving in the nitric acid present. Thus:

$2MnO_2 + H_2O + 3O \rightarrow 2HMnO_4$;
$3PbO_2 + 6HNO_3 \rightarrow 3Pb(NO_3)_2 + 3H_2O + 3O$;

i.e., $2MnO_2 + 3PbO_2 + 6HNO_3 \rightarrow 2HMnO_4 + 3Pb(NO_3)_2 + 2H_2O$.

Reducing agents.—Some important reducing agents are:

(1.) Nascent hydrogen and metals:
$SnCl_4 + 2H \rightarrow SnCl_2 + 2HCl$.
$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$.

(2.) Hydrogen sulphide ($H_2S + O \rightarrow H_2O + S$):
$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$.
$K_2Cr_2O_7 + 8HCl + 3H_2S \rightarrow 2KCl + 2CrCl_3 + 7H_2O +$
$3S$.

(3.) Stannous chloride ($SnCl_2 + 2Cl \rightarrow SnCl_4$):
$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$,
$HgCl_2 + SnCl_2 \rightarrow Hg + SnCl_4$.
$K_2Cr_2O_7 + 14HCl + 3SnCl_2 \rightarrow 3SnCl_4 + 7H_2O +$
$2KCl + 2CrCl_3$.

(4.) Sulphurous acid ($H_2SO_3 + O \rightarrow H_2SO_4$):
$2KMnO_4 + 5H_2SO_3 \rightarrow 2KHSO_4 + 2MnSO_4 +$
$H_2SO_4 + 3H_2O$.

(5.) Oxalic acid ($H_2C_2O_4 + O \rightarrow H_2O + 2CO_2$):
$2KMnO_4 + 5H_2C_2O_4 + 4H_2SO_4 \rightarrow 10CO_2 + 8H_2O +$
$2KHSO_4 + 2MnSO_4$.

(6.) Alcohol ($C_2H_6O + O \rightarrow C_2H_4O + H_2O$):
$K_2Cr_2O_7 + 8HCl + 3C_2H_6O \rightarrow 2KCl + 2CrCl_3 +$
$7H_2O + 3C_2H_4O$.

GROUP III.

AMMONIUM SULPHIDE GROUP.

This group contains the metals whose sulphides, though soluble in dilute acids, are insoluble in water in the presence (or absence) of ammonium salts. These metals are all precipitated from neutral solution by $(NH_4)_2S$; zinc, manganese, iron, cobalt, and nickel are precipitated as sulphides, while chromium and aluminium, owing to hydrolysis, are precipitated as hydroxides by $(NH_4)_2S$. Fe^{+++}, Al^{+++}, and Cr^{+++} are precipitated as hydroxides upon the addition of NH_4OH, even in the presence of ammonium salts; Fe^{++}, Co^{++}, Ni^{++}, Mn^{++}, and Zn^{++}, in the presence of ammonium salts, are not precipitated by NH_4OH (but in the presence of air, iron and manganese, owing to oxidation, are slowly precipitated), unless phosphates, etc., are present.

In the presence of phosphates, borates, oxalates, fluorides, etc., calcium, strontium, barium, and magnesium may also be precipitated with this group upon the addition of NH_4OH.

This group is divided into two sub-groups:

A. The Aluminium Group.—To this belong **aluminium, chromium,** and **zinc,** whose hydroxides are readily soluble in a mixture of NaOH and Na_2O_2 (or H_2O_2).

B. The Iron Group.—To this belong **manganese, iron, cobalt,** and **nickel,** whose hydroxides are insoluble in a mixture of NaOH and Na_2O_2 (or H_2O_2).

PRELIMINARY EXPERIMENTS.

Aluminium.—To an aluminium salt solution add NH_4Cl, boil and add NH_4OH. Filter, wash, and dissolve the precipitate in a little dil. HCl. Dilute the solution to 10 or 15 c.c., make it alkaline with NaOH solution, cool, and add 1–2 grams solid Na_2O_2, with stirring (the $Al(OH)_3$ will dissolve just as well in an excess of NaOH, without the addition of Na_2O_2). Boil, acidify the solution containing $NaAlO_2$ with dil. HNO_3, and add gradually to the hot solution NH_4OH until the solution smells of it after shaking. Dissolve the precipitate of $Al(OH)_3$ in about 5 c.c. dil. HNO_3, and to the solution add about 5 mg. of cobalt as cobalt nitrate solution. Evaporate almost to dryness in a porcelain dish, add a drop or two of water, and take up the solution in a small piece of filter paper. Roll up the paper, wind a platinum wire around it to form a spiral, incinerate the paper in a small flame, and finally heat the residue strongly. The blue substance, whose formula is not definitely known, is a compound of the two oxides, CoO and Al_2O_3; it may be simply cobalt aluminate, $Co(AlO_2)_2$.

Chromium.—To a chromium salt solution add NH_4Cl, boil, and add NH_4OH until the liquid smells of it after shaking. Filter, wash, dissolve the precipitate in a little dil. HCl. Dilute the solution to 10–15 c.c., make it alkaline with NaOH solution, cool, and add 1–2 grams solid Na_2O_2, in small portions, with stirring. Boil to decompose the excess of Na_2O_2, acidify the solution containing Na_2CrO_4 with dil. HNO_3, and add to the hot solution an excess of NH_4OH. Acidify the resulting solution with $HC_2H_3O_2$, and add $BaCl_2$. The yellow precipitate is $BaCrO_4$. Dissolve it, after filtering in a very little dil. HNO_3, add 9–10 volumes of water, and to a portion of the cold solution in a test-tube add about 2 c.c. ether and 1 c.c. H_2O_2, and shake. The blue compound is a perchromic acid, probably H_3CrO_7. It is very unstable; by its decomposition oxygen is evolved and the chromium is reduced to a chromic salt. Its decomposition is greatly accelerated by an excess of H_2O_2, by the presence of much acid, and by raising the temperature.

Acidify a solution of $K_2Cr_2O_7$ with HCl, and saturate it with H_2S. Boil, filter, add NH_4Cl and NH_4OH. What is the precipitate? Account for the change in the color of the solution.

Zinc.—To a zinc salt solution add NH_4Cl, and NH_4OH in excess; then add $(NH_4)_2S$ (or H_2S). Warm, filter, dissolve the precipitate of ZnS in dil. HCl, boil to expel the H_2S (why expel it?), dilute to 10–15 c.c., and add NaOH in excess. Acidify the solution containing Na_2ZnO_2 with dil. HNO_3, and add NH_4OH in excess. Acidify the solution containing $[Zn(NH_3)_4](NO_3)_2$ with $HC_2H_3O_2$, and pass into it H_2S. The precipitate is ZnS. Filter, and pour a 10 c.c. portion of dil. HNO_3 repeatedly through the filter. To the resulting solution add 4–5 mg. cobalt as cobalt nitrate solution. Evaporate in a porcelain dish almost to dryness, neutralize with Na_2CO_3 solution, and add about 0.5 c.c. in excess. Evaporate to dryness, ignite gently until the purple color disappears, and allow the dish to cool. The green substance is a compound of cobalt and zinc oxides, possibly cobalt zincate, $CoZnO_2$.

Acidify a zinc salt solution with about 1 c.c. dil. HCl, and pass into it H_2S. Acidify a second portion in the same way, add to it an equal volume of saturated $NaC_2H_3O_2$ solution, and again pass in H_2S. Explain the results by the ionic theory and the law of mass action.

Manganese.—To a manganese salt solution add NH_4OH. shake, and note carefully what happens. Can you redissolve the precipitate by adding NH_4Cl? Why?

To another portion of the same solution add an equal volume of NH_4Cl solution, boil, and then add NH_4OH (is there any difference?). Now add $(NH_4)_2S$ (or H_2S), warm, and filter. Dissolve the precipitate in a little dil. HCl, boil to expel H_2S, dilute the solution to 10–15 c.c., make it alkaline with NaOH solution, cool, and add 1–2 grams solid Na_2O_2, in small portions, with stirring. Filter off and wash the precipitate of $MnO(OH)_2$, transfer it to a porcelain dish, add 15–20 c.c. dil. HNO_3 and 2–3 c.c. 3 per cent. H_2O_2, with stirring. Evaporate the solution to 1–2 c.c. in a porcelain dish; then, *under a hood*, add 10–15 c.c. conc. HNO_3, heat to boiling, add about 0.5 gram solid $KClO_3$ and boil gently for 2–3 minutes. (MnO_2 is not soluble in HNO_3, but upon the addition of H_2O_2 to the mixture it is reduced to MnO, which is readily soluble in the HNO_3. Manganese salts are rapidly oxidized to hydrated MnO_2 by $HClO_3$ in nitric acid solution, with evolution of ClO_2 gas.) Filter off the precipitate with an asbestos filter, made by pouring a suspension of washed asbestos over a compact wad of glass wool in a glass funnel. Transfer the precipitate to a porcelain dish, add 1–2 grams PbO_2, and about 10 c.c. dil. HNO_3; boil for a short time, pour the mixture into a test-tube, and allow the excess of PbO_2 to settle. The solution is violet red in color, owing to the presence of $HMnO_4$.

Iron.—Saturate an acid solution containing a ferric salt with H_2S, boil to expel H_2S, filter, and add to the filtrate containing Fe^{++}-ions NH_4OH to alkaline reaction, and then a little $(NH_4)_2S$. Filter off and wash the precipitate, dissolve it in a little dil. HCl, dilute to 10–15 c.c., and make the solution alkaline with NaOH; then add about 1 gram solid Na_2O_2. The $Fe(OH)_2$ is changed to dark red $Fe(OH)_3$ by the Na_2O_2. Dissolve the precipitate, after filtering, in dil. HCl, and divide the solution into three portions. To one add NH_4OH; to another add $K_4Fe(CN)_6$ solution; and to the third add KSCN solution. The two precipitates are $Fe(OH)_3$ and $Fe_4[Fe(CN)_6]_3$, respectively, and the third portion of the solution is colored red, owing to the formation of un-ionized $Fe(SCN)_3$. This test may be made in the presence of much HCl, for HSCN is also a highly ionized acid, which is therefore not displaced from its salt. Much HNO_3 must not, however, be present: for, by its action on KSCN, NO_2, which also gives a deep red color with KSCN, may be formed. The test is extremely delicate, and if only a faint red color is obtained, the acids used must be tested for iron.

Cobalt.—To a cobalt salt solution add NH_4Cl and NH_4OH, then add $(NH_4)_2S$. Filter, wash, add to the precipitate 5 c.c. dil. HCl and stir. Then add about 1 c.c. dil. HNO_3 and warm. Make the resulting solution alkaline with NaOH, and then add about 1 gram solid Na_2O_2. The precipitate is $Co(OH)_3$; dissolve it in dil. HCl, and to the $CoCl_2$ solution add NH_4OH and a little $(NH_4)_2S$. Dissolve the precipitate in a very little aqua regia (*hood*), evaporate nearly to dryness, add 5 c.c. water, and then NaOH solution drop by drop, with shaking, until a permanent precipitate just forms. Add 3 c.c. $HC_2H_3O_2$ and then 5 c.c. 30 per cent. KNO_2; dilute to 15 c.c. and allow to stand. The yellow precipitate is $K_3Co(NO_2)_6$. Test the precipitate in a borax bead. The deep blue color of the bead is due to cobalt.

In the formation of $K_3Co(NO_2)_6$ the cobaltous salt is oxidized to cobaltic by the nitrous acid set free from its salt by the $HC_2H_3O_2$, the cobaltic salt combining as fast as formed with the KNO_2, according to the equations:

$$Co(NO_2)_2+2HNO_2 \rightarrow Co(NO_2)_3+H_2O+NO,$$
$$\text{and } Co(NO_2)_3+3KNO_2 \rightarrow K_3Co(NO_2)_6.$$

The $K_3Co(NO_2)_6$ is somewhat soluble in water but very difficultly soluble in a concentrated KNO_2 solution, owing to the common-ion effect of the potassium ion.

Nickel.—With a nickel salt solution, perform the same experiments as with cobalt, up to the addition of $HC_2H_3O_2$. Instead of $HC_2H_3O_2$, add to the neutral solution 10 per cent. KCN solution (**Caution:** KCN is an extremely dangerous poison) drop by drop until the precipitate at first formed is redissolved, and then add about 0.5 c.c. more. To the resulting solution add 5 c.c. of 10 per cent. NaOH solution, and then saturated bromine water, until a piece of filter paper moistened with KI and starch solutions, when dipped into the solution is colored blue or brown. The black precipitate is $Ni(OH)_3$.

The NaOBr formed in the solution first decomposes the excess of KCN present; it then oxidizes the nickel to the nickelic state, whereupon it is precipitated as $Ni(OH)_3$ by the NaOH present.

The Effect of the Presence of Phosphates, Borates, Oxalates, etc., upon the Precipitation of Group III.—Dissolve a little solid $Ca_3(PO_4)_2$ in a few c.c. dil. HCl, and add to the solution NH_4Cl,

NH_4OH to alkaline reaction, and $(NH_4)_2S$. The precipitate is $Ca_3(PO_4)_2$. Try the same experiment with a solution of $CaCl_2$ or $Ca(NO_3)_2$. Explain the formation of the $Ca_3(PO_4)_2$ precipitate.

ANALYSIS.

III. Ammonium Sulphide Group.

(16.) Precipitation.—Boil the filtrate from Group II. **(5.)** till the H_2S is expelled. Transfer it to a flask, add NH_4OH until its odor persists slightly after shaking, and then 3–4 c.c. more; note the appearance of any precipitate that may be formed. Then pass H_2S into the mixture until, after shaking, the vapors in the flask blacken a piece of filter paper moistened with a drop of $Pb(C_2H_3O_2)_2$ solution.[1] Shake the mixture or heat it nearly to boiling (to coagulate the precipitate).

a. *No precipitate is formed.* Group III. is absent. Proceed to **(24.)**.

b. *A precipitate is obtained.* Filter off the precipitate and wash it, first with water containing a few drops $(NH_4)_2S$, and then with a little pure water. During the filtration, keep the funnel covered with a watch glass, in order to prevent oxidation to soluble sulphates. To the filtrate add a few drops $(NH_4)_2S$, boil the mixture for a few seconds, and filter if there is a precipitate, uniting it with the preceding one. Treat the precipitate by **(17.)** and the filtrate by **(24.)**.

The H_2S is boiled out, and the effect produced by NH_4OH alone is noted, because it often gives a useful indication as to what elements are present. Instead of adding $(NH_4)_2S$ to the alkaline solution, H_2S is passed into it because in this way the solution of any NiS is entirely prevented. (If, however, it is preferred to use $(NH_4)_2S$, and the filtrate is brown or nearly black, the NiS may be precipitated from it by boiling the solution for a few minutes. It should then be united with the main precipitate.)

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[1] Instead of H_2S, $(NH_4)_2S$ may be used at this point.

The presence of a considerable amount of NH_4Cl (or other ammonium salt), such as is formed by the neutralization of the acid already in the solution, lessens the solubility of $Al(OH)_3$ (a so-called amphoteric substance which ionizes both as a base and as an acid) in NH_4OH, and also serves to prevent the precipitation of the $Mg(OH)_2$, etc. For the elements of Group III., and also for magnesium, the value of the solubility product for the saturated hydroxide solution is so small that even if 1 mg. of the element is present in 50 c.c. of solution, the product $[M^{++}] \times [OH^-]^2$ (or $[M^{+++}] \times [OH^{-3}]$) exceeds it, and precipitation results upon the addition of a slight excess of NH_4OH. In the presence of much NH_4Cl, however, owing to the common-ion effect, the ionization of the NH_4OH and, therefore, the value of $[OH^-]$ in the solution is so reduced that for certain elements the product $[M^{++}] \times [OH^-]^2$ does not reach the value of the solubility product, even when $[M^{++}]$ is moderately large. But in the cases of ferric iron, aluminium, and chromium the solubility of the hydroxides in water is so slight that even in the presence of NH_4- salts their solubility is not appreciable. In the cases of zinc, nickel, and cobalt (and of chromium to a much lesser extent), just as with silver, copper, and cadmium, the excess of NH_3 combines with the simple cation M^{++} to form complex cations such as $Zn(NH_3)_4{}^{++}$, etc., thus displacing the equilibrium, $M(OH)_2$ solid$\rightleftarrows M(OH)_2$ dissolved$\rightleftarrows M^{++} + 2OH^-$, and rendering the hydroxide more soluble.

When phosphate, fluoride, borate, or oxalate is present, magnesium, calcium, strontium, barium, and manganese may be precipitated by NH_4OH. Fluoride will ordinarily have been removed, however, in the evaporation with acids in the preparation of the solution;[1] the borates of the alkali earth elements are not sufficiently insoluble to be precipitated,[2] unless they are

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[1] See Part II.

[2] The solubility of the alkali earth borates (and fluorides) is increased by the presence of ammonium salts.

present in large quantity; and oxalate, even if present, does not make any change necessary in the usual process of analysis; for much of the oxalate is separated from the alkali earths in (**17.**), and the rest of it is destroyed in (**21.**). It is necessary, however, when phosphate is present, to provide for the detection of the alkali earth metals in the analysis of the precipitate. The tertiary and secondary phosphates of these elements are difficultly soluble in water, but they are readily soluble in acids, owing to the formation of the much more soluble primary phosphates or of free phosphoric acid (by the union of H^+-ion with HPO_4^{--} or PO_4^{---}-ion). Upon the addition of a base to such a solution, H^+-ions are removed, $H_2PO_4^-$ -ion and H_3PO_4 dissociate to give HPO_4^{--} and PO_4^{---}, and these ions cause the precipitation of the alkali earth metals. If, however, ferric iron, which forms a more insoluble phosphate, is also present, it combines with the phosphate radical, and the alkali earth metals remain in solution.

(**17.**) **Separation of The Aluminium and Iron Groups.**—Transfer the $(NH_4)_2S$ precipitate (with the filter if necessary) to a porcelain dish; add 5–20 c.c. dil. HCl, according to the size of the precipitate, stir for a minute in the cold and then boil the mixture; if a black residue remains, add to the mixture a few drops conc. HNO_3 and boil again. Add a little water, filter from any sulphur, and evaporate the filtrate to 1–2 c.c. to remove most of the acid. Dilute the solution to 15–20 c.c.; make it alkaline with NaOH solution (avoiding a large excess), and if the precipitate is very large add 10–20 c.c. more water. Cool the mixture, and add to it 1–3 grams solid Na_2O_2, in small portions with constant stirring. Then add 5 c.c. 10 per cent. Na_2CO_3 solution, unless the alkali earth metals are known to be absent. *Boil to decompose the excess of* Na_2O_2, cool, and dilute with an equal volume of water.

a. *No precipitate is obtained.* The iron group is absent. Treat the solution by (**18.**).

b. *A precipitate is obtained.* Filter it off (with suction, if possible), and wash it with hot water. Treat the filtrate by (**18.**); the precipitate by (**21.**).

All the hydroxides and all the sulphides of the group, except CoS and NiS, usually dissolve readily in cold, dil. HCl. The fact that these two sulphides dissolve so much less readily in dilute acids than the others seems to be due to an unusually slow rate of solution, and not to a lesser solubility in water. By NaOH, Fe, Mn, Co and Ni are completely precipitated and do not dissolve in excess, while the hydroxides of Al, Cr, and Zn, being amphoteric substances, are soluble in a sufficient excess, forming with the NaOH aluminate ($NaAlO_2$), chromite ($NaCrO_2$), and zincate (Na_2ZnO_2). When zinc and chromium are both present they are precipitated together, possibly as zinc chromite, $Zn(CrO_2)_2$, or as chromium zincate, $Cr_2(ZnO_2)_3$. Upon the addition of Na_2O_2, $Fe(OH)_2$ is changed to $Fe(OH)_3$, $Mn(OH)_2$ to hydrated MnO_2, $Co(OH)_2$ to $Co(OH)_3$, and $Ni(OH)_2$ partially to $Ni(OH)_3$, all of which are insoluble in excess of NaOH. The $NaCrO_2$ in the solution is changed by Na_2O_2 into Na_2CrO_4, which remains in solution. The Na_2CO_3 is added in order to completely precipitate any alkali earth metals which may be present; it also decomposes the chromates of these metals, *and if it is not added, chromium may remain in the precipitate and escape detection.* This separation with NaOH, Na_2O_2, and Na_2CO_3 is very satisfactory, except in the case of zinc. This metal, when present in small quantities, is completely carried down in the precipitate if much iron, nickel, or cobalt, or especially manganese, is present. Provision must therefore also be made in sub-group B for the detection of zinc.

THE ALUMINIUM GROUP.

ANALYSIS.

(**18.**) **Aluminium.**—Acidify the alkaline filtrate from (**17.**) with HNO_3, avoiding a large excess; add NH_4OH till its odor persists after shaking, and then add 2–3 c.c. more to keep the zinc in solution. Heat to boiling, filter if there is a precipitate, and wash it thoroughly with hot water. Treat the filtrate by **(19.)**. Dissolve the precipitate in 5 c.c. dil. HNO_3, and to the solution add about one-fourth as much cobalt (as cobalt nitrate) as there was aluminium estimated in the precipitate; add, however, at least 0.2 mg. Evaporate almost to dryness in a dish, add 1–2 drops water, and absorb the solution in a small piece of filter paper. Make a roll of the paper, incinerate it in a platinum spiral in a small flame, and finally heat the residue strongly. A blue residue shows the presence of aluminium.

Since aluminium and silica are likely to be present in the NaOH and Na_2O_2 used as reagents, a blank test should be made with these reagents by following **(18.)** and comparing the NH_4OH precipitate with that obtained in a regular analysis. It is also well at the same time to make a blank test for zinc by acidifying the filtered NH_4OH solution with $HC_2H_3O_2$ and following **(20.)**.

(19.) Chromium.—Acidify the filtrate from **(18.)** with $HC_2H_3O_2$, avoiding a large excess. The presence of 1 mg. chromium as chromate in 100 c.c. of solution makes the solution distinctly yellow; therefore, if the solution is colorless, chromium is absent.[1] In that case, proceed at once to **(20.)**. If, however, the solution is at all yellow, add about 10 c.c. 10 per cent. $BaCl_2$ solution, allow the mixture to stand for 5 minutes, filter, and treat the filtrate by **(20.)**. A yellow precipitate is $BaCrO_4$; unless the precipitate is distinctly yellow, the following confirmatory test must be tried. Pour repeatedly through the filter containing the precipitate a cold mixture of 1 c.c. dil. HNO_3 and 9 c.c. water; to the cold solution in a test-tube add about 2 c.c. ether and 1 c.c. 3 per cent. H_2O_2 solution, and shake. Chromium is present if the ether layer is colored blue.

(20.) Zinc.—Warm the acetic acid solution from **(19.)** to about 50°, saturate it in a small flask with H_2S, cork the flask

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[1] In artificial light, a yellow solution may appear colorless.

and allow it to stand for 10 minutes if no precipitate separates at once. A white *flocculent* precipitate is ZnS. If only a small, non-flocculent precipitate, which may be sulphur, results, or if, owing to the presence of other elements, the precipitate is dark colored, the following confirmatory test must be tried. Pour a 5 c.c. portion of dil. HNO_3 several times through the filter containing the H_2S precipitate. To the solution add an amount of cobalt (as cobalt nitrate) equal to about one-fourth the amount of zinc estimated to be present, but do not add less than 0.2 mg. cobalt. Evaporate in a dish almost to dryness, neutralize with Na_2CO_3 solution, adding about 0.5 c.c. in excess. Evaporate to dryness, ignite gently till the purple color disappears, and allow the dish to cool. Zinc is present if the residue is green.

THE IRON GROUP.

ANALYSIS.

(21.) Manganese.—Transfer the precipitate from **(17.)**—which may contain $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_{2\text{-}3}$, $Zn(OH)_2$, $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$, and phosphates of these metals—to a porcelain dish (together with the filter, if necessary), add 5–30 c.c. dil. HNO_3, then add slowly with stirring 3 per cent. H_2O_2 solution until the precipitate has completely dissolved. Heat to boiling, filter to remove the paper, and evaporate the filtrate under a hood to 1–5 c.c.[1] Add 10–20 c.c. conc. HNO_3, heat to boiling (under a hood), add about 0.5 gram solid $KClO_3$ and boil gently. If a large precipitate forms, gradually add more $KClO_3$. A dark brown or black precipitate shows the presence of manganese. Filter it off through an asbestos filter, heat the filtrate to boiling, add more $KClO_3$, boil, and, if more

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[1] Instead of treating it with dil. HNO_3 and H_2O_2, the precipitate may be boiled gently with 5–30 c.c. HCl (sp. gr. 1.12) until it is dissolved; it should then be filtered off from the paper, evaporated to 1–2 c.c., and the HCl should be decomposed by adding 5 c.c. conc. HNO_3 and boiling under a hood as long as oxides of nitrogen are given off. To the resulting solution add 10–20 c.c. conc. HNO_3 and proceed as directed above.

of the precipitate separates, filter through the same filter. Treat the filtrate by **(22.)**. Wash the precipitate with a little conc. HNO_3, which has just been warmed with a little $KClO_3$ (to remove the oxides of nitrogen, which would cause MnO_2 to dissolve); transfer not more than 5–10 mg. of it to a dish; add 1–2 grams PbO_2, and about 10 c.c. dil. HNO_3; heat to boiling, boil for 1–2 minutes, and then pour the mixture into a test-tube and allow the PbO_2 to settle. A violet-red color indicates the presence of manganese.

(22.) Iron.—Add about one-tenth of the HNO_3 solution from **(21.)** to three or four times its volume of ammonium molybdate reagent, and heat to 60–70°.

a. *A yellow, finely crystalline precipitate is not obtained.*—Phosphate is absent. Make the HNO_3 solution from **(21.)** strongly alkaline with NH_4OH, using an excess of 4–5 c.c. A dark red precipitate is $Fe(OH)_3$. Filter and treat the filtrate by **(23.)**. Wash the precipitate, dissolve it in dil. HCl and to one-half the solution add $K_4Fe(CN)_6$ solution. A blue precipitate is caused by Fe. To the other half add KSCN, which will give a deep red color if iron is present.

b. *A yellow, finely crystalline precipitate is obtained.*—Phosphate is present. Test one-tenth of the HNO_3 solution from **(21.)** for iron by evaporating it just to dryness, adding 1–2 c.c. HCl, evaporating again to decompose the HNO_3 (cf. preliminary experiments in regard to the necessity of removing the HNO_3), diluting to 10 c.c. and adding 5 c.c. KSCN solution. A permanent red color indicates the presence of iron. To the remainder of the solution from **(21.)** slowly add NH_4OH until the precipitate just fails to redissolve on shaking. (If, owing to the addition of too much NH_4OH a large precipitate separates or the solution becomes alkaline, make it distinctly acid with $HC_2H_3O_2$.) Add 5 c.c. 50 per cent. $NH_4C_2H_3O_2$ solution, and, unless the mixture is already brownish-red, add $FeCl_3$ drop by drop, with stirring, until such a color is produced. Dilute the mixture to about 100 c.c., boil for 5 minutes in a 250 c.c. flask, adding more water if a very large precipitate is formed, and allow the mixture to stand for a short time. Filter while still hot, rejecting the precipitate. Add 4–5 c.c. more $NH_4C_2H_3O_2$ solution to the filtrate, boil, and if a precipitate forms, filter it off on a fresh filter, and reject it. Make the filtrate alkaline with NH_4OH, adding an excess of 2–3 c.c.; filter off and reject any precipitate. Treat the solution by **(23.)**.

This method of separation depends upon the facts that all the phosphate radical present combines with ferric iron when the latter is present in excess, leaving the bivalent metals in solution (since $FePO_4$ is much less soluble than are the phosphates of the bivalent metals), and that, upon boiling an acetic acid solution containing much acetate, ferric iron is completely precipitated. If the solution becomes brownish-red upon the addition of the $NH_4C_2H_3O_2$, it shows that an excess of iron is already present; for a cold solution of $Fe(C_2H_3O_2)_3$ is of a deep red color. If, however, a colorless solution (with or without a precipitate) results, it shows that iron is not present in excess, and $FeCl_3$ must be added to cause the precipitation of $FePO_4$ as a yellowish-white precipitate. Upon boiling, the excess of iron is completely precipitated as basic ferric acetate, $Fe(OH)_2(C_2H_3O_2)$.

(**23.**) **Cobalt and Nickel.**—Into the NH_4OH solution from (**22.**) pass H_2S until, after shaking, the vapors above the liquid blacken lead acetate paper.[1]

a. *No precipitate is obtained.*—Cobalt and nickel (and zinc) are absent. Treat the solution by (**23 a.**).

b. *A precipitate is obtained.*—It may contain CoS, NiS (and ZnS). Filter, and wash the precipitate with water containing a few drops of $(NH_4)_2S$. Treat the filtrate by (**23 a.**). If zinc has already been detected, treat the precipitate at once as directed in the following paragraph. If, however, zinc has not already been found in sub-group A, transfer the precipitate (with the filter) to a porcelain dish, and add 10–30 c.c. of a cold mixture of 1 volume

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[1] Instead of H_2S,$(NH_4)_2S$ may of course be used at this point.

HCl (sp. gr. 1.12) and 5 volumes water. Stir the mixture in the cold for 5 minutes, and filter. Boil the HCl solution until the H_2S is completely expelled, add NaOH solution to alkaline reaction, transfer to a porcelain dish, cool, and add about 1 gram Na_2O_2 in small portions, with stirring. Boil to decompose the excess Na_2O_2, and cool the mixture; filter off the precipitate, unite it (together with the filter) with the black residue left by the dil. HCl, and treat the mixture according to the next paragraph. Acidify the Na_2O_2 filtrate with $HC_2H_3O_2$, warm it to 60°–70°, and pass in H_2S for a few minutes. A white, flocculent precipitate is ZnS. Apply to it the confirmatory test described under (**20.**). A small proportion of the nickel and cobalt present (5–20 per cent.) always dissolves in the dil. HCl, and the treatment with NaOH and Na_2O_2 serves to separate them from the zinc. This separation is satisfactory when, as in the dil. HCl solution, the nickel and cobalt are present in such small quantity that only an insignificant amount of zinc is carried down with them.

Transfer the precipitate, with the filter paper, to a porcelain dish, add 5–15 c.c. dil. HCl and a few drops conc. HNO_3, warm until the black precipitate is dissolved, and filter off the paper. Evaporate the filtrate almost to dryness to expel most of the acid, add 5 c.c. water, and then NaOH solution drop by drop until, on shaking, the precipitate just fails to redissolve. Test one-half of this mixture for cobalt, and the rest for nickel as follows:

To one-half of the neutral solution add 3 c.c. 30 per cent. $HC_2H_3O_2$ solution, and then 10 c.c. 30 per cent. KNO_2 solution; dilute to 20 c.c., and allow to stand at least 30 minutes, unless the precipitate forms sooner. A yellow precipitate is $K_3Co(NO_2)_6$. Apply to it the borax bead test for cobalt. Nickelous salts are not oxidized by HNO_2, and are not precipitated by KNO_2 except in a very concentrated solution, when a dark yellow or reddish precipitate of $K_2Ni(NO_2)_4$ may separate.

To the remainder of the neutral solution add 10 per cent.

KCN solution, drop by drop (**Caution**: KCN is a dangerous poison), until all or nearly all of any precipitate formed at first redissolves; then add 0.5–3 c.c. more (according to the size of the KCN precipitate). Heat to 50°–60° in an open dish (**Hood**), with frequent stirring, for at least 5 minutes (or longer, if the solution has not become light colored), and filter off and reject any small residue that may remain. To the filtrate add 5–10 c.c. 10 per cent. NaOH solution, and then saturated Br_2 solution until a piece of KI-starch paper is colored blue by a drop of the mixture. Allow the mixture to stand 5–10 minutes, unless a precipitate forms sooner. A black precipitate is $Ni(OH)_3$.

When a little KCN is added to the neutral solution, green $Ni(CN)_2$ and dark brown $Co(CN)_2$ result unless only small amounts of these metals are present. The precipitates dissolve in more KCN to form the soluble complex salts $K_2Ni(CN)_4$ and $K_4Co(CN)_6$. The nickel complex is stable in the air, but the cobalt salt is readily oxidized according to the equation:

$$4K_4Co(CN)_6 + O_2 + 2H_2O \rightarrow 4K_3Co(CN)_6 + 4KOH.$$

After having decomposed the excess of KCN, the NaOBr then oxidizes Ni^{++}-ion (formed according to the equation $Ni(CN)_4^{--} \rightleftarrows Ni^{++} + 4CN^{-}$) to Ni^{+++}-ion, and this is at once precipitated by the NaOH present. The cobalt is not precipitated as $Co(OH)_3$ because the complex ion, $Co(CN)_6^{---}$ is so very slightly ionized into Co^{+++} and CN^{-}.

(**23 a.**) Add to the solution from (**23.**) dil. HCl just to acid reaction, and evaporate the mixture to a volume of 25–30 c.c.; filter from any sulphur. To the filtrate add NH_4OH drop by drop until its odor persists after shaking; heat to boiling; add $(NH_4)_2CO_3$ solution as long as a precipitate continues to form, and then allow the mixture to stand for 10 minutes.

a. *No precipitate forms.* Add to the clear solution a few drops each of $(NH_4)_2SO_4$, and $(NH_4)_2C_2O_4$ solution, and warm. Filter from any precipitate, and test *the whole filtrate* for magnesium by **(26.)**. Since this solution is known to contain potassium (See **(21.)**), it should then be rejected.

b. *A precipitate may contain* $BaCO_3$, $SrCO_3$ and $CaCO_3$. Filter, and wash the precipitate with hot water. Test the filtrate for magnesium according to the preceding paragraph; to the precipitate on the filter add any precipitate which may be obtained in **(24.)** (by filtering it off through the same filter), and analyze the mixture by **(25.)**.

GROUP IV.

AMMONIUM CARBONATE GROUP.

To this group belong **barium, strontium,** and **calcium,** whose hydroxides and sulphides are not precipitated in the presence of ammonium salts, but whose carbonates are precipitated in the presence of ammonium salts. The hydroxides of these metals are soluble with difficulty in water, but are quite readily soluble in the presence of ammonium salts. (The hydroxide and carbonate of magnesium are practically insoluble in water, but they dissolve readily if ammonium salts are present.)

PRELIMINARY EXPERIMENTS.

Barium.—To about 5 c.c. of a boiling barium salt solution add $(NH_4)_2CO_3$ solution, allow the mixture to settle, filter, and dissolve the precipitate by repeatedly pouring a hot 5 c.c. portion of 30 per cent. $HC_2H_3O_2$ solution through the filter. To one-third of the solution add an equal volume of a clear saturated solution of $CaSO_4$; notice whether $BaSO_4$ is formed immediately or not. To the remainder of the solution, diluted to 75–100 c.c., add $K_2Cr_2O_7$, and filter (the filtrate should be yellow in color). The precipitate is $BaCrO_4$. Filter, and test the filtrate for barium with NH_4OH and $(NH_4)_2CO_3$. Dissolve the $BaCrO_4$ in dil. HCl, add 0.5 c.c. alcohol, and boil until the solution has become light green in color; neutralize the boiling solution with NH_4OH, and filter off from the $Cr(OH)_3$. Evaporate the filtrate nearly to dryness, and introduce a little of it, on a clean platinum wire, into the colorless flame of a Bunsen burner. The green color is due to the barium.

Strontium.—To about 5 c.c. of a boiling solution containing strontium add $(NH_4)_2CO_3$ solution, allow the mixture to settle, filter, and dissolve the precipitate in $HC_2H_3O_2$ as described under Barium. To one-third of the solution add an equal volume of saturated $CaSO_4$ solution, warm, if necessary, and notice the difference between the behavior of barium and strontium. Dilute the remainder of the solution to about 100 c.c., add $K_2Cr_2O_7$, then NH_4OH and $(NH_4)_2CO_3$; filter, and wash the precipitate of $SrCO_3$. Dissolve the $SrCO_3$ in $HC_2H_3O_2$, and test one-third of the solution with $CaSO_4$ solution. To the remainder add $(NH_4)_2SO_4$ in slight excess, boil, filter, and add to the filtrate NH_4OH to alkaline reaction, and then a little $(NH_4)_2C_2O_4$. (If the strontium salt used was free from calcium, no precipitate will be obtained here.) Introduce a little of a concentrated solution of $SrCl_2$, on a clean platinum wire, into the flame of a Bunsen burner, and note the effect.

Calcium.—Use a solution of $CaCl_2$. Try the same experiments as with strontium. The last precipitate is calcium oxalate, CaC_2O_4.

If a spectroscope is available, study carefully the spectrum of each metal of the group, using saturated solutions of the chlorides.

ANALYSIS.

IV. Ammonium Carbonate Group.

(**24.**) **Precipitation.**—Add to the solution from (**16.**) a., or to the filtrate from (**16.**) b. dil. HCl just to acid reaction, and evaporate the mixture to a volume of 25–30 c.c.; filter off any sulphur. To the filtrate add NH_4OH drop by drop until its odor persists after shaking; heat to boiling; add $(NH_4)_2CO_3$ solution as long as a precipitate continues to form, and then allow the mixture to stand for 10 minutes.

a. *No precipitate forms.* Absence of more than traces of barium, strontium, or calcium. Divide in two portions. To one add a few drops $(NH_4)_2SO_4$ solution and warm. A precipitate is $BaSO_4$. To the other add a very little $(NH_4)_2C_2O_4$ solution and warm. A precipitate is CaC_2O_4. Reunite the two portions, filter off from any precipitate, and treat the filtrate by (**26.**).

b. *A precipitate may contain* $BaCO_3$, $SrCO_3$, and $CaCO_3$. Filter,[1] and wash the precipitate. To the filtrate add a few drops each of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ solutions, noting if either gives a precipitate; heat to boiling; filter, rejecting any precipitate; and treat the filtrate by (**26.**). Dissolve the $(NH_4)_2CO_3$ precipitate by repeatedly pouring a hot, 5–10 c.c. portion of 30 per cent. $HC_2H_3O_2$ solution through the filter, and test the solution as follows:

(**25.**) Add to a small portion of the solution in acetic acid an equal volume of saturated $CaSO_4$ solution.

a. *No precipitate forms even after some time and warming.* **Ba** and **Sr** are absent. Confirm the presence of **Ca** by adding to the remainder of the solution a little $(NH_4)_2C_2O_4$ solution. A white pulverulent precipitate is CaC_2O_4.

b. *A precipitate forms slowly or after warming.* **Ba** is absent. **Sr** is present. Dilute the remainder of the solution to 20–25 c.c., heat to boiling, add $(NH_4)_2SO_4$ solution as long as a precipitate continues to form, boil for 2–3 minutes, and filter off the $SrSO_4$ (and $CaSO_4$). To the filtrate, which may contain $CaSO_4$, add NH_4OH to alkaline reaction, and then a little $(NH_4)_2C_2O_4$ solution. A precipitate is CaC_2O_4. Filter it off, ignite a little of it on a *clean* platinum wire, barely moisten the residue on the wire with HCl, and test it in the flame.

c. *A precipitate forms immediately.* **Ba** is present. Dilute the remainder of the solution to about 100 c.c., add 5 c.c. saturated $NaC_2H_3O_2$ solution, heat to boiling, and add gradually $K_2Cr_2O_7$ solution until it is present in slight excess. Boil, and filter while boiling hot (the filtrate should be yellow in color). The precipitate is $BaCrO_4$. Apply to it the confirmatory flame test described under barium in the preliminary experiments. To the filtrate add NH_4OH to alkaline reaction, heat to boiling, and add $(NH_4)_2CO_3$ solution in excess. A precipitate may

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[1] See (**23 a.**).

contain $SrCO_3$ and $CaCO_3$. Filter it off (rejecting the filtrate), wash it, and dissolve it on the filter in a little hot $HC_2H_3O_2$. To a small portion of the solution add $CaSO_4$ solution, and boil. If a precipitate of $SrSO_4$ forms, treat the remainder of the solution as in b. If strontium is absent, test the remainder of the solution for calcium with NH_4OH and $(NH_4)_2C_2O_4$ solution.

The analysis of this group by the method here given does not permit an estimate to be formed as to the relative quantities in which the members of the group are present.[1] The method is based entirely upon the relative solubilities of the sulphates, chromates, and oxalates of the metals. In the following table are given, *in milligrams*, the amounts of the salts that are held in solution at 18° by 1 liter of pure water. The solubility is of course less in the presence of an excess of a common-ion. The arrows emphasize the order of increasing solubility.

	CO_3	CrO_4	SO_4	C_2O_4	$(OH)_2$
Ba	23	3.8	2.3	86. ↑	37000 ↑
Sr	11	1200	110	46.	7700
Ca	13	4000 ↓	2000 ↓	5.6	1700

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[1] If it is desired to form such an estimate, dissolve the precipitate of $SrCO_3$ and $CaCO_3$ (obtained with $(NH_4)_2CO_3$ after the removal of the Ba) in a few c.c. dil. HNO_3, evaporate the solution to dryness in a small porcelain dish, and heat strongly on an iron plate until no odor of HNO_3 can be detected. After cooling, at once rub the contents of the dish to a powder with the blunt end of a glass rod, add 5 c.c. absolute alcohol and 5 c.c. absolute ether, and triturate with the rod for 2–3 minutes. Filter and wash the residue on the filter with small portions of the alcohol-ether mixture until the last washings show no turbidity with a drop of dil. H_2SO_4. The residue is $Sr(NO_3)_2$; dissolve it in water and add $(NH_4)_2CO_3$ solution. Evaporate the ether-alcohol filtrate and washings to dryness on a steam bath. The residue is $Ca(NO_3)_2$; dissolve it in water and add $(NH_4)_2CO_3$ solution.

GROUP V.

SOLUBLE GROUP.

To this group belong **magnesium, sodium, potassium, lithium,** and **ammonium.** There is no common precipitant for the group and very few insoluble salts of the last four metals are known.

PRELIMINARY EXPERIMENTS.

Magnesium.—To one portion of a magnesium salt solution add an equal volume of NH_4Cl, and then add NH_4OH. To another portion add NH_4OH directly; then add NH_4Cl and shake. Explain the results according to the ionic theory. Perform the same experiment, using $(NH_4)_2CO_3$ solution in the place of NH_4OH. *See* pp. 50 and 60.

To a solution containing Mg^{++}-ions add NH_4OH to alkaline reaction, NH_4Cl solution until the precipitate of $Mg(OH)_2$ is dissolved, and then a little Na_2HPO_4 solution, and shake. The precipitate is $MgNH_4PO_4$.

To a magnesium salt solution add $Ba(OH)_2$ solution in excess, filter, heat the filtrate to boiling, and precipitate the excess of barium from the boiling solution with dil. H_2SO_4. Filter, and test the filtrate for magnesium according to the preceding paragraph. By means of $(BaOH)_2$, in the absence of ammonium salts, magnesium may be separated from the alkali metals.

Sodium.—Use a solution of NaCl. Test in the flame. Add 1 drop of a solution of NaCl to 10 drops of a solution of KCl and test in the flame. No satisfactory precipitant for sodium is known. The flame test is so exceedingly delicate that only when the yellow flame is intense and persistent, and only when its light will change the color of a solution, or a crystal, of

$K_2Cr_2O_7$ from orange-red to pale yellow, is sodium likely to be present in appreciable quantity. Even then there may be very little sodium present.

Potassium.—Use a solution of KCl. Test in the flame, using a *clean* platium wire. To a few drops of the solution in a watch glass add a few drops of H_2PtCl_6 solution. The yellow crystalline precipitate is potassium chloroplatinate, K_2PtCl_6. Test a few drops of KCl solution in the same way with $HClO_4$ solution (sp. gr. 1.12). The white crystalline precipitate is $KClO_4$.

To a 1–2 c.c. portion of concentrated NH_4Cl solution add a very little $MgCl_2$ solution and also a small quantity of NaCl solution. To one-half of the mixed solution add a few drops of H_2PtCl_6 solution. The precipitate is $(NH_4)_2PtCl_6$. To the remainder of the mixed solution add 10–15 drops of $HClO_4$ solution, allow the mixture to stand, and note whether a precipitate is formed; to the solution add a little conc. KCl solution. The precipitate is $KClO_4$. $KClO_4$ and NH_4ClO_4 are soluble to the extent of 1.667 grams and 20 grams, respectively, in 100 c.c. cold water; K_2PtCl_6 and $(NH_4)_2PtCl_6$ are soluble to the extent of 0.92 gram and 0.67 gram, respectively, in 100 c.c. cold water. Potassium can therefore readily be detected in the presence of ammonium by means of $HClO_4$ solution; but not by means of H_2PtCl_6 solution.

Lithium.—Use a solution of LiCl. Test in the flame, using a clean platinum wire. Examine the spectrum of the lithium and compare it with that given by potassium, noting especially the relative positions of the red lines.

Lithium resembles magnesium in giving a fairly insoluble carbonate, phosphate, and fluoride.

Ammonium.—Evaporate a small quantity of NH_4Cl solution to dryness in a porcelain dish and heat the residue. Warm another portion with NaOH in a test-tube. Notice the odor of the gas evolved, and its effect upon a piece of moist red litmus paper. Also hold a glass rod moistened with conc. HCl at the mouth of the tube.

ANALYSIS.

V. SOLUBLE GROUP.

(26.) **Magnesium.**—Evaporate the solution from (24.) which may contain the members of this group, in a porcelain dish until ammonium salts begin to crystallize out. Acidify the liquid with HCl, filter, and add to about one-fourth of the filtrate in a test-tube a third its volume of NH_4OH and 1–2 c.c. Na_2HPO_4 solution. Shake vigorously for 2–3 minutes, and if no precipitate appears, rub the sides of the tube with a glass rod (see the remarks in (13.) in regard to the precipitation of arsenic as $MgNH_4AsO_4$). A white *crystalline* precipitate is $MgNH_4PO_4$; if flocculent, the precipitate may be $AlPO_4$, which may be present here (owing to the solubility of $Al(OH)_3$ in NH_4OH) if too large a quantity of NH_4OH was used in the precipitation of Group III.

(27.) **Potassium, Sodium, and Lithium.**—Evaporate the remainder of the solution (from 26.) to dryness in a small porcelain dish, and ignite the residue gently (not above a faint red heat) until most of the ammonium salts are expelled, being careful to heat the sides as well as the bottom of the dish. Introduce a little of the residue into the Bunsen flame on a *clean* platinum wire. If a violet flame is obtained, potassium is present and sodium is absent. A red flame indicates the presence of lithium. If a bright, persistent yellow flame is obtained, which changes the color of a crystal or a solution of $K_2Cr_2O_7$ held near it from orange-red to pale yellow, sodium is present in appreciable quantity. Also determine by means of the spectrum given by the residue whether lithium is present (if the yellow sodium line in the spectrum is persistently brilliant, sodium is likely to be present in appreciable quantity). Treat the remainder of the residue with not more than 1 c.c. of hot water, cool, filter the solution into a test-tube, add 0.5 c.c. $HClO_4$ solution (sp. gr.

1.12), and allow the mixture to stand for about 5 minutes, unless a precipitate forms sooner. A white, crystalline precipitate is $KClO_4$.[1] This test, while not so delicate as that with H_2PtCl_6 solution, has the advantage that ammonium salts do not give a precipitate with the reagent. It is directed to expel most of the ammonium salts simply in order to avoid the dilution of any potassium salt that may be present with the water required to dissolve the large quantity of ammonium salts always present at this point.

If Mg or K, or both, are present in quantity, and it is desired to form an estimate of the amount of Na present, first completely expel the NH_4-salts (from the residue obtained by evaporation) by gentle ignition in a small crucible. Dissolve the residue in a little water, remove the Mg by means of $Ba(OH)_2$ solution, filter, heat the filtrate to boiling and precipitate the excess of Ba with $(NH_4)_2CO_3$ solution. Filter, evaporate the filtrate to dryness, expel the NH_4-salts, dissolve in the least possible quantity of cold water, add 10 per cent. H_2PtCl_6 solution in excess, allow to stand for 5 minutes, and filter off the K_2PtCl_6. Evaporate the filtrate to dryness in a porcelain crucible, ignite the residue to a dull red heat as long as the odor of chlorine can be detected, extract it with water (after cooling), filter, and evaporate the filtrate to dryness. The residue is NaCl. (If lithium was also present, the residue may be freed from LiCl by dissolving it in the least possible quantity of water, saturating the solution with HCl gas, and adding an equal volume of alcohol. The precipitate is NaCl.)

(28.) **Ammonium.**—Test a portion of the *original substance* for ammonium salts by mixing it in a small beaker with an excess of NaOH solution. Cover the beaker with a watch glass, on the under side of which is placed a piece of moist red litmus

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[1] Concerning the delicacy of this test, the addition of one-fourth its volume of $HClO_4$ (sp. gr. 1.12) to a portion of 0.1 normal KCl produces a distinct precipitate of $KClO_4$; if to 10 c.c. of 0.25 normal KCl solution 0.5 c.c. $HClO_4$ is added, a good test is obtained. The addition of 0.05 c.c. $HClO_4$ to a 10 c.c. portion of normal KCl solution gives an instantaneous precipitate.

paper, and warm gently. If the litmus turns blue, ammonium salts are present. In that case, the odor of NH_3 will generally be perceptible. Care must be taken that the litmus paper does not absorb any of the alkaline NaOH solution, and for that reason the mixture should be only gently heated; *do not boil it.*

B. DETECTION OF THE NON-METALS.

In most cases the non-metallic elements do not exist in solution in the form of simple anions containing only an atom of the single element (the most important ones which do occur in this manner are chlorine, bromine, iodine, and sulphur); they combine mostly with other elements to form compound anions such as CO_3^{--}, NO_3^{-}, PO_4^{---}, etc. It is therefore usual in the detection of the non-metals to first convert the elements into acids (unless they are already present in the form of simple or compound ions); these furnish anions which contain the elements in question, and which can be readily recognized by means of their characteristic reactions.

In the analysis of an unknown substance, the number of anions to be tested for is generally restricted by the solubility of the substance taken in connection with the metals already found in it. A substance soluble in water and containing a certain cation cannot contain any anion known to form an insoluble salt with that cation; for example, a soluble substance giving a neutral (or slightly acid) solution which contains Zn^{++}- and Ba^{++}-ions need not be tested for any of the following anions; $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, S^{--}, SO_3^{--}, CO_3^{--}, $C_2O_4^{--}$, $C_4H_4O_6^{--}$, PO_4^{---}, AsO_3^{---}, AsO_4^{---}, CrO_4^{--}, $S_2O_3^{--}$, SO_4^{--}, F_2^{--}, SiO_3^{--}, SiO_4^{----}, etc.[1] However, if a substance is insoluble, certain acid radicals forming soluble salts with the metals present may nevertheless be present; for such salts may be held back by certain insoluble substances (*e.g.*, $Ba(NO_3)_2$ by $BaSO_4$). Moreover, many basic salts are insoluble, although readily soluble when normal (*e.g.*, $Pb(OH)NO_3$). In order to determine what acid radicals are excluded by the

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[1] See, however, the remarks on p. 106 in regard to the effect of the presence of ammonium salts.

solubility of the substance, the solubility of the various salts of the metals present must be considered. The table of solubilities on the back cover-sheet will be of assistance in this connection.

GROUPS OF THE ACIDS.

The detection of the anions, unlike that of the cations, does not, in general, require their separation from one another. They are, nevertheless, divided into groups according to their behavior toward a few general reagents, which serve simply to show the presence or the absence of members of a whole group of anions, and not to separate one group from another. If a group is found to be absent, it is of course unnecessary to test for any anion in that group. But if a certain group is found to be present, every anion in that group which may be present (see p. 69) must be tested for.

The reactions of the anions are, by a somewhat loose use of language, called reactions of the acids of which these ions form the characteristic part. Thus the reactions which serve for the detection of the ion SO_4^{--} are said to be reactions for sulphuric acid. For the sake of convenience this usage, which is historic in origin, and which is common among chemists, will be followed.

The ordinary grouping of the acids depends on the solubility of their barium and silver salts in neutral and acid solutions. It is given in slightly modified form below.

Group I.—Acids whose silver salts are insoluble in water or dilute nitric acid; but whose barium salts are soluble in water. *Hydrochloric, hydrobromic, hydriodic, hydrocyanic, thiocyanic, hydroferrocyanic, hydroferricyanic* and *hydrosulphuric* (H_2S) *acids.*

Group II.—Acids whose silver salts are soluble in dilute nitric acid, but difficultly soluble in water; and whose barium salts are soluble in water. *Nitrous and acetic acids.*

Group III.—Acids whose silver and barium salts are insoluble in water, but soluble in dilute nitric acid.

a. Acids whose silver salts are colorless (white). *Sulphurous, carbonic, oxalic, boric, and tartaric acids.*

b. Acids whose silver salts are colored. *Phosphoric, arsenic, arsenious, thiosulphuric,*[1] *and chromic acids.*

Group IV.—Acids whose silver and barium salts are soluble in water. *Nitric, chloric, permanganic, acetic and nitrous acids.* $AgC_2H_3O_2$ and $AgNO_2$ are difficultly soluble (cf. Group II.).

Group V.—Acids whose silver salts are soluble in water, but whose barium salts are insoluble in water or in dilute acids. *Sulphuric, and hydrofluoric acids.* BaF_2 is difficultly soluble in dil. HNO_3.

Group VI.—Non-volatile acids, giving soluble alkali salts, which on evaporation and digestion with HCl give insoluble residues. *The silicic acids.*

Group VII.—Organic acids which carbonize on heating. *Tartaric acid, citric acid, acetic acid, malic acid, succinic acid, benzoic acid, salicylic acid, lactic acid, propionic acid, butyric acid, and hundreds of others.*

GENERAL TESTS.

The solution to be tested for acids should contain no cations other than those of the alkalies and alkali earths (see Part II. for its preparation). Strongly acidify a 3–4 c.c. portion of the solution with HNO_3, and add 1–2 c.c. $AgNO_3$ solution Filter off any precipitate, noting its appearance, and add to the filtrate a little more $AgNO_3$ to insure complete precipitation. Then carefully pour a little dilute ammonia down the sides of the tube containing the clear filtrate so as to form a layer on top. Note the appearance of any precipitate that forms at the junction of the two liquids.—AgI, Ag_3PO_4, and

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[1] Thiosulphates give with silver nitrate a white precipitate of $Ag_2S_2O_3$, which soon decomposes, the color changing very rapidly, through yellow to black, Ag_2S being formed. (Certain other thiosulphates of heavy metals decompose in the same way.)

Ag_3AsO_3 are yellow; AgBr is yellowish-white; $Ag_3Fe(CN)_6$ is brownish-red; Ag_2CrO_4 is dark red; Ag_3AsO_4 is chocolate colored; Ag_2S is black. The other silver salts are white; but Ag_2CO_3 rapidly turns yellow, and $Ag_2S_2O_3$ rapidly changes from white to yellow, to reddish, and finally to black. All of the precipitates except AgI, Ag_2S and $Ag_4Fe(CN)_6$ are soluble in NH_4OH. It is for this reason that the NH_4OH is added on top, since the whole solution is not easily made exactly neutral. A grayish-brown precipitate of Ag_2O may form, even when the second and third groups of acids are absent.

Make another 3–4 c.c. portion of the solution *slightly* alkaline with carbonate-free NaOH solution; add about 1 c.c. $BaCl_2$ solution and allow the mixture to stand for 4 or 5 minutes. If a precipitate forms, add, without filtering, 2–3 c.c. dilute HNO_3, and, if doubtful whether any of the precipitate has dissolved, shake, filter and make the filtrate alkaline with carbonate-free NaOH solution.

Compare the results obtained in the $AgNO_3$ and $BaCl_2$ tests with the following scheme and draw conclusions as to which groups of acids cannot be present, and are therefore excluded from further consideration. It should be noted, however, that the solution used in these tests will generally not contain sulphides, sulphites, thiosulphates, nitrites (or carbonates), since these will previously have been expelled by boiling with dil. HNO_3 in the preparation of this solution (See Part II. B.).

Precipitated by $AgNO_3$				Not precipitated by $AgNO_3$.		
$AgNO_3$ precipitate insoluble in dil. HNO_3	$AgNO_3$ precipitate soluble in dil. HNO_3.					
Not precipitated by $BaCl_2$.		$BaCl_2$ gives a precipitate which is soluble in HNO_3.		Not precipitated by $BaCl_2$.	$BaCl_2$ gives a precipitate which is insoluble or nearly so in dil. HNO_3.	
Group I.	Group II.	Group III. a.	b.	Group IV.	Group V.	Group VI. See Part II.
		Ag salts, White	Ag precipitate, colored:			
HCl	$HC_2H_3O_2$	H_2SO_3		HNO_3	H_2SO_4	Silicic acids.
HBr	HNO_2	H_2CO_3	H_3PO_4	$HClO_3$	H_2F_2	
HI		$H_2C_2O_4$	$H_2S_2O_3$	$HMnO_4$		
HCN		H_3BO_3	H_3AsO_3	(HNO_2)		
HCNS		$H_2C_4H_4O_6$	H_3AsO_4	$(HC_2H_3O_2)$		
$H_4Fe(CN)_6$			H_2CrO_4			
$H_3Fe(CN)_6$						
H_2S						

Moisten a small quantity of the finely powdered solid (obtained by evaporation, if necessary) in a small test-tube with water, and then add about 1 cc. conc. H_2SO_4; in this way considerable heat is evolved, and it is usually unnecessary to warm the tube. The indications which may be derived from this test are given below; they should not be taken as conclusive (especially when the results are negative), but should be confirmed by the special tests for the acids in question:

Chlorides evolve HCl [illegible] which gives a precipitate of AgCl with a drop of $AgNO_3$ solution held on the end of glass rod, and may also be recognized by its odor.

Bromides evolve HBr, together with brown fumes of Br_2 (and also SO_2 from the H_2SO_4).

Iodides evolve violet fumes of I_2 (and also H_2S and SO_2 from the H_2SO_4). Solid iodine may also separate.

Cyanides evolve HCN, recognized by its odor (**Caution!**).

Thiocyanates evolve $HCHO_2$, CO_2, COS and SO_2, with the separation of sulphur.

Sulphides evolve H_2S.

Acetates evolve $HC_2H_3O_2$, recognized by its odor.

Nitrites evolve brown fumes (mainly NO_2).

Sulphites evolve SO_2 gas, recognized by its odor; *thiosulphates* evolve SO_2 and give a precipitate of sulphur.

Carbonates and *oxalates* give off CO_2 (together with CO in the case of oxalates). The gas when poured into a tube containing lime water renders the latter turbid.

Tartrates char and blacken the H_2SO_4, SO_2 being evolved at the same time.

Chlorates sputter, and evolve ClO_2 a greenish gas which colors the H_2SO_4 intensely yellow.

Permanganates evolve Mn_2O_7, which is explosive.

Fluorides evolve H_2F_2, which etches the test-tube; the SiF_4 formed renders turbid a drop of water, suspended on the end of a glass rod. It may be necessary to heat the tube.

Silicates may decompose with separation of gelatinous silicic acid.

SPECIAL TESTS.

By the considerations already stated, and by the $AgNO_3$, $BaCl_2$, and H_2SO_4 tests, the examination for acids is greatly simplified. Moreover, in the analysis for metals, the presence or absence of H_2CO_3, H_2S, HCN, H_2SO_3, and $H_2S_2O_3$ will have been demonstrated upon the addition of HCl to the solution; that of H_3AsO_3, H_3AsO_4, H_2CrO_4, and $HMnO_4$ will have been demonstrated in the precipitation of Group II. with H_2S; and finally, the presence or absence of H_3PO_4 will generally have been demonstrated in the analysis of Group III. For the acids not already detected with certainty, or not proved absent, special tests must be tried as follows:

GROUP I.

Hydrochloric Acid.—If the precipitate with silver nitrate in acid solution is white and (HBr), HCN, HSCN, and $H_4Fe(CN)_6$ are absent, it must consist of AgCl.

Cyanides, thiocyanates, ferrocyanides, and ferricyanides, if present, should first be removed as follows: Add to the HNO_3 solution $AgNO_3$ as long as a precipitate continues to form, heat to boiling, and filter; dry the precipitate, and ignite it to a dull red heat in a *porcelain* crucible. (By this treatment the cyanogen compounds are decomposed with the separation of Ag, while the halides remain unchanged.) Fuse the residue in the same crucible with about 1 gram of pure Na_2CO_3, cool, boil with about 10 c.c. of water, and filter. Acidify the solution with HNO_3, and test it with $AgNO_2$.

The simplest and most certain method for the detection of chlorides in the presence of bromides and iodides is as follows: Dilute about 0.25 c.c. of the solution to be tested with 2–3 c.c. of water, acidify with dil. HNO_3, and add *one drop* of dil. $AgNO_3$ solution; heat to boiling, and shake. If bromides or iodides are present, a yellow precipitate will be obtained. Filter, add to the filtrate *one drop* of the $AgNO_3$ solution, etc., until, finally, either a *pure white* precipitate of AgCl, or, in the absence of chlorides, no precipitate at all is obtained—(If cyanogen compounds are present, they must first be removed as described above.)

Hydrobromic Acid.—Add to a small portion of the solution dil. H_2SO_4 to acid reaction, then add a few drops of carbon disulphide, which will sink to the bottom, and a single drop of chlorine water (*be sure the latter has not lost its chlorine by standing*), and shake. The Cl_2 will displace iodine or bromine, if iodides or bromides are present; bromine colors the CS_2 yellow if only a little is present and reddish-brown if much is present, while iodine colors it violet. If iodine is liberated, add Cl_2 solution slowly, shaking after each addition; in this way the I_2 is oxidized to colorless HIO_3, and, if bromides are present, the liberated Br_2 imparts its color to the CS_2. If care is not taken to avoid an excess of Cl_2, the solution will be decolorized, owing to the formation of BrCl.

Hydriodic Acid.—(See preceding test.) If minute quantities of iodides are to be detected, dilute KNO_2 solution should be added to the acid solution instead of chlorine water, since an excess of nitrous acid does not oxidize the liberated iodine. The reaction is $2HI + 2HNO_2 \rightarrow 2H_2O + 2NO + I_2$.

Chlorides, Bromides, and Iodides may be detected in the presence of one another as follows: Dilute the solution largely and use, at first, 1 c.c. or less for the tests. Add 5 c.c. dil. H_2SO_4 and a few drops of a solution of ferric sulphate. Boil in an 8-inch test-tube, shaking vigorously to prevent bumping. Test the steam which escapes for iodine with starch paper. If iodine is found, boil until it is completely expelled, adding more $Fe_2(SO_4)_3$ from time to time. Add some water and a few drops of $K_2Cr_2O_7$ solution, boil again and test the steam with potassium iodide starch paper. The bromine, if present, sets iodine free and this turns the paper blue. Care must be taken, however, that the liquid does not touch the paper. Boil till the bromine is completely expelled, adding more $K_2Cr_2O_7$ from time to time, and water, if necessary, to prevent the liquid from becoming too concentrated. Test the solution remaining with $AgNO_3$; a white precipitate is AgCl.

Under the conditions of this test, the $Fe_2(SO_4)_3$ oxidizes only the HI, according to the equation, $Fe_2(SO_4)_3 + 2HI \rightarrow 2FeSO_4 + H_2SO_4 + I_2$; the $K_2Cr_2O_7$ then oxidizes only the HBr, according to the equation, $K_2Cr_2O_7 + 5H_2SO_4 + 6HBr \rightarrow 2KHSO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Br_2$; and the HCl remains unaltered in the solution.

Hydrocyanic Acid.[1]—Dissolve a little of the original substance in water or in dil. HCl without warming. Add a few drops each of $FeSO_4$ and $Fe_2(SO_4)_3$ solutions. These should produce no precipitate if the solution is acid. (If a blue precipitate is formed, $H_4Fe(CN)_6$ or $H_3Fe(CN)_6$ is present; in that case see Fresenius.) Add NaOH to alkaline reaction, boil for a short time, and then acidify with HCl. Cyanides, if present, are con-

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[1] Owing to the fact that hydrocyanic acid is volatile and a most deadly poison, cyanides will not be given for analysis in this course.

verted into ferrocyanides according to the equation, $FeSO_4 + 6KCN \rightarrow K_4Fe(CN)_6 + K_2SO_4$, and, on acidifying, a precipitate of Prussian blue is obtained with the ferric salt present.

Thiocyanic Acid.—Add a few drops of $FeCl_3$ solution to a portion of the neutral or very slightly acid solution. A red color, not destroyed by boiling, indicates thiocyanic acid. The color will disappear on adding $HgCl_2$ solution.

Certain organic acids, like acetic acid, give a red color with ferric salts, but, on boiling, a reddish-brown precipitate is formed, and the supernatant liquid is rendered colorless, unless thiocyanic acid is also present.

Hydroferrocyanic and Hydroferricyanic Acids.—Add to one portion of the slightly acid solution a few drops of $FeSO_4$ solution (which must be free from ferric salt), and to another portion a few drops of $FeCl_3$ solution.

*Ferro*cyanides give with *ferrous* salts (in the absence of air) a white precipitate of $Fe_2^{II}[Fe(CN)_6]^{IV}$. The precipitate obtained is generally light blue, and it rapidly turns darker, owing to oxidation.

*Ferro*cyanides give with *ferric* salts a dark blue precipitate of $Fe_4^{III}[Fe(CN)_6]_3^{IV}$ ("Prussian blue").

*Ferri*cyanides give with *ferrous* salts a dark blue precipitate of $Fe_3^{II}[Fe(CN)_6]_2^{III}$ ("Turnbull's blue").

*Ferri*cyanides give with *ferric* salts no precipitate, but only a brownish coloration, due to the formation of soluble $Fe^{III}[Fe(CN)_6]^{III}$.

Hydrosulphuric Acid (H_2S).—Warm some of the finely powdered original substance in a test-tube with dil. HCl, hold a piece of filter paper moistened with $Pb(C_2H_3O_2)_2$ solution in the top of the tube, and if it is not blackened, add some pure powdered zinc; cork the tube loosely, with the paper suspended in the top, and allow it to stand.

The nascent hydrogen evolved by the zinc reduces sulphides like HgS, FeS_2, etc., which are not decomposed by HCl alone, with evolution of H_2S. Sulphides, if present in quantity, should be detected in the analysis for the metals upon the addition of acid to the solution, or, if a solid was started with, by the action of HCl (odor of H_2S) or of HNO_3 or *aqua regia* (separation of sulphur).

GROUP II.

Nitrous Acid.—Nitrities, if present in quantity, evolve a reddish-brown mixture of NO and NO_2 when the solution is acidified with dil. HCl (or H_2SO_4). The fumes are best seen by looking down through the tube. The acid solution liberates iodine from iodides. It also decolorizes $KMnO_4$ solution.

Solutions of α-naphthylamine and sulphanilic acid, when both are added to an acid solution of a nitrite, give a rose color which develops slowly in very dilute solutions. This reaction is very sensitive (1 : 1,000,000,000, at least) and is especially suited for water analysis.[1] To about 50 c.c. of the water to be tested add 2 c.c. of the reagent, stir, and allow to stand 5–10 minutes in a tube or beaker covered to exclude the oxides of nitrogen in the air of the laboratory.

Acetic Acid.—To a small quantity of the solid substance on a watch glass add 3–4 drops of water and then about 0.5 c.c. conc. H_2SO_4. Triturate with a glass rod, and note the odor.

To a little of the solid substance in a test-tube add about 0.5 c.c. alcohol and 1 c.c. conc. H_2SO_4; heat *gently*, and note the odor. Until familiar with the odor, the beginner should always make a comparative experiment with a pure acetate. The odor is due to the presence of ethyl acetate, $(C_2H_5)C_2H_3O_2$.

For a third test, see under **Thiocyanic Acid.**

GROUP III.

Sulphurous and Thiosulphuric ("Hyposulphurous") **Acids.**—Both sulphites and thiosulphates evolve SO_2 on warming with

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[1] The reagent is prepared as follows: Dissolve 0.5 gram sulphanilic acid in 150 c.c. dil. $HC_2H_3O_2$; boil 0.2 gram solid α-naphthylamine with 20 c.c. water, pour off the colorless solution from the residue (rejecting the latter), and add to the liquid 150 c.c. dil. $HC_2H_3O_2$; then mix the two solutions. If the solution becomes reddish in color, shake it with zinc dust, and filter.

dil. HCl. Sulphur dioxide is readily recognized by its odor. Free sulphurous acid is a reducing agent, and it instantly decolorizes a drop of potassium permanganate solution. It is thereby converted into sulphuric acid which may be detected by $BaCl_2$. Sulphates must be removed by means of $BaCl_2$ before the test is applied.

Sulphites are easily oxidized to sulphates, and the solution of a sulphite will usually contain a little sulphate.

Thiosulphates, upon the addition of HCl, give a white or yellow precipitate of S at the same time that SO_2 is evolved.

With silver nitrate, in cold neutral solution, sulphites give a white precipitate of Ag_2SO_3; thiosulphates give a white precipitate of $Ag_2S_2O_3$, which quickly becomes yellow, brown, and finally black, owing to the separation of Ag_2S.

Carbonic Acid.—Cover some of the pulverized substance in a test-tube with a little water, boil, and then add dil. HCl. If effervescence takes place, pour the gas into a second test-tube containing 2–3 c.c. lime water, cover the latter tube with the thumb, and shake; note whether the lime water becomes turbid. The test is more delicate if, instead of pouring the gas into lime water, a drop of $Ba(OH)_2$ solution suspended on the end of a glass rod is held just above the surface of the liquid in which gas is being formed.

Oxalic Acid.—To the acidified solution first add a considerable quantity of saturated $NaC_2H_3O_2$ solution, and then add $CaSO_4$ solution. A white precipitate may be CaC_2O_4 or CaF_2. Boil the mixture, allow the precipitate to settle, and decant the liquid. Add to the solid a little powdered MnO_2 and 2–3 c.c. dil. H_2SO_4; heat gently, and test the gas evolved with $Ca(OH)_2$, or $Ba(OH)_2$ solution. If an oxalate is boiled with MnO_2 and dil. H_2SO_4, the oxalic acid is oxidized to carbon dioxide according to the equation, $MnO_2+H_2SO_4+H_2C_2O_4 \rightarrow MnSO_4+2H_2O+2CO_2$.

Boric Acid.—Add to a small portion of the solution HCl just to acid reaction. Dip a piece of turmeric paper in the solution and dry it on the water-bath. If boric acid is present, the turmeric paper will turn brownish-red, and the color is not destroyed upon dipping the paper into very dilute H_2SO_4. (Turmeric paper is turned brown by alkalies, but in this case the color is destroyed by dil. H_2SO_4.)

Add to a little of the solid substance (obtained if necessary by evaporating the solution, first made alkaline with NaOH, since H_3BO_3 is volatile with steam), in a small dish 2–3 c.c. conc. H_2SO_4 and 2–3 c.c. alcohol. Warm gently, and set fire to the vapors. Note whether the borders of the flame are colored green. The green color is due to the presence of $(C_2H_5)_3BO_3$ in the vapors. In the presence of chlorides this test is not very reliable, since C_2H_5Cl also tinges the flame green. Also, if copper is present, it must first be removed with H_2S.

Tartaric Acid.—Solid tartaric acid and tartrates when heated blacken and give a characteristic odor resembling that of burnt sugar. If tartaric acid is indicated by this test, make the solution slightly alkaline with NH_4OH, add $CaCl_2$ solution in excess and allow the mixture to stand a short time. If a precipitate forms, filter it off, and digest it in the cold with NaOH solution. Dilute slightly, filter and boil the filtrate. If a precipitate forms, tartaric acid is indicated. Filter hot, wash, introduce the precipitate into a test-tube, add 1 drop of NH_4OH and a little $AgNO_3$ and warm. If tartaric acid is present, it will be oxidized by the $AgNO_3$ and the latter will be reduced to metallic silver, which will give a black precipitate, or form a silver mirror on the walls of the tube.

Phosphoric Acid.—To about 5 c.c. of ammonium molybdate reagent in a test-tube add a few drops of the solution to be tested, having first acidified the latter with HNO_3. Warm the mixture and if no precipitate forms add 2 or 3 c.c. of the solution to be tested, warm again and allow to stand. A yellow precipitate is ammonium phospho-molybdate, of the approximate composition $(NH_4)_3PO_4.12MoO_3$.

Arsenic acid gives with ammonium molybdate a similar pre-

cipitate; so that arsenic, if present, must first be removed from the solution by means of H_2S.

Arsenious Acid, Arsenic Acid, and Chromic Acid, if present, will have been found in testing for the metals.

GROUP IV.

Nitric Acid.—Mix the solution to be tested with an equal volume of saturated $FeSO_4$ solution, acidify with dil. H_2SO_4, and pour the mixture carefully down the sides of a tube containing about 2 c.c. conc. H_2SO_4, so that the two liquids do not mix.

Allow the mixture to stand a short time. If a nitrate is present, a brown ring will form at the zone of contact of the two liquids.[1]

Starting with $NaNO_3$, the reactions are:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3;$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO;$$

and $FeSO_4 + NO \rightarrow FeSO_4.NO$.

The brown compound, $FeSO_4.NO$, is easily decomposed by heat; for that reason the liquids must be kept cold during the test.

Chlorates, iodides, and chromates interfere with the test, so that, if present, they must first be removed. To remove chlorates, mix the substance in a porcelain crucible with dry Na_2CO_3 and ignite gently for 5–10 minutes. The chlorate is thus changed to chloride; the nitrate is at the same time partially reduced to nitrite, which gives the same reaction with $FeSO_4$ solution. To remove chromates, warm the solution which has been previously acidified with dil. H_2SO_4, with the addition of Na_2SO_3 solution, drop by drop, till the color becomes a pure green. Add NH_4OH, and filter off the $Cr(OH)_3$; test the filtrate with $FeSO_4$ and H_2SO_4. To remove iodides, add to the solution, acidified with dil. H_2SO_4, Ag_2SO_4 solution, as long as a precipitate continues to form, filter, and test the filtrate as described abvoe.

Chloric Acid.—Add conc. H_2SO_4 to a very little of the solid

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[1] Nitrous acid gives with the slightly acid $FeSO_4$ solution the same dark colored compound, but in this case the brown coloration appears before the mixture is poured into the tube containing the conc. H_2SO_4.

substance in a test-tube and warm gently. Greenish-yellow ClO_2 gas is evolved with sputtering, according to the equation:

$$3KClO_3+2H_2SO_4 \rightarrow 2KHSO_4+H_2O+KClO_4+2ClO_2.$$

The ClO_2 colors the H_2SO_4 intensely yellow.

Acidify the solution to be tested with HNO_3, add $AgNO_3$ as long as a precipitate forms, and filter. Make the filtrate alkaline with pure Na_2CO_3, evaporate to dryness, ignite at a low red heat, dissolve in water, and add dil. HNO_3 and $AgNO_3$. This test is very delicate, but it is given by perchlorates as well.

Permanganic Acid.—This acid will have been detected in the analysis for metals. All solutions containing salts of the acid are colored intensely red or violet.

GROUP V.

Sulphuric Acid.—In most cases, if a white pulverulent precipitate, insoluble in HCl, is obtained with $BaCl_2$, it may be taken as $BaSO_4$. In case of doubt, heat the precipitate with Na_2CO_3 in the R. F. on charcoal, place the residue on a silver coin and moisten. If the precipitate is $BaSO_4$, Na_2S will be formed and a black stain of Ag_2S will appear.

Hydrofluoric Acid.—Mix a small portion of the solid substance with $KHSO_4$. Dip in the mixture a borax bead prepared in the usual way, and test in the Bunsen flame. A green flame, appearing only for an instant, indicates the formation of BF_3. Always confirm, either by the drop-of-water test (p. 74), or by mixing some of the substance with enough conc. H_2SO_4 in a lead dish to form a thin paste, laying over the dish a piece of glass covered with beeswax or paraffin in which letters have been traced with a pointed piece of wood, and heating very gently, but not enough to melt the wax. If the substance is a fluoride, lines will be etched on the glass.

If a fluoride is dissolved by means of HCl in a glass vessel, H_2SiF_6 is formed, which gives with $BaCl_2$ a precipitate insoluble in HCl and sometimes mistaken for $BaSO_4$. BaF_2, itself, is not very soluble in HCl.

GROUP VI.

Silicic Acid.—The only common silicates soluble in water are those of K and Na. If HCl is added drop by drop to a strong solution of a silicate, most of the silicic acid separates in the gelatinous form. If the acid is added quickly, the silicic acid sometimes remains entirely in solution. If the acid solution is evaporated completely to dryness, but with care not to heat the residue after it is dry, on moistening it with conc. HCl (or HNO_3 if Ag is present) and then treating it with hot water, the silicic acid will remain undissolved. The same method serves for the detection and separation of silicic acid in silicates which are decomposed by conc. HCl or HNO_3.

The silica obtained above or the silica in any silicate will dissolve with effervescence in a bead of Na_2CO_3, but both are insoluble in a bead of sodium metaphosphate (obtained from $NaNH_4HPO_4$, "microcosmic salt").

GROUP VII.

Organic Acids.—The presence of organic acids, or rather of organic matter in general, can be detected by the carbonization which occurs when the substance is heated in a closed tube. The number of the organic acids is so great that any systematic scheme of analysis for them all is impossible. Practically, the examination for such acids resolves itself into special tests for those which are suspected to be present in a given case.

Many organic acids are precipitated on adding an acid to solutions of their salts. Such acids can often be identified by their melting-points, determined with the dry acid in a capillary tube. Many acids may also be extracted from aqueous HCl solutions by means of ether and are left as a liquid or solid residue when the solvent is evaporated. On distilling aqueous solutions, many acids, especially monobasic ones, pass over with the water vapor. It seems scarcely desirable to select particular acids for further discussion.

REACTIONS OF THE METALS.

Group I.

Reagent.	Silver. $AgNO_3$.	Mercury (ous). $Hg_2(NO_3)_2$.	Lead. $Pb(NO_3)_2$.
Hydrochloric Acid. HCl.	Silver Chloride. $AgCl$. White pr., insol. in acids, soluble in NH_4OH, in KCN, in $Na_2S_2O_3$. Darkens in the light.	Mercurous Chloride. Hg_2Cl_2. White pr. Sol. in HNO_3, in aqua regia. Converted to $NH_2HgCl+Hg$ by NH_4OH.	Lead Chloride. $PbCl_2$. White pr., slightly soluble in cold water, more easily in hot water. Converted to an insoluble basic salt by NH_4OH.
Hydrogen Sulphide. H_2S.	Silver Sulphide. Ag_2S. Black pr., insol. in $(NH_4)_2S$. Sol. in hot HNO_3.	Mercuric Sulphide and Mercury. $HgS+Hg$. Black pr., partly sol. in HNO_3. Sol. in aqua regia.	Lead Sulphide. PbS. Black pr., insol. in $(NH_4)_2S$. Sol. in HNO_3.
Sulphuric Acid. H_2SO_4.	Silver Sulphate. Ag_2SO_4. White precip., only in concentrated solutions.	Mercurous Sulphate. Hg_2SO_4. White pr., slightly sol. in water.	Lead Sulphate. $PbSO_4$ White pr., insol. in excess, slightly sol. HNO_3. Soluble in $NH_4C_2H_3O_2$.
Sodium Hydroxide. $NaOH$.	Silver Oxide. Ag_2O. Brown pr., sol. in HNO_3, in NH_4OH.	Mercurous Oxide. Hg_2O. Black pr., soluble in HNO_3, insol. in NH_4OH.	Lead Hydroxide. $Pb(OH)_2$. White pr. Sol. in excess, in HNO_3, insol. in NH_4OH.
Ammonium Hydroxide. NH_4OH.	Silver Oxide. Ag_2O. Brown precip., soluble in excess.	Ammonobasic Mercuric Salt and Mercury. Black precip., insol in excess.	Basic Salt. White pr., insol. in excess.
Sodium Carbonate. Na_2CO_3.	Silver Carbonate. Ag_2CO_3. White precip., soluble in NH_4OH.	Basic Salt. Yellow pr., quickly becoming black.	Basic Lead Carbonate. $2PbCO_3Pb(OH)_2$. White pr., "White Lead."
Potassium Chromate. K_2CrO_4.	Silver Chromate. Ag_2CrO_4. Dark red precip., soluble in HNO_3, in NH_4OH.	Mercurous Chromate. Hg_2CrO_4. Dark red pr.	Lead Chromate. $PbCrO_4$. Yellow pr. Slightly sol. in HNO_3. Sol. in $NaOH$.
Potassium Ferrocyanide. $K_4Fe(CN)_6$.	Silver Ferrocyanide. $Ag_4Fe(CN)_6$. White precip., insoluble in NH_4OH.	Mercurous. Ferrocyanide. $Hg_4Fe(CN)_6$. White precipitate.	Lead Ferrocyanide. $Pb_2Fe(CN)_6$. White precipitate.
Stannous Chloride. $SnCl_2$.	Silver Chloride. $AgCl$. White precip.	Mercury. Hg. Dark gray precip.	Lead Chloride. $PbCl_2$. White precipitate.

Group II—A. The Copper Group.

Reagent.	Mercury (ic). $HgCl_2$	Copper. $CuSO_4$.	Bismuth. $BiCl_3$.	Cadmium. $CdSO_4$.
Hydrogen Sulphide. H_2S.	Mercuric Sulphide. HgS. First white, then yellow, reddish brown and black pr., insol. in HNO_3, in $(NH_4)_2S$. Sol. in aq. regia, in $Na_2S + NaOH$.	Copper Sulphide. CuS. Black pr., sol. in HNO_3, in KCN. Very slightly sol. in $(NH_4)_2S_x$ Insol. in hot dil. H_2SO_4.	Bismuth Sulphide. Bi_2S_3. Dark brown pr. sol. in HNO_3, insol. in $(NH_4)_2S$.	Cadmium Sulphide. CdS. Yellow pr. sol. in HNO_3, in hot diluted H_2SO_4, insol. in $(NH_4)_2S$.
Sulphuric Acid. H_2SO_4.	No precipitate.	No precipitate.	No precipitate	No precipitate.
Ammonium Hydroxide. NH_4OH.	Ammonobasic Mercuric Chloride. $HgNH_2Cl$. White precip.	Basic Copper salt. Greenish-blue pr. sol. in excess to a blue solution.	Bismuthyl Hydroxide. $BiO\ OH$. White pr., insol. in excess.	Cadmium Hydroxide. $Cd(OH)_2$. White precip., sol. in excess.
Sodium Hydroxide. $NaOH$.	Mercuric Oxide. HgO. Yellow pr. In presence of NH_4Cl, white pr. of $HgNH_2Cl$.	Copper Hydroxide. $Cu(OH)_2$. Blue pr. changed to black CuO by boiling.	Bismuthyl Hydroxide. $BiO\ OH$. White precip.	Cadmium Hydroxide. $Cd(OH)_2$. White precip.
Sodium Carbonate. Na_2CO_3.	Mercuric Oxychloride. $HgCl_2 + nHgO$. Reddish br. pr., changed to yellow HgO by boiling.	Basic Copper Carbonate. Blue pr. changed to black CuO by boiling.	Bismuthyl Carbonate. $(BiO)_2CO_3$. White precip.	Cadmium Carbonate. $CdCO_3$. White precip.
Potassium Chromate. K_2CrO_4.	Mercuric Chromate. $HgCrO_4$. Reddish-yellow pr., soluble in HNO_3.	Copper Chromate. $CuCrO_4$. Reddish-brown precip., sol. in NH_4OH to a green solution.	Bismuthyl Dichromate. $(BiO_2)Cr_2O_7$. Yellow pr., sol. in $HC_2H_3O_2$.	———
Potassium Ferrocyanide $K_4Fe(CN)_6$	———	Copper Ferrocyanide. $Cu_2Fe(CN)_6$. Reddish-brown pr. slightly sol. in NH_4OH, insol. in $HC_2H_3O_2$.	Bismuth Ferrocyanide. White pr., insol. in HCl.	Cadmium Ferrocyanide. $Cd_2Fe(CN)_6$. Yellowish-white precip., sol. in HCl.
Stannous Chloride. $SnCl_2$.	Mercurous Chloride. Hg_2Cl_2. White pr. An excess of $SnCl_2$ gives gray Hg.	Cuprous Chloride. Cu_2Cl_2. White precip., only in conc. solutions.	Darkens a pr. of Bi O O H, changing it to Bi.	———
Water. H_2O.	———	———	Basic Bismuth Salt. $BiOCl$. White pr., sol. in HCl.	———

Group II—

Reagent.	Arsenic.		Antimony.	
	Arsenious Salts. K_3AsO_3.	Arsenic Salts. KH_2AsO_4.	Antimonious Salts. $SbCl_3$.	Antimonic Salts. $KSbO_3$.
Hydrogen Sulphide. H_2S.	Arsenic trisulphide. As_2S_3. Yellow pr., sol. in alkalies and alkali sulphides. Insol. in conc. HCl.	Arsenic trisulphide and sulphur. As_2S_3+2S. Yellow precip. forming slowly and on warming.	Antimony trisulphide. Sb_2S_3. Orange pr. sol. in conc. HCl, in Alkalies and alkali sulphides.	Antimony pentasulphide. Sb_2S_5. Orange pr. sol. in conc. HCl in alkalies and alkali sulphides.
Ammonium Sulphide. $(NH_4)_2S$.	Arsenic trisulphide. As_2S_3. Only in acid solutions. Sol. in excess.	Arsenic. pentasulphide. As_2S_5. Only in acid solutions. Sol. in excess.	Antimony trisulphide. Sb_2S_3. Sol. in excess.	Antimony pentasulphide. Sb_2S_5. Sol. in excess.
Sodium Hydroxide. NaOH.	——	——	Antimonious Hydroxide. $Sb(OH)_3$. White pr., sol. in excess.	Sodium Metantimonate. $NaSbO_3$. White pr. sol. in excess.
Potassium Hydroxide. KOH.	——	——	Antimonious Hydroxide. $Sb(OH)_3$.	——
Ammonium Hydroxide. NH_4OH.	——	——	Antimonious Hydroxide. $Sb(OH)_3$. Insol. in excess.	Ammonium Metantimonate. NH_4SbO_3. Nearly insol. in excess.
Sodium Carbonate. Na_2CO_3.	——	——	Antimonious Hydroxide. $Sb(OH)_3$. Sol. in excess on boiling.	——
Silver Nitrate. $AgNO_3$.	Silver Arsenite. Ag_3AsO_3. Yellow pr., sol. in HNO_3, in. NH_4OH.	Silver Arsenate. Ag_3AsO_4. Reddish-brown pr., sol. in HNO_3, in NH_4OH.	Silver Chloride and Antimony trioxide. $AgCl+Sb_2O_3$ White precip.	Silver Antimonate. $AgSbO_3$. White pr., sol. in NH_4OH.
Copper Sulphate. $CuSO_4$.	Copper Arsenite. $Cu_3(AsO_3)_2$. Yellowish-green, pr. sol. in HNO_3, in NH_4OH, in NaOH.	Copper Arsenate. $Cu_3(AsO_4)_2$. Greenish-blue pr. soluble in HNO_3, in NH_4OH.	Antimony Oxychloride. SbOCl. White pr. caused by dilution.	Copper Antimonate. Brown precip.
Mercuric Chloride. $HgCl_2$.	Mercuric Arsenite. $Hg_3(AsO_3)_2$. White pr., sol. in acids.	——	Antimony Oxychloride. Caused by dilution. Sol. in conc. HCl.	——
Stannous and Stannic Chlorides. $SnCl_2+SnCl_4$.	——	——	——	——
Magnesia Mixture. NH_4Cl, NH_4OH, $MgCl_2$	——	Magnesium Ammonium Arsenate. $MgNH_4AsO_4$. White crys. pr., sol. in $C_2H_4O_2$.	Same pr. as by NH_4OH.	Same precip. as by NH_4OH.
Metallic Zinc and Hydrochloric Acid. (Marsh's test.)	Hydrogen and Hydrogen Arsenide. The flame deposits a spot on porcelain. Sol. in sodium hypochlorite. Sol. in $(NH_4)_2S$; on evaporation the yellow residue is insol. in conc. HCl.		Hydrogen and Hydrogen Antimonide. The flame deposits a spot on porcelain. Insol. in sodium hypochlorite. Sol. in $(NH_4)_2S$. On evaporation the orange residue is sol. in conc. HCl.	

B. The Tin Group.

Tin.		Platinum.	Gold.
Stannous Salts. $SnCl_2$.	Stannic Salts. $SnCl_4$.	H_2PtCl_6.	$HAuCl_4$.
Stannous Sulphide. SnS. Dark brown pr., sol. in conc. HCl. in alkalies. Difficultly sol. in yellow $(NH_4)_2S$.	Stannic Sulphide. SnS_2. Yellow pr., sol. in conc. HCl, in alkalies and alkali sulphides, in alkali carbonates.	Platinic Sulphide. PtS_2. Dark brown pr., insol. in conc. HCl. Difficultly sol. in alkali sulphides. Sol. in aqua regia.	Gold Sulphide. Au_2S_3. Black pr. insol. in conc. HCl. Sol. in alkali sulphides, sol. in aqua regia.
Stannous Sulphide. SnS. Sol. in yellow $(NH_4)_2S$.	Stannic Sulphide. SnS_2. Sol. in excess.	Platinic Sulphide. PtS_2. Sol. in excess.	Gold Sulphide. Au_2S_3. Sol. in excess.
Stannous Hydroxide. $Sn(OH)_2$. White pr., sol. in excess.	Stannic Hydroxide. $Sn(OH)_4$. White pr., sol. in excess.	——	——
Stannous Hydroxide. $Sn(OH)_2$.	Stannic Hydroxide. $Sn(OH)_4$.	Potassium Chloroplatinate. K_2PtCl_6. Yellow pr. in presence of free HCl.	——
Stannous Hydroxide. $Sn(OH)_2$. Insol. in excess. Darkens on boiling.	Stannic Hydroxide. $Sn(OH)_4$. Slightly sol. in excess.	Ammonium Chloroplatinate. $(NH_4)_2PtCl_6$. Yellow pr., sol. in great excess.	Fulminating Gold. $\left[Au\begin{matrix}(NH_3)_2\\(OH\ )_2\end{matrix}\right]OH$. Yellow pr., insol. in excess.
Stannous Hydroxide. $Sn(OH)_2$. Insol. in excess.	Stannic Hydroxide. $Sn(OH)_4$. Slightly sol. in excess.	——	——
Silver Chloride and Silver. $AgCl+Ag$.	Silver Chloride. $AgCl$.	Silver Chloride and Platinum Oxide. $AgCl+PtO_2$. Brown precipitate.	Silver Chloride and Gold Oxide. $AgCl+Au_2O_3$. Brown precipitate.
Cuprous Chloride. Cu_2Cl_2. White pr., sol. in acids.	——	——	——
Mercurous Chloride. Hg_2Cl_2. White pr., insol. in cold conc. HCl.	——	——	——
——	——	——	Purple of Cassius. Purple red precip. or coloration.
Same precip. as by NH_4OH.	Same precip. as by NH_4OH.	Same precip. as by NH_4OH.	Same precip. as by NH_4OH.
Metallic Tin.		Platinum.	Gold.
	In neutral solution, also Stannic Hydroxide.	Black precipitate.	Brown precipitate.

Group

Reagent.	Aluminium $KAl(SO_4)_2$.	Chromium. $KCr(SO_4)_2$.	Zinc. $ZnCl_2$.	Manganese. $MnCl_2$.
Ammonium Sulphide. $(NH_4)_2S$.	Aluminium Hydroxide. $Al(OH)_3$. White flocculent pr.	Chromium Hydroxide. $Cr(OH)_3$ Grayish-green pr.	Zinc Sulphide. ZnS. White pr. insol. in $C_2H_4O_2$. Sol. in HCl.	Manganese Sulphide. MnS Flesh col'd pr. sol. in HCl, in $C_2H_4O_2$. Oxidizes in the air.
Hydrogen Sulphide. H_2S.	———	———	Zinc Sulphide. Only in neutral alkaline acid or acetic acid solution.	Manganese Sulphide. Only in neutra or alkaline solutions.
Ammonium Hydroxide. NH_4OH.	Aluminium Hydroxide. $Al(OH)_3$. White flocculent pr. very slightly sol. in excess.	Chromium Hydroxide. $Cr(OH)_3$. Grayish-blue or green precip. slightly sol. in excess with a red color.	Zinc Hydroxide, Zn $(OH)_2$. White pr. sol. in excess. In presence of NH_4Cl no pr.	Manganese Hydroxide. $Mn(OH)_2$. White pr. becoming brown. In presence of NH_4Cl a dark brown pr. forms slowly by oxidation.
Sodium Hydroxide. NaOH.	Aluminium Hydroxide. $Al(OH)_3$. White pr. sol. in excess as $NaAlO_2$.	Chromium Hydroxide. $Cr(OH)_3$. Sol. in excess to a green sol. reprecipitated by boiling.	Zinc Hydroxide Zn $(OH)_2$. White pr. sol. in excess. Reprecipitated by boiling.	Manganese Hydroxide. $Mn(OH)_2$. White pr. becoming brown. Insol. in excess.
Barium Carbonate. $BaCO_3$.	Aluminium Hydroxide. $Al(OH)_3$. White pr.	Basic Salt. Greenish pr.	No pr. in the cold except in presence of a sulphate.	No pr. in the cold except in presence of a sulphate.
Sodium Phosphate. Na_2HPO_4.	Aluminium Phosphate. $AlPO_4$. White pr. sol. in NaOH, insol. in $C_2H_4O_2$.	Chromium Phosphate. $CrPO_4$. Green pr.	Zinc Phosphate $Zn_3(PO_4)_2$. White pr. sol. in excess.	Manganese Phosphate. $Mn_3(PO_4)_2$. White pr. sol. in NH_4OH.
Ammonium Carbonate. $(NH_4)_2CO_3$.	Aluminium Hydroxide. $Al(OH)_3$. White pr.	Chromium Hydroxide. $Cr(OH)_3$. Grayish-green pr. sol. excess.	Basic Zinc Carbonate. White pr. sol. in excess.	Manganese Carbonate. $MnCO_3$. White pr. insol. in excess.
Potassium Ferrocyanide. $K_4Fe(CN)_6$.	White pr. forms slowly.	———	Zinc Ferrocyanide. $Zn_2Fe(CN)_6$. White pr. sol. in HCl.	Manganese Ferrocyanide. $Mn_2Fe(CN)_6$. Reddish-white precip. sol. in HCl.
Potassium Ferricyanide. $K_3Fe(CN)_6$.	———	———	Zinc Ferricyanide. $Zn_3[Fe(CN)_6]_2$. Yellowish-brown pr. sol. in HCl.	Manganese Ferricyanide. $Mn_3[Fe(CN)_6]_2$. Brown pr. insol, in HCl.
Potassium Thiocyanate. KCNS.	———	———	———	———
Borax bead.	———	Yellowish-green hot. Emerald green, cold.	———	Violet red, hot Amethyst red cold. Colorless in R.F.

III.

Ferric Salts. $FeCl_3$	Ferrous Salts. $FeCl_2$.	Cobalt. $CoCl_2$.	Nickel. $NiCl_2$.	Uranium. $UO_2(NO_3)_2$.
Iron Sulphide. Fe_2S_3. Black pr. Sol. in acids to a ferrous salt.	Iron Sulphide. FeS. Black pr. sol. in HCl, in $C_2H_4O_2$. Oxidizes in the air.	Cobalt Sulphide. CoS. Black pr. insol. in $C_2H_4O_2$, very slowly sol. in HCl. Sol. in aq. reg.	Nickel Sulphide. NiS. Black pr. slightly sol. in exc. very slowly sol. in HCl. Sol. in aq. reg.	Uranyl Sulphide. UO_2S Dk. br. pr, somewhat sol. in exc. of colorless $(NH_4)_2S$-
Reduced to a ferrous salt with separation of sulphur.	No pr. in acid solution.	Cobalt Sulphide. Only in neutral or alkaline solutions.	Nickel Sulphide. Only in neutral or alkaline solutions.	—
Ferric Hydroxide. $Fe(OH)_3$ Reddish-brown pr. insol. in excess.	Ferrous Hydroxide. $Fe(OH)_2$. White pr. becoming green and reddish-brown. In presence of NH_4Cl, $Fe(OH)_3$ forms slowly.	Basic Salt. Blue pr. sol. in excess to a red sol. In presence of NH_4Cl, no pr.	Nickel Hydroxide. $Ni(OH)_2$. Green pr. sol. in excess to a blue sol. in presence of NH_4Cl no pr.	Ammonium Uranate. $(NH_4)_2U_2O_7$. Yellow pr.
Ferric Hydroxide. $Fe(OH)_3$. Reddish-brown pr. insol. in excess.	Ferrous Hydroxide. $Fe(OH)_2$. White pr. becoming green and reddish brown, insol. in excess.	Basic Salt. Blue pr. insol. in excess. Sol. in $C_2H_4O_2$, in NH_4OH.	Nickel Hydroxide. $Ni(OH)_2$. Apple green pr. insol. in excess, sol. in $C_2H_4O_2$. in NH_4OH.	Sodium Uranate. $Na_2U_2O_6$. Yellow pr. sol. in $(NH_4)_2CO_3$.
Basic Salt. Reddish-brown pr.	No pr. in the cold except in the presence of a sulphate.	No pr. in the cold except in presence of a sulphate.	No pr. in the cold except in presence of a sulphate.	Uranly Hydroxide. $UO_2(OH)_2$. Yellow pr.
Ferric Phosphate. $FePO_4$. Yellowish-white pr. sol. in excess. Insol. in $C_2H_4O_2$.	Ferrous Phosphate. $Fe_3(PO_4)_2$ White pr. becoming blue in the air.	Cobalt Phosphate. $Co_3(PO_4)_2$. Red pr. sol. in NH_4OH.	Nickel Phosphate. $Ni_3(PO_4)_2$. Green pr. sol. in NH_4OH.	Uranyl Phosphate. UO_2HPO_4. Yellowish-white pr.
Basic Salt. Reddish-brown pr.	Ferrous Carbonate. $FeCO_3$. White pr. sol. in excess.	Basic Carbonate Pink pr. sol. in excess.	Basic Carbonate. Green pr. sol. in excess.	Ammonium Uranyl Carbonate $2(NH_4)_2CO_3+UO_2CO_3$. Yellow pr. sol. in excess, reprecipitated by alkalies.
Ferric Ferrocyanide. $Fe_4[Fe(CN)_6]_3$. Dark blue pr. insol. in HCl. Decomposed by NaOH.	Ferrous Ferrocyanide. $Fe_2Fe(CN)_6$. Bluish-white pr. becoming blue.	Cobalt Ferrocyanide. $Co_2Fe(CN)_6$. Green pr. becoming greenish-blue, insol. in HCl.	Nickel Ferrocyanide. $Ni_2Fe(CN)_6$. Greenish-white pr. insol. in HCl.	Uranyl Ferrocyanide $(UO_2)_2[Fe(CN)_6]$. Reddish-brown pr.
Reddish-brown color.	Ferrous Ferricyanide. $Fe_3[Fe(CN)_6]_2$. Dark blue pr. insol. in HCl. Decomposed by NaOH.	Cobalt Ferricyanide. $Co_3[Fe(CN)_6]_2$. Dark brown pr. insol. in HCl.	Nickel Ferricyanide. $Ni_3[Fe(CN)_6]_2$. Yellowish-green pr. insol. in HCl.	—
Blood red solution. $Fe(CNS)_3$. Most delicate with HCl.	No color.	—	—	Red color.
Yellow in O. F. Green in R. F.	Yellow in O. F. Green in R. F.	Blue.	Violet, hot. Reddish-brown, cold, gray and turbid in R. F.	Yellow in O. F. Green in R. F.

Group IV.

Reagent.	Barium. $BaCl_2$.	Strontium. $SrCl_2$.	Calcium. $CaCl_2$.	Magnesium. $MgSO_4$.
Ammonium Carbonate. $(NH_4)_2CO_3$.	Barium Carbonate. $BaCO_3$. White pr. sol. in acids.	Strontium Carbonate. $SrCO_3$. White pr. sol. in acids.	Calcium Carbonate. $CaCO_3$. White pr. sol. in acids.	Basic Magnesium Carbonate. $MgCO_3 + nMg(OH)_2$. White pr. on warming and in absence of NH_4 salts.
Sodium Hydroxide. NaOH.	Barium Hydroxide. $Ba(OH)_2$. White pr. only in conc. solutions.	Strontium Hydroxide. $Sr(OH)_2$. White pr. difficultly sol. in water.	Calcium Hydroxide. $Ca(OH)_2$. White pr. difficultly sol. in water.	Magnesium Hydroxide. $Mg(OH)_2$. White pr. sol. in NH_4Cl.
Ammonium Hydroxide. NH_4OH.	No pr.	No pr.	No pr.	Magnesium Hydroxide. $Mg(OH)_2$. Sol. in NH_4Cl.
Sulphuric Acid. H_2SO_4.	Barium Sulphate. $BaSO_4$. White pr. insol. in water or in acids.	Strontium Sulphate. $SrSO_4$. White pr. very little sol. in water or in $(NH_4)_2SO_4$.	Calcium Sulphate. $CaSO_4$. White pr. somewhat sol. in water. In sol. in alcohol.	———
Ammonium Oxalate. $(NH_4)_2C_2O_4$.	Barium Oxalate. BaC_2O_4. White pr. sol. in HCl, slightly sol. in $C_2H_4O_2$.	Strontium Oxalate. SrC_2O_4. White pr. sol. in HCl, slightly sol. in $C_2H_4O_2$.	Calcium Oxalate. CaC_2O_4. White pr. sol. in HCl, almost insol. in $C_2H_4O_2$ or $H_2C_2O_4$.	No precipitate in dilute solutions.
Potassium Dichromate. $K_2Cr_2O_7$.	Barium Chromate. $BaCrO_4$. Yellow pr. insol. in $C_2H_4O_2$ in presence of $K_2Cr_2O_7$. Sol. in HCl.	Strontium Chromate. $SrCrO_4$. Yellow pr. sol. in $C_2H_4O_2$.	Calcium Chromate. $CaCrO_4$. Yellow pr. sol. in $C_2H_4O_2$.	———
Hydrofluosilicic Acid. H_2SiF_6.	Barium Fluosilicate. $BaSiF_6$. White pr. insol. in HCl.	———	———	———
Sodium Phosphate. Na_2HPO_4.	Barium Hydrogen Phosphate. $BaHPO_4$. White pr. sol. in acids.	Strontium Hydrogen Phosphate. $SrHPO_4$. White pr. sol. in acids.	Calcium Hydrogen Phosphate. $CaHPO_4$. White pr. sol. in acids.	Magnesium Hydrogen Phosphate. $MgHPO_4$. White pr. in presence of NH_4OH and NH_4Cl a white cryst. pr. of $MgNH_4PO_4$ is formed. Sol. in $C_2H_4O_2$.
Flame.	Yellowish-green.	Bright red.	Yellowish-red.	———

Group V.

Reagent.	Lithium. LiCl.	Ammonium. NH_4Cl.	Sodium. NaCl.	Potassium. KCl.
Sodium Carbonate. Na_2CO_3.	Lithium Carbonate. Li_2CO_3. White pr. slightly sol. in water.	Ammonia. NH_3. On boiling.	—	—
Sodium Phosphate. Na_2HPO_4.	Lithium Phosphate. Li_3PO_4. White pr. slightly sol. in H_2O. Sol. in HCl.	—	—	—
Chloro-platinic Acid. H_2PtCl_6.	—	Ammonium Chloroplatinate. $(NH_4)_2PtCl_6$. Yellow pr. slightly sol. in water. Insol. in alcohol.	—	Potassium Chloroplatinate. K_2PtCl_6. Yellow precip. slightly sol. in water, insol. in alcohol.
Perchloric acid. $HClO_4$.	—	—	—	White cryst. precip. $KClO_4$. Slightly sol. in water.
Tartaric Acid. $H_2C_4H_4O_6$.	—	Mono-Ammonium Tartrate. $NH_4HC_4H_4O_6$. White cryst. pr. on shaking. Slightly sol. in water.	—	Mono-Potassium Tartrate. $KHC_4H_4O_6$. White cryst. pr. on shaking and rubbing. Somewhat sol. in water.
Potassium Pyroantimonate. $K_2H_2Sb_2O_7$.	—	—	Sodium Pyroantimonate. $Na_2H_2Sb_2O_7$. White cryst. pr., best in slightly alkaline solutions.	—
Nessler's Reagent. K_2HgI_4+KOH.	—	Reddish - brown pr. or yellow color, very delicate.	—	—
Sodium Hydroxide. NaOH.	—	Evolves NH_3 on warming.	—	—
Hydrofluosilicic Acid. H_2SiF_6.	—	—	Sodium Fluosilicate. Na_2SiF_6. White pr. somewhat sol. in water.	Potassium Fluosilicate. K_2SiF_6. Transparent pr. slightly sol. in H_2O.
Flame.	Red.	—	Yellow.	Violet.

REACTIONS OF

I.—Inorganic

Salts of	Barium Chloride.	Calcium Chloride.	Silver Nitrate.
Sulphuric Acid. H_2SO_4.	White pr. insol. in acids.	White pr. somewhat sol. in water and in acids.	White pr. only in conc. solutions.
Hydrofluosilicic Acid. H_2SiF_6.	White pr. insol. in HCl.	——	——
Sulphurous Acid. H_2SO_3.	White pr. sol. in HCl.	White pr. sol. in HCl.	White pr. decomposed by boiling into Ag, Ag_2SO_4 and SO_2.
Thiosulphuric Acid. (Hyposulphurous.) $H_2S_2O_3$.	White pr. only in conc. solutions.	——	White pr. sol. in $Na_2S_2O_3$. Decomposes into H_2SO_4 and black Ag_2S.
Phosphoric Acid. H_3PO_4.	White pr. sol. in acids.	White pr. sol. in acids, even in $HC_2H_3O_2$.	Yellow pr. sol. in HNO_3, in NH_4OH.
Pyrophosphoric Acid. $H_4P_2O_7$.	White pr. sol. in HCl.	White pr. sol. in an excess of the pyrophosphate.	White pr. sol. in HNO_3. NH_4OH.
Metaphosphoric Acid. HPO_3.	White pr. sol. in. excess of the metaphosphate.	White pr.	White pr. sol. in HNO_3, in NH_4OH.
Arsenic Acid. H_3AsO_4.	White pr. sol. in acids.	White pr. sol. in $HC_2H_3O_2$.	Reddish-brown pr. sol. in HNO_3, in NH_4OH.
Arsenious Acid. H_3AsO_3.	White pr. sol. in acids.	White pr. sol. in $HC_2H_3O_2$.	Yellow pr. sol. in HNO_3, in NH_4OH.
Chromic Acid. H_2CrO_4.	Yellow pr. sol. in HCl, in HNO_3, insol. in $HC_2H_3O_2$.	——	Dark red pr. sol. in HNO_3.
Boric Acid. $H_3BO_3(H_2B_4O_7)$.	White pr. difficultly sol. in water, sol. in acids.	White pr. sol. in acids.	White pr. sol. in HNO_3, in NH_4OH.
Phosphorous Acid. H_3PO_3.	White pr. sol. in $HC_2H_3O_2$.	White pr. sol. in NH_4Cl.	White pr. but deposits black Ag on warming.
Silicic Acid. H_2SiO_3.	White pr.	White pr.	Yellow pr. sol. in conc. solutions, sol. in HNO_3.
Carbonic Acid. H_2CO_3.	White pr. sol. in acids.	White pr.	White pr. sol. in HNO_3.

THE ACIDS.

Acids.

Lead Acetate.	Characteristic Reactions.
Wh. pr. sol. in NaOH, in ammonium tartrate, in am. acetate.	Sulphates when heated with Na_2CO_3, in the reducing flame on charcoal give a hepar (Na_2S) which blackens silver, when moistened with water.
——	The potassium salt is difficultly soluble. Fluosilicates give with conc. H_2SO_4, H_2F_2 and SiF_4.
White pr.	Sulphites reduce $KMnO_4$, give a hepar with Na_2CO_3 on charcoal. Give SO_2 without separation of S, on warming with HCl.
White pr. on boiling becomes gray, $PbS+PbSO_4$.	Gives on warming with HCl, SO_2 and a pr. of S. Gives a hepar with Na_2CO_3 on charcoal. $Na_2S_2O_3$ dissolves Ag Cl.
White pr. sol. in NaOH, insol. in NH_4OH.	Added to a solution of ammonium molybdate in HNO_3, gives a yellow pr. of ammonium phosphomolybdate; $MgCl_2+NH_4OH+NH_4Cl$ precipitate white cryst. $MgNH_4PO_4$.
White pr. sol. in an excess of the pyrophosphate.	Does not coagulate albumen. Changed to H_3PO_4 by boiling with HNO_3.
White pr.	Coagulates albumen. Changed to H_3PO_4 by boiling with HNO_3.
White pr. sol. in HNO_3 insol. in $HC_2H_3O_2$.	Yellow precip. with $(NH_4)_2MoO_4$. White precip. with $NH_4Cl+NH_4OH+MgCl_2$.
White pr. sol. in HNO_3 soluble in $HC_2H_3O_2$.	Marsh's test gives an arsenic mirror. H_2S precipitates yellow As_2S_3 from the warm acid solution.
Yellow pr. sol. in NaOH.	Reduced to green $CrCl_3$ by warming with HCl and alcohol.
White pr. sol. in excess of the lead salt.	With alcohol and conc. H_2SO_4 colors flame green. Turmeric paper dipped in the HCl solution becomes red on drying.
White pr. insol. in $HC_2H_3O_2$.	Reducing agent. Very concentrated solutions evolve PH_3 on heating.
White pr. insol. in HNO_3.	Evolves CO_2 with Na_2CO_3 bead. Gives a skeleton of SiO_2 with $NaPO_3$ bead. SiO_2 separates on evaporating the acid solution to dryness.
White pr. sol. in HNO_3.	Effervesces with HCl giving CO_2 which renders lime water turbid.

I.—Inorganic

Salts of	Barium Chloride.	Calcium Chloride.	Silver Nitrate.
Hydrofluoric Acid. H_2F_2.	White pr. sol. in hot HCl.	White, gelatinous pr., sol. in HCl, insol. in $HC_2H_3O_2$.	———
Iodic Acid. HIO_3.	White pr. sol. in HCl.	———	White pr., sol. in NH_4OH. Reduced to AgI by SO_2.
Hyhrochloric Acid. HCl	———	———	White pr., insol. in HNO_3, soluble in NH_4OH, in KCN.
Hydrobromic Acid. HBr.	———	———	Yellowish-white pr., difficultly sol. in NH_4OH. Insol. in HNO_3.
Hydriodic Acid. HI.	———	———	Yellow precip. insol. in NH_4OH, in HNO_3.
Hydrocyanic Acid. HCN.	———	———	White precip. sol. in NH_4OH, in KCN.
Hydroferrocyanic Acid. $H_4Fe(CN)_6$.	———	———	White pr. soluble in KCN, insoluble in HNO_3.
Hydroferricyanic Acid. $H_3Fe(CN)_6$.	———	———	Orange pr. sol. in NH_4OH, in KCN, insol. in HNO_3.
Thiocyanic Acid. HCNS.	———	———	White precipitate, difficultly sol. in NH_4OH.
Nitrous Acid. HNO_2.	———	———	White pr. sol. in hot water.
Hypochlorous Acid. HClO.	———	———	White pr. of Ag Cl.
Hydrosulphuric Acid. H_2S.	———	———	Black precipitate, soluble in hot HNO_3.
Nitric Acid. HNO_3.	———	———	———
Chloric Acid. $HClO_3$.	———	———	———

Acids.

Lead Acetate.	Characteristic Reactions.
White precipitate, sol. in HNO_3.	With conc. H_2SO_4 gives H_2F_2, which etches glass.
White precipitate.	With KI and $HC_2H_3O_2$, gives free I_2.
White precipitate, soluble in hot water.	With H_2SO_4 and MnO_2 gives Cl_2. With conc. H_2SO_4 and $K_2Cr_2O_7$ gives CrO_2Cl_2.
White precipitate, slightly soluble in hot water.	Cl_2 water liberates Br_2 which dissolves in CS_2 to a reddish-yellow solution.
Yellow precipitate, slightly soluble in hot water.	Cl_2 water, or nitrous acid, liberates I_2, which dissolves in CS_2 to a violet red solution, or colors starch paste blue.
White precipitate, soluble in HNO_3.	After warming with $FeSO_4$, $FeCl_3$ and NaOH, on adding HCl, Prussian blue remains undissolved. When warmed with yellow $(NH_4)_2S$, NH_4CNS is formed.
White precipitate.	Gives Prussian blue with ferric salts. Gives a red precipitate with Cu Salts.
No pr. in alkaline solutions, but on warming PbO_2 is precipitated.	Gives a dark blue precipitate with ferrous salts.
White precipitate.	Blood red color with $FeCl_3$, not destroyed by boiling, but which vanishes on adding $HgCl_2$.
———	Gives a yellow color with meta-phenylene-diamine in acid solution.
White pr. changing to orange, red and br'n on boiling.	Gives with $MnSO_4$ a brownish-black pr. of MnO_2.
Black precip. sol. in hot HNO_3.	Sulphides give a hepar with Na_2CO_3. See sulphates. Soluble sulphides give a violet color with Sodium nitroprussiate.
———	Mixed with $FeSO_4$ and poured on conc. H_2SO_4, gives a dark brown zone. Colors a solution of brucine in H_2SO_4, red.
———	Chlorates deflagrate on charcoal. Added to conc. H_2SO_4 they give yellow ClO_2.

II.—Organic

Salts of	Calcium Chloride.	Silver Nitrate.
Formic Acid. $HCHO_2$.	——	White precipitate in conc. solutions, becoming dark from reduction to Ag.
Acetic Acid. $HC_2H_3O_2$.	——	White precipitate, soluble in hot water.
Oxalic Acid. $H_2C_2O_4$.	White precipitate, insoluble in $HC_2H_3O_2$.	White precipitate, soluble in HNO_3.
Tartaric Acid. $H_2C_4H_4O_6$.	White precipitate, soluble in NaOH, reprecipitated by boiling but dissolves again on cooling.	White precipitate with alkali salts, soluble in HNO_3 and in NH_4OH. Precipitate or mirror of Ag on warming.
Malic Acid. $H_2C_4H_4O_5$.	White precipitate only in presence of strong alcohol.	White precipitate.
Citric Acid. $H_3C_6H_5O_7$.	White precipitate, less soluble in hot than in cold water. Insoluble in NaOH, soluble in NH_4Cl.	White precipitate.

Salts of	Ferric Chloride.	Silver Nitrate.
Benzoic Acid. $HC_7H_5O_2$.	Flesh colored precipitate, soluble in HCl.	White precipitate, soluble in hot water.
Succinic Acid. $H_2C_4H_4O_4$.	Pale red precipitate.	White precipitate.
Salicylic Acid. $HC_7H_5O_3$.	Deep violet color.	White precipitate, soluble in hot water.
Gallic Acid. $C_7H_6O_5$.	Blue black precipitate.	Reduces to metallic Ag.
Tannic Acid. (Tannin.) $C_{14}H_{10}O_9$.	Blue black color.	White precipitate.

Acids.

Lead Acetate.	Characteristic Reactions.
———	Reducing agent, with conc. H_2SO_4 gives CO.
———	Gives with $FeCl_3$ a reddish-brown solution and a precipitate on boiling. Alcohol and conc. H_2SO_4 give ethyl acetate, $(C_2H_5)C_2H_3O_2$, recognized by its odor.
White pr. sol. in HNO_3 and in NH_4OH.	Heated with conc. H_2SO_4 gives CO_2 and CO. With dil. H_2SO_4 and MnO_2 gives CO_2.
White pr. sol. in NaOH.	The acid K and NH_4 salts are difficultly soluble.
White pr. which melts under boiling water.	
White pr. sol. in ammonium citrate.	Tartaric, malic and critic acids prevent the precipitation of $FeCl_3$ by alkalies.

Lead Acetate.	Characteristic Reactions.
White pr.	Mets at 121°.
White pr.	Melts at 180°.
White pr.	Melts at 156°.
———	Melts at 200°. The alkaline sol. absorbs O_2.
Yellow pr.	Amorphous, with an astringent taste. It precipitates a solution of glue.

PART II.

SYSTEMATIC ANALYSIS.

Before beginning the analysis of an unknown substance, the analyst should consider the amount at his disposal. Portions will be needed for preliminary examination, for the detection of metals, and for the detection of acids; *such quantities should be used in these operations that at least one-third may remain for cases of emergency.*

The quantity of substance taken for analysis should always be approximately known, for a good qualitative analysis should show, besides the presence or absence of various elements, also their approximate relative quantities. Commercial calcium bisulphite solution, for example, which is largely used in the manufacture of paper, almost always contains as impurities relatively small amounts of sodium, magnesium, iron, sulphate, chloride, etc. If an analyst, after having found all these substances, should report simply that the substance was a solution in water of the chlorides, sulphites, and sulphates of sodium, magnesium, calcium, iron, etc., his report would be very misleading. The report should be, that the substance is approximately a 10 per cent. solution of calcium bisulphite in water, containing very small quantities of sodium, magnesium, chloride, sulphate, etc., as impurities.

A. DETECTION OF THE METALS.

PREPARATION OF THE SOLUTION.

Preliminary Examination.—If the substance is a solid, note its color, odor, and texture: determine, if possible, whether it is a mixture and, if so, note the appearance of its components.[1] Especially note whether it is an alloy, and, if it is not an alloy,

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[1] A lens or a microscope, if necessary, should be used at this point.

determine whether it contains organic matter or water by heating about 0.1 gram of the finely powdered substance in a hard glass tube closed at one end; heat gently at first, keeping the upper part of the tube cool so that any water present may condense there, and then heat strongly. Note whether the substance blackens, whether a tarry or aqueous deposit forms on the cold part of the tube, and whether a burnt odor is emitted.

If the substance is a solution containing a volatile solvent, note its odor, test it with litmus paper, and evaporate to dryness enough to furnish about 1 gram of residue, first adding carefully 3–5 c.c. conc. HNO_3 if arsenic or mercury is to be tested for. Test a small quantity of the residue as described in the preceding paragraph.

a. Organic Matter is Present.—Certain kinds of organic matter, especially hydroxy compounds such as the sugars, tartaric acid, etc., prevent the precipitation of aluminium and chromium hydroxides, and must therefore be removed.[1] Moreover, a large quantity of organic matter of any kind interferes with the operations of solution, filtration and evaporation.

I.—Powder, or cut into small pieces 1–5 grams of the substance (according to the amount of organic matter present). Add to it in a porcelain dish about 5 c.c. conc. H_2SO_4; warm gently until well charred; cool; add slowly, with constant stirring, under a hood, conc. HNO_3 until violent action ceases; digest for some time on a steam bath, and then heat over a flame, stirring constantly, until the substance is thoroughly charred. Cool, again add conc. HNO_3 as before, and heat until dense white fumes of H_2SO_4 are evolved; cool, and add a little conc. HNO_3. Repeat this process till the H_2SO_4 becomes light colored and remains so when strongly heated. Evaporate the remaining H_2SO_4 under a hood to about 1.5 c.c. Cool thoroughly and add the contents of the dish to about 10 c.c. of water in

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[1] In the case of substances like oil paints, it is often best to simply extract the oil with ether, and then to treat the residue by *b*.

another dish; then pour the liquid back into the first dish, rinsing out the second dish with a little water. If there is a residue, cover the dish and boil for some time (to extract slowly dissolving sulphates, such as anhydrous $Fe_2(SO_4)_3$). Cool, filter, and wash, first with dil. H_2SO_4 and then with a little water, rejecting the washings. Treat the residue[1] by VI. To the solution add a drop of dil. HCl. [If a precipitate forms, add dil. HCl drop by drop *only as long as the precipitate continues to form;* filter, wash the precipitate, and test it for silver. Dilute the solution to a volume of 40 c.c., and treat it by (**5.**), Part I.

b. Organic Matter is Absent.

II.—*In case the substance is not an alloy,* powder it, and weigh out into a porcelain dish about 1 gram of it. Add 10–30 c.c. of water, heat to boiling, and test the solution with litmus paper. If the substance has dissolved completely to a neutral or acid solution, treat the solution by (**1.**), Part I. But if there is a residue, or if the solution is alkaline, add carefully, without filtering, 5–10 c.c. conc. HNO_3, and evaporate just to dryness.[2] Treat the residue by IV.

III.—*In case the substance is an alloy,* convert it into small particles, and weigh out into a porcelain dish about 0.5 gram of it. Under a hood, add 10 c.c. dil. HNO_3; cover the dish with a watch glass; heat on a steam bath as long as any action continues, adding a little conc. HNO_3 from time to time if action is renewed thereby, or a little water if crystalline salts are deposited. Finally evaporate just to dryness.

IV.—Gently heat the residue from II. or III. over a small flame, kept in constant motion, until it is perfectly dry, or, better, heat it in a drying oven at 120–130° for at least half

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[1] This residue may contain silicates; all the Pb, Ba, and Sr that were present in any form; all the silica; some of the Ca, Bi, Sb, and Sn; and practically all of the Cr.

[2] In the case of non-metallic substances which do not contain silica, the evaporation and subsequent heating at 120–130°, etc. (see IV.), may be omitted. In that case, heat on a steam bath for 10 minutes, and proceed as described in IV. With respect to the use of HCl instead of HNO_3, see p. 101.

an hour. Rub the residue to a fine powder with a blunt glass rod; add to it 5–10 c.c. dil. HNO_3, cover the dish, and heat on a steam bath for 10 minutes. Dilute with 20 c.c. water, heat to boiling, filter, and wash the residue. Treat the residue by V. To the solution add 5 c.c. conc. HCl, filter, and wash the precipitate with a little cold water, adding the washings to the filtrate. Treat the precipitate by (**2.**), Part I. Save the filtrate for V.

In dissolving non-metallic substances either HNO_3 or HCl may be first used, each having advantages and disadvantages of its own. Owing to its oxidizing properties, HNO_3 dissolves many alloys and sulphides not attacked by HCl, but it fails to dissolve certain oxides (such as MnO_2, Sb_2O_5, and hydrated SnO_2) which dissolve in HCl. HCl may cause the precipitation of Group I.; while strong HNO_3 on heating oxidizes sulphides partially to sulphates and may cause the precipitation of Pb, Ba, Sr, and Ca as sulphates. HNO_3 oxidizes mercurous, arsenious, antimonious, stannous, and ferrous compounds to the higher state of oxidation. If HCl alone were used as a solvent, Hg, and As, if present in the arsenious condition, would be partly or wholly lost (owing to the volatility of their chlorides) in the subsequent evaporation, which is necessary in order to remove silica. For this last reason, and also because the procedure is a more general one, the use of HNO_3 is recommended. *If, however, organic matter and silica are absent and the substance dissolves completely in HCl, considerable time may be saved by using HCl.*

By the treatment of alloys with strong HNO_3, all the more common elements are dissolved except Sb, Sn, and Si, which are oxidized to antimonic acid ($Sb_2O_5.nH_2O$), metastannic acid (nH_2SnO_3), and silicic acid. The evaporation and heating at 120–130° serve to partially dehydrate these compounds and render them nearly insoluble in HNO_3; if after having thoroughly dried the mixture at this temperature there is no residue insoluble in the HNO_3, Sn and Si cannot be present in quantity as large as 1 mg., and not more than 3 mg. Sb can be present.

In that case, the subsequent procedures for Sn and Sb may generally be omitted. Since, however, in the dehydrated condition, even a very slight residue or turbidity may correspond to an appreciable quantity of one of these elements, if no residue is visible in the white dish, rub its sides gently with the rubber-covered end of a glass rod, pour the liquid into a small flask, allow it to stand 2–3 minutes, and note whether there is any residue whatever. In addition to the substances already named the residue may contain considerable stannic phosphate or arsenate when tin and phosphorus or arsenic are simultaneously present, or of bismuth hydroxide when antimony and bismuth are both present. Various other elements may be enclosed in small quantities, in the residue. A black or metallic residue may contain carbon or carbides, certain alloys of iron (such as ferrochrome or ferrosilicon), gold, or platinum metals.

If the original substance was non-metallic, the residue insoluble in HNO_3 probably contains one or more of the following substances: partially dehydrated hydroxides of Sn, Sb, Si; the native or ignited oxides of the same elements, of Al, and of Cr; anhydrous chromic salts; MnO_2 and PbO_2; $BaSO_4$, $SrSO_4$, $PbSO_4$; HgS; the silicates and fluosilicates of many elements; CaF_2; the halides of Ag and Pb; the phosphate or arsenate of Sn; ferric ferrocyanide; sulphur; carbon; SiC. The nonexistence of a residue shows the absence of Si, but it does not furnish conculsive evidence of the absence of Sb and Sn; the presence of chloride or sulphate, for example, may cause a considerable quantity of Sn or Sb to dissolve.

V.—To the residue from IV., in a porcelain dish, add gradually 5–10 c.c. conc. HCl, and heat under a hood as long as action continues, adding more HCl if necessary. If the substance does not dissolve completely, add without filtering one-third volume conc. HNO_3 and heat gently as long as action continues, adding more of the acids if necessary.

To this solution in HCl alone, or in *aqua regia,* add, without filtering off any residue, the HCl filtrate obtained in IV., and evaporate nearly to dryness. In order to expel the HNO_3, add to the residue 3–5 c.c. conc. HCl, and evaporate to dryness. Thoroughly dry the residue by heating it in an oven at 120–130°, or by heating it with a small flame kept in constant motion. Add to the residue 4 c.c. HCl (sp. gr. 1.12) from a graduate, and about 20 c.c. water; boil gently for a few minutes if there is a residue; filter; and wash the residue thoroughly with boiling water. Treat the residue by VI. Pour the filtrate into a graduate and dilute it to 40 c.c; treat the resulting solution by (**5.**), Part I.

MnO_2 and PbO_2 are reduced and dissolved by conc. HCl; antimonic acid, stannic phosphate and arsenate, and much metastannic acid are also dissolved by it. Upon the addition of the HNO_3, gold, platinum, and HgS are entirely dissolved; and AgBr, AgI, AgCN, etc., are completely converted into AgCl. Such substances as AgCl, $SrSO_4$, and $PbSO_4$ are fairly soluble in the concentrated acids, but very much less so in the small quantity of dil. HCl added after the evaporation.

If the original substance was an alloy, a residue after treatment with *aqua regia* probably consists of metastannic or silicic acid; or of C, a platinum metal, or an alloy of Fe with Cr, Si, etc.

VI.—Transfer the residue from I. or V. to a platinum crucible, add 2 c.c. conc. H_2SO_4 from a small graduate, heat with a moving flame until white fumes are evolved, and cool completely. Add carefully from the loop of a platinum wire 5–6 drops of pure 40 per cent. H_2F_2, and warm the mixture over a steam bath. If gas bubbles are formed, silica is present.[1] Now add about 5 c.c. more of the H_2F_2, cover with a platinum cover, digest for about 15 minutes on a steam bath, unless the residue

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[1] As little as 1 mg. SiO_2 may be detected by this test, whether free or in a decomposable silicate. It should be remembered that a small quantity of silica will have been introduced if ordinary filters have been used and have been destroyed by acids or by ignition, or if an alkaline solution has been boiled in glass vessels, or if a substance has been fused with sodium carbonate in a porcelain vessel.

dissolves more quickly; remove the cover and evaporate carefully until white fumes of H_2SO_4 begin to come off, heating the sides of the crucible with a moving flame. If there is reason to believe that the residue from I. or V. consisted only of SiO_2, determine this by evaporating off the H_2SO_4 under a hood, taking care not to ignite the residue. If a residue remains, showing the presence of other substances than SiO_2, add from a graduate 1.5 c.c. conc. H_2SO_4, and heat until the residue is redissolved, not allowing any acid to evaporate. Cool, pour the contents of the crucible into 10 c.c. water, and rinse out the crucible with a little water. Boil to extract slowly dissolving sulphates, cool, shake, filter, and wash the residue, first with dil. H_2SO_4 and then with a little water, rejecting the washings. Treat the residue by VII., *but first see the following paragraph* (*footnote*).

To the filtrate add HCl drop by drop *only as long as a precipitate continues to form;*[1] filter, wash the precipitate, and test it for Ag. Dilute the filtrate to a volume of 40 c.c. and treat the resulting solution by (**5.**), Part I., subsequently testing for all the metals except Pb, Ba, and Sr.

The digestion with H_2F_2 decomposes most silicates and removes the silica. The evaporation with H_2SO_4 expels the excess of H_2F_2 and decomposes the fluorides formed, as well as some other substances that may have been left undissolved by the HNO_3 and HCl.

VII.—Transfer the residue from VI. to a porcelain dish, add about 25 c.c. of saturated Na_2CO_3 solution, cover the dish, and

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[1] If a precipitate forms here, the residue insoluble in H_2SO_4 is likely to still contain AgCl, which is only slowly decomposed by hot conc. H_2SO_4. In order to remove this, add to the residue in a small dish 5 c.c. conc. H_2SO_4, heat till white fumes are evolved, cover the dish with a watch glass, and boil gently for 10 minutes. Cool, pour into 10 c.c. water, boil, cool, filter, and add HCl to the filtrate as long as a precipitate continues to form. Wash the residue and treat it by VII. If AgCl is not completely removed in this way, the residue will turn dark upon boiling it with Na_2CO_3 solution (see VII.); in such a case, it must be removed by further treatment with H_2SO_4 before a fusion is made with Na_2CO_3 in a platinum crucible; for, if not, AgCl will be reduced to metallic silver, and this will alloy with the platinum and spoil the crucible.

boil for 10 minutes. Filter, and wash the residue thoroughly, rejecting the filtrate. (*If the residue turned dark on boiling it with* Na_2CO_3 *solution, see VI., footnote to the second paragraph.*) Heat the residue with 5 c.c. HCl (sp. gr. 1.12), measured in a graduate, add 10 c.c. water; filter, and wash the residue. Treat the residue[1] (which can contain only $BaSO_4$, anhydrous $Cr_2(SO_4)_3$, or some of the original substance, consisting probably of one of the native oxides or silicates) by VIII.

Dilute the filtrate to 40 c.c., treat the solution with H_2S, and test only for Pb, Bi, Sb, Cr, Ba, Sr, and Ca.

VIII.—Transfer the residue from VII., with the filter, to a platinum crucible, ignite until the filter is destroyed, mix the residue with 5–10 grams anhydrous Na_2CO_3 and 0.1–0.5 gram solid KNO_3, cover the crucible, and heat for 5–10 minutes over a blast lamp, adding if necessary more Na_2CO_3. Cool, place the crucible in a dish, add carefully dil. HCl till the solution remains strongly acid, evaporate to dryness, and heat at 120–130° to render silica insoluble; add from a graduate 4 c.c. HCl (sp. gr. 1.12) and 10–20 c.c. water, boil and filter. Dilute the filtrate to 40 c.c. and treat it by (**5.**), Part I., subsequently testing for all the metals except the alkalies. Treat the residue by IX.

IX.—A residue from VIII. probably consists of SiO_2, $BaSO_4$, Al_2O_3, or SnO_2. Such a residue is best treated first with H_2SO_4 and H_2F_2, as described in VI., to detect and remove SiO_2; then with Na_2CO_3 solution, according to VII., to remove $BaSO_4$. If a residue still remains, treat it as follows: Grind it to a very fine powder, add to it in a silver or nickel crucible 5–10 grams of pure solid KOH, and fuse for 10–20 minutes. Cool, extract with 25–30 c.c. water, and filter. Exactly neutralize the filtrate with dil. HCl. Treat the residue[2] with 5 c.c. HCl (sp. gr. 1.12), filter off any undecomposed residue, and unite the filtrate with

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[1] If Ba is found in the filtrate, however, first repeat the treatment with Na_2CO_3 solution, and see if the resulting residue is not entirely soluble in 5 c.c. dil. HCl.

[2] The residue undissolved by water may be black NiO from the nickel crucible, or it may consist of stannic hydroxide or other hydroxides coming from the original substance. All of these dissolve in HCl.

the neutral solution already obtained. Treat the mixture by the regular procedure, testing especially for Sn and Al.

B. DETECTION OF THE ACIDS.

Preliminary Examination.—Moisten a small quantity of the finely powdered solid in a small test-tube with water, and then add about 1 c.c. conc. H_2SO_4; in this way considerable heat is evolved, and it is usually unnecessary to warm the tube. The indications which may be derived from this test have already been discussed in Part I., which see.

PREPARATION OF THE SOLUTION.

The solution to be tested for acids should be free from heavy metals, since these often interfere with the special tests. In their presence, the solution often cannot even be made alkaline without the formation of a precipitate.

a. Salts and Industrial Products.

If the substance is soluble in water, and only alkali and alkali earth metals are present, dissolve about 1 gram of it in 20–30 c.c. water, and use this solution for the $AgNO_3$ and $BaCl_2$ tests,[1] and for the various special tests described in Part I.; if, however, other metals are present, add to the boiling-hot solution of the substance in water Na_2CO_3 solution as long as a precipitate continues to form. Filter off, and reject the precipitate; use the filtrate for the $AgNO_3$ and $BaCl_2$ tests and for the various special tests, as described below.

If the substance is insoluble, and metals not precipitated by H_2S are present, boil 1 gram of the finely powdered substance in a porcelain dish with about 10 c.c. conc. Na_2CO_3 solution for at least 10 minutes, replacing the water which evaporates.

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[1] H_3BO_3 is precipitated by $BaCl_2$ only from fairly concentrated solutions; it should also be noted that BaF_2 as well as many of the barium salts of Group III. are fairly soluble in ammonium salt solutions. For that reason, ammonium salts, if present, should first be removed by boiling with carbonate-free NaOH solution.

Filter, and neutralize half of the filtrate with HNO_3; filter off any precipitate, slightly acidify the filtrate with HNO_3, boil to expel the CO_2, and use the solution for the $AgNO_3$ and $BaCl_2$ tests, and for the special tests which may be made in the presence of HNO_3. Acidify fresh portions of the Na_2CO_3 solution with $HC_2H_3O_2$ for the oxalic and tartaric acid tests, and with H_2SO_4 for the nitric acid test. If, however, only metals which are precipitated by H_2S are present, and if chlorates and nitrates[1] are known to be absent, suspend a gram of the finely powdered substance in 50 c.c. of water, saturate with H_2S, heat to boiling, and filter; boil the filtrate till the H_2S is entirely expelled, and use it for the $AgNO_3$ and $BaCl_2$ tests, and for the various special tests.

If not already detected or proved absent, test the original substance for H_2S, H_2CO_3 H_2SO_3 and $H_2S_2O_3$.

All the metals except arsenic and the alkalies are precipitated from solution by Na_2CO_3 as carbonates, basic carbonates, or hydroxides. Moreover, most insoluble salts are more or less completely decomposed by a boiling-hot, concentrated solution of Na_2CO_3, the acid radical going into solution; many of the carbonates and hydroxides are somewhat soluble in the excess of Na_2CO_3, but they are re-precipitated when the solution is neutralized. The solution must be slightly acidified, and the CO_2 expelled before testing with $AgNO_3$ and $BaCl_2$; otherwise Ag_2CO_3 and $BaCO_3$ will precipitate.

The removal of the metals with H_2S, while more complete than with Na_2CO_3, is of course inapplicable in the presence of strong oxidizing agents, such as chlorates, etc.

b. Minerals and Metallurgical Products.

First try the special tests for H_2S and H_2CO_3 with portions of the finely powdered substance, unless they have already been detected.

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[1] In the presence of such oxidizing substances it is better to prepare the solution by the Na_2CO_3 method; otherwise, in the presence of chlorates, the tests for HCl and H_2SO_4 would be valueless, and in that of nitrates the H_2SO_4 test would be uncertain.

Boil about 1 gram of the powdered substance with 5 c.c. conc. HNO_3 for 2–3 minutes, add 15 c.c. water, boil again, and filter from any residue. Test portions of the filtrate for H_3PO_4 with ammonium molybdate reagent, and for HCl with $AgNO_3$ solution. If sulphides are absent, test a portion for H_2SO_4 with $BaCl_2$ solution; if the substance was not completely dissolved by the HNO_3, fuse the residue with 3–4 parts solid Na_2CO_3, boil the fused mass with water, filter, and test the filtrate for H_2SO_4 by acidifying it with HCl and adding $BaCl_2$ solution.[1] If sulphides are present, boil some of the finely powdered original substance with conc. Na_2CO_3 solution for 5–10 minutes, filter, acidify the filtrate with HCl, and add $BaCl_2$.[2]

The presence or absence of silicic acid will always have been determined in the analysis for metals. If silicates are absent, test for H_2F_2 with H_2SO_4, and for H_3BO_3 with H_2SO_4 and alcohol. If silicates are present, it is necessary in testing for these acids to fuse about 1 gram of the powdered substance with 4–5 parts of Na_2CO_3.[3] Boil the fused mass with 15–20 c.c. of water and filter; slightly acidify a portion of the filtrate with HCl and test it for H_3BO_3 with turmeric paper; evaporate half of the remaining filtrate to dryness and test for H_3BO_3 with H_2SO_4 and alcohol. Acidify the remainder of the filtrate with $HC_2H_3O_2$, allow the mixture to stand, filter off the precipitate of silicic acid, and add $CaCl_2$ solution; allow the mixture to stand, filter, and test the precipitate for H_2F_2 with H_2SO_4.

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[1] If Ag has been found among the metals, the solution obtained by boiling or fusing with Na_2CO_3 must also be tested for HCl, etc.

[2] Sulphides are partially oxidized to sulphates by boiling with HNO_3 and by fusing with Na_2CO_3; hence the substance should be boiled with Na_2CO_3 solution, or, if completely soluble in acid, it may be dissolved in HCl and the solution tested for H_2SO_4 in the presence of H_2S.

[3] All silicates are not decomposed by H_2SO_4, and even if they were, H_2F_2 might be completely changed to SiF_4 by the SiO_2 present.

SPECIAL PART.

In many cases the method of procedure in qualitative analysis can be shortened because the chemist knows beforehand what substances are likely to be present. In other cases special methods are necessary for the purpose of detecting minute amounts of elements or compounds. In the directions given below it is presupposed that a knowledge of the methods of analysis has already been acquired, and that the student will know how to interpret his results.

POTABLE WATERS.

By noticing carefully the amounts of the precipitates and the intensity of the reactions obtained, a qualitative analysis may give considerable information with regard to the character of a given water.

Evaporate 250 c.c. of the water in a porcelain dish to one-third, filter, and save both precipitate and filtrate.

EXAMINATION OF THE PRECIPITATE.

Dissolve in the least possible amount of dil. HCl, noting the presence or absence of **carbonates**. Test separate portions of the solution:

1. For $\mathbf{Fe^{+++}}$ with KCNS.

2. For $\mathbf{Ca^{++}}$ with NH_4OH and $(NH_4)_2C_2O_4$. Warm, filter and test filtrate for $\mathbf{Mg^{++}}$ with Na_2HPO_4.

3. For $\mathbf{SO_4^{--}}$ with $BaCl_2$. If found, $\mathbf{CaSO_4}$ is indicated.

4. For $\mathbf{PO_4^{---}}$. Add HNO_3, evaporate to dryness, moisten with HNO_3, filter from any **Silica** which remains, add to the filtrate an equal volume of molybdic solution and allow to stand over night.

EXAMINATION OF THE FILTRATE.

Test separate portions:

1. For **SO_4^{--}** with dil. HCl and $BaCl_2$.

2. For **Cl^-** with dil. HNO_3 and $AgNO_3$.

3. A larger portion for **PO_4^{---}** by evaporating with HNO_3 as above in 4.

4. About 10 c.c. for **NO_3^-** by evaporating to a few drops and adding carefully to 2 c.c. of con. H_2SO_4 in which a minute amount of brucine has been dissolved. The solution must be almost or quite colorless before the water is added, otherwise the H_2SO_4 contains nitric acid and is unfit for the test.

5. Add to the remainder of the solution NH_4Cl, NH_4OH and $(NH_4)_2C_2O_4$ to test for **Ca^{++}**. If much Ca is found here, it must have been present as a sulphate, chloride or nitrate. Warm for some time, filter and test a *small portion* of the filtrate with Na_2HPO_4 and NH_4OH for **Mg^{++}**. Evaporate the remainder of the solution to a few drops and test with the spectroscope for **K** and **Na**. **Lithium** may sometimes be found here. The oridnary tests for K and Na may also be used after removing the Mg.

FURTHER TESTS.

Carbonic Acid.—Put 3 c.c. of lime water in a test-tube and add a little of the water. A precipitate which redissolves on adding more of the water indicates free H_2CO_3.

Nitrous Acid.—To about 50 c.c. of the water to be tested add 2 c.c. of the α-naphthylamine sulphanilic acid reagent (see *Nitrous Acid,* p. 78), stir, and allow the mixture to stand for 5–10 minutes.

Ammonia and Nitrogenous Organic Matter.—Take a *clean* 300 c.c. distilling bulb, closed with a *cork,* put in it 100 c.c. of distilled water and 2 c.c. of a solution of Na_2CO_3. Distil through a Liebig's condenser till 10 c.c. of the distillate gives no reaction for ammonia with Nessler's solution. Add 100 or 150 c.c. of the water, distil 10 c.c. and test the distillate with Nessler's solution. If ammonia is found, distil till the distillate is free from ammonia, then add 10 c.c. of an alkaline solution of potassium permanganate[1] which has been diluted with 20 c.c. of water and boiled down to its original volume in a 100 c.c. flask. Distil 10 c.c. and test the distillate with Nessler's solution. The potassium permanganate oxidizes the organic matter in the water and at the same time a part of the nitrogen of the organic matter is converted into ammonia. Such ammonia is commonly called "albuminoid ammonia."

These tests require the most extreme care in every detail, and are entirely worthless if any one works with solutions containing ammonia in the neighborhood of the apparatus.

Organic Matter.—Put 200 c.c. of the water in a clean flask, add 10 c.c. dil. H_2SO_4 and then a dilute solution of $KMnO_4$[2] drop by drop till the water acquires a faint pink color which does not disappear on standing 2 or 3 minutes. Then add 1 c.c. $KMnO_4$ and heat to boiling. If the pink color disappears, add more of the solution, noting the amount. The $KMnO_4$ is reduced by the organic matter in the water.

Hydrogen Sulphide.—Fill a bottle two-thirds full with the water, suspend a strip of paper moistened with a solution of lead acetate from the stopper, and allow to stand for about 1 hour. If the paper turns dark, H_2S is indicated. If the paper does not blacken, add to the water dil. HCl and repeat the test. Blackening now indicates a *sulphide.*

Lead.—Add 5 c.c. of NH_4OH to 2 or 3 liters of the water, then acetic acid to acid reaction, evaporate to about 10 c.c., filter and test the filtrate with H_2S. If a black precipitate forms, test this for lead.

Aluminium.—Take 500 c.c. of the water, add 100 c.c. of lime water, heat rapidly till a copious precipitate forms and filter as quickly as possible, best with a filter plate and pump. Dis-

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[1] Eight grams $KMnO_4$ and 200 grams KOH to one liter of water.

[2] 0.395 gram $KMnO_4$ to 1 liter. One c.c. contains 0.1 milligram available oxygen.

solve the precipitate in dil. HCl, evaporate to dryness in a platinum dish and dry at 120–130° to separate silica, moisten the residue with conc. HCl, dilute slightly, filter and test the filtrate for Fe and Al by adding NH_4OH. It is usually possible to tell whether Al is present or not by the appearance of the precipitate. If the result is doubtful, filter, dissolve in HCl, add a little pure NaOH and boil in a platinum dish, filter and test the filtrate for Al by adding HCl and NH_4OH. This method will enable the chemist to distinguish between soluble aluminium compounds and clayey matters, only the former being shown by this treatment.

IRON AND STEEL.

The following tests may be of considerable value in the comparison of specimens of iron and steel if the amounts taken are weighed roughly and the methods of testing the two specimens are exactly alike.

Phosphorus.—Take 0.2 gram, dissolve in 5 c.c. HNO_3,[1] filter, add a little $KMnO_4$ and boil, then a drop of ammonium tartrate or of tartaric acid, boil till clear, add NH_4OH till nearly neutral but still perfectly clear and distinctly acid, and then add 5 c.c. of molybdic solution.

Sulphur.—Dissolve from 1–5 grams in dil. HCl and pass the gas evolved through a solution of caustic soda to which a little lead acetate has been added.

Silicon.—Dissolve 0.2 gram in 5 c.c. HNO_3, add 8 c.c. dil. H_2SO_4 and evaporate till fumes of H_2SO_4 appear. Cool, add water and dil. HCl; warm, filter, wash thoroughly and ignite the residue in a porcelain crucible over the blast till only white SiO_2 remains. Test this with H_2SO_4 and H_2F_2 in a platinum crucible (VI, p. 103).

Graphite.—This will be found in the residue left when iron is dissolved in dil. HCl.

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[1] In all tests given here, sp. gr. = 1.20.

Combined Carbon.—Dissolve 0.4 gram in 4 c.c. of HNO_3 by heating in a test-tube immersed in boiling water. The depth of color indicates the amount of combined carbon present and may be used for the comparison of specimens of steel of the same character. Both graphite and combined carbon are left undissolved when iron or steel is dissolved in a solution of the double chloride of copper and ammonium.

Manganese.—Dissolve 0.1 gram in 10 c.c. HNO_3, filter, evaporate to a volume of 2–3 c.c., add about 0.5 gram solid $KClO_3$, and boil gently. If a brown substance separates, filter it off, using an asbestos filter, and warm it with 5–10 c.c. HNO_3 and about 0.5 gram PbO_2. Pour the mixture into a test-tube, allow the excess of PbO_2 to settle, and note the color of the solution.

SILVER AND GOLD ORES.

If the amount of silver is considerable, the tests given in the regular course of analysis may be applied. The silver is frequently present as a chloride, however, and must be dissolved in a solution of KCN, precipitated with H_2S or $(NH_4)_2S$, and the Ag_2S dissolved by boiling with HNO_3.

When the amount of silver or gold is small, the most satisfactory method is to fuse 25–100 grams of the powdered ore with $NaHCO_3$, PbO and argol (crude cream of tartar). The lead button obtained is then scorified and cupelled. The following charge answers well with most siliceous ores: Ore, 60 grams; $NaHCO_3$, 60 grams; PbO, 50 grams; argol, 4 grams. If the ore is basic, add 40 grams of silica and use a little less soda. Ores containing sulphides must be roasted. The fusion may be made in a Hessian crucible in a gas furnace, or in an ordinary coal fire. For fuller details, a book on assaying should be consulted.

APPENDIX.

Form of Record.

It is essential that in performing the preliminary experiments such a record shall be kept of the work that afterward it will be possible, by referring to it, to determine where each metal goes at every stage of the analysis. *This thought should be kept constantly in mind in making the record.* It is not necessary, however, to repeat statements from the text-book, and the more concise the record can be made the better, provided it contains all essential facts and is clear. An illustration will, perhaps, be of service.

Silver.

$$AgNO_3 + HCl = \underset{\text{White ppt.}}{\underline{AgCl}} + HNO_3.$$

$AgCl$ + hot water—does not dissolve, since the filtrate gives no ppt. with H_2S.

$$AgCl + 2NH_3 = \underset{\text{Clear sol.}}{\underline{Ag(NH_3)_2Cl.}}$$

$$Ag(NH_3)_2Cl + 2HNO_3 = \underset{\text{White ppt.}}{\underline{AgCl}} + 2NH_4NO_3.$$

In recording analyses, one of the following forms will be found convenient.

No.	Substance.	Reagent.	Result.	Inference.	Precip. or residue.	Solution.
1	Colorless sol.	HCl.	Wh. pr.	Gr. I.	$AgCl, Hg_2Cl_2, PbCl_2$.	
2	Pr. 1.	Hot H_2O.	Partial sol.		$AgCl$, Hg_2Cl_2.	$PbCl_2$.
3	Sol. 2.	H_2SO_4.	Wh. pr.	Pb.	$PbSO_4$.	
4	Res. 2.	NH_4OH.	Blackens.	Hg.	$NH_2HgCl + Hg$.	$Ag(NH_3)_2Cl$.
5	Sol. 4.	HNO_3.	No pr.	No Ag.		

The numbers in the second column refer to the operation which gave the precipitate or solution referred to, and any metal can be followed by these numbers from the beginning to the end of the analysis. The columns headed "Precip. or Residue" and "Solution" give the compounds which would be present in each case if all metals of the group were present.

Slightly acid solution: added HCl.

<table>
<tr><td colspan="3">Precipitate: $AgCl$, Hg_2Cl_2, $PbCl_2$.
Extracted with hot water.</td><td rowspan="4">Filtrate:
Groups II.—V.</td></tr>
<tr><td colspan="2">Residue: $AgCl$, Hg_2Cl_2.
Treated with NH_4OH.</td><td>Filtrate: $PbCl_2$.
Added $K_2Cr_2O_7$ solution.</td></tr>
<tr><td rowspan="2">Black residue:
$NH_2HgCl+Hg$.</td><td>Filtrate:
$Ag(NH_3)_2Cl$.
Acidified with HNO_3.</td><td rowspan="2">Yellow precipitate:
$PbCrO_4$.</td></tr>
<tr><td>No precipitate; therefore silver not present.</td></tr>
<tr><td colspan="3">Found present: Lead and mercurous mercury.</td><td></td></tr>
</table>

It is important that the record should be made in the laboratory as the experiments are performed.

Be prepared to recite upon the following questions and equations, as far as the point assigned in the lectures.

GROUP I.

Lead.

1. Lead nitrate and hydrochloric acid give?
2. Lead chloride and hot water.
3. Lead chloride and hydrogen sulphide give?
4. Lead chloride and sulphuric acid give?
5. Lead chloride, potassium dichromate and? give lead chromate, chromic acid and?

Mercury in Mercurous Salts.

1. Mercurous nitrate and hydrochloric acid give?
2. Mercurous chloride and hot water.
3. Mercurous chloride and ammonia give ammonobasic mercuric chloride and?

4. Ammonobasic mercuric chloride, mercury and *aqua regia* give mercuric chloride, ammonium chloride, nitric oxide, and water. Write first a reaction between ammonobasic mercuric chloride and hydrochloric acid, giving mercuric chloride and ammonium chloride; then a reaction between mercury and *aqua regia*, giving mercuric chloride, nitric oxide and water.

Silver.

1. Silver nitrate and hydrochloric acid give?
2. Silver chloride and hot water.
3. Silver chloride and ammonia give?
4. Ammonio-silver chloride and nitric acid give?

What ions are furnished by ammonio-silver chloride? Account for the solubility of silver chloride in ammonia, and for its reprecipitation upon acidifying the solution. What equilibria are here involved?

The chlorides of lead, mercurous mercury, and silver are appreciably soluble in concentrated hydrochloric acid. Account for this fact.

Show by means of equations the action of each of the following reagents upon lead, mercurous, and silver salt solutions: Hydrogen sulphide, sodium hydroxide, sodium carbonate.

GROUP II.

A. THE COPPER GROUP.

Mercury in Mercuric Salts.

1. Mercuric chloride and hydrogen sluphide give?
2. Mercuric sulphide and nitric acid.
3. Mercuric sulphide and aqua regia give mercuric chloride, nitric oxide, sulphur and water.
4. Mercuric chloride and stannous chloride give?
5. Mercuric sulphide and bromine solution give?

What causes the white ppt. formed on the addition of a drop of $SnCl_2$ to $HgCl_2$ solution to turn gray on the addition of more $SnCl_2$?

Lead.

1. Lead chloride and hydrogen sulphide give?

2. Lead sulphide and nitric acid give lead nitrate, nitric oxide, sulphur and water. Write first lead sulphide and nitric acid give lead nitrate and hydrogen sulphide; then hydrogen sulphide and nitric acid give nitric oxide, sulphur and water; then combine the two reactions.

3. Lead nitrate and sulphuric acid give?

Why is it directed in the procedure to evaporate with sulphuric acid at this point to white fumes, and then to dilute the solution again with water?

4. Lead sulphate and ammonium acetate give?

5. Lead acetate and potassium dichromate give?

How does it happen that lead, if present, should always be found in group II., while it may or may not be detected in Group I?

Bismuth.

1. Bismuth chloride and hydrogen sulphide give?

2. Bismuth sulphide and nitric acid give?

3. Bismuth nitrate and sulphuric acid give? Why is it directed in the procedure at this point to use as much as 3 c.c. of concentrated sulphuric acid?

4. Bismuth sulphate and ammonium hydroxide give?

5. Bismuth hydroxide and hydrochloric acid give?

6. Bismuth chloride and water give?

Explain the directions given in the procedure for making this confirmatory test.

7. Bismuth oxychloride and sodium stannite give metallic bismuth, sodium chloride, sodium stannate, and water. Write first an equation with bismuth oxychloride and sodium hydrox-

ide; then an equation with bismuth hydroxide and sodium stannite; and combine the two.

Copper.

1. Copper sulphate and hydrogen sulphide give?
2. Copper sulphide and nitric acid give? (Cf. 2., under Lead.)
3. Copper nitrate and sulphuric acid give?
4. Copper sulphate and ammonia in excess give?
5. Ammonio-cupric sulphate and sulphuric acid give copper sulphate and?
6. Copper sulphate and iron give?

Cadmium.

1. Cadmium nitrate and hydrogen sulphide give?
2. Cadmium sulphide and nitric acid give? (Cf. 2., under Copper.)
3. Cadmium nitrate and sulphuric acid give?
4. Cadmium sulphate and ammonia in excess give?
5. Ammonio-cadmium sulphate and sulphuric acid give?
6. Cadmium sulphate and iron give?
7. Cadmium sulphate and hydrogen sulphide give?

Account for the solubility of copper and cadmium hydroxides in ammonium hydroxide, giving the equilibria which are involved in the action.

Explain why iron displaces copper ions but not cadmium ions from solution. Could we use zinc instead of iron for the removal of copper, before testing for cadmium? Why?

Explain why copper, while not soluble in hydrochloric acid, will dissolve readily in nitric acid.

Explain the non-precipitation of cadmium by hydrogen sulphide in the presence of much hydrochloric acid. Describe and explain the conditions under which cadmium may be completely precipitated from acid solution by hydrogen sulphide.

Show by means of equations the action of sodium hydroxide, and of sodium carbonate, upon solutions of mercury, lead, bismuth, copper, and cadmium salts.

B. THE TIN GROUP.

Arsenic.

1. Arsenious oxide and hydrochloric acid give arsenic trichloride and?

2. Arsenic trichloride and hydrogen sulphide give?

3. Arsenious sulphide and ammonium persulphide give?

4. Arsenic acid and hydrogen sulphide give?

5. Arsenic sulphide and ammonium sulphide give?

6. Ammonium sulpharsenate and hydrochloric acid give?

7. Arsenic sulphide, hydrochloric acid, water, and potassium chlorate give arsenic acid, chlorine dioxide, potassium chloride, hydrochloric acid, and sulphur. First write an equation to show the main reaction between potassium chlorate and hydrochloric acid, then write an equation to show the interaction of arsenic sulphide, chlorine, and water; and combine the two.

8. Arsenic acid and ammonium hydroxide give?

9. Ammonium arsenate and magnesium chloride give?

Antimony.

1. Antimony trichloride and hydrogen sulphide give?

2. Antimony pentachloride and hydrogen sulphide give antimony trisulphide and? Explain.

3. Antimony trisulphide and ammonium persulphide give?

4. Ammonium sulphantimonate and dilute hydrochloric acid give?

5. Antimony pentasulphide and concentrated hydrochloric acid give antimony trichloride and?

6. Antimony trichloride and tin give?

Tin.

1. Stannous chloride and hydrogen sulphide give?

2. Stannous sulphide and ammonium persulphide give?

3. Stannic chloride and hydrogen sulphide give?

4. Stannic sulphide and ammonium sulphide give?

5. Ammonium sulpho-stannate and dilute hydrochloric acid give?

6. Stannic sulphide and concentrated hydrochloric acid give?
7. Stannic chloride and zinc give?
8. Tin and strong hydrochloric acid give?
9. Stannous chloride and mercuric chloride give?

Show by means of equations the action of sodium hydroxide, and of sodium carbonate, upon arsenious, antimonious, stannous, and stannic chlorides.

Ammonium persulphide and hydrochloric acid give?

How may we determine whether the hydrogen sulphide precipitate (Group II.) contains only sulphides of the copper group, only those of the tin group, or both?

Why is a long time sometimes required for the formation of the magnesium ammonium arsenate precipitate? How may its formation be hastened? Explain.

Explain the formation of antimony trichloride when antimony pentasulphide is dissolved in concentrated hydrochloric acid.

Name, and explain the nomenclature of the following compounds: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$ and $(NH_4)_2SnS_3$.

Explain by means of the ionic theory and the law of mass action the fact that stannic sulphide dissolves readily in concentrated hydrochloric acid, but not in the diluted acid. If you had a strongly acid solution of stannic chloride, how would you quantitatively precipitate the tin?

In what three ways may the presence of an element be detected? (See the confirmatory tests for arsenic, antimony, and tin.)

Why may we not prepare hydrogen sulphide by the action of nitric acid upon ferrous sulphide?

GROUP III.

A. THE ALUMINIUM GROUP.

Aluminium.

1. Alum and ammonium hydroxide give?
2. Alum, ammonium sulphide, and water give?

3. Sodium peroxide and water give?
4. Aluminium hydroxide and sodium hydroxide give?
5. Sodium aluminate ($NaAlO_2$) and nitric acid give?
6. Aluminium nitrate and ammonium hydroxide give?

If a precipitate of aluminium hydroxide is obtained in this test, does it necessarily indicate that the unknown contained aluminium? Explain your answer.

7. Aluminium hydroxide and nitric acid give?
8. Aluminium nitrate upon ignition gives?

Chromium.

1. Potassium chromate and hydrochloric acid give?
2. Potassium dichromate, hydrochloric acid, and hydrogen sulphide give?
3, Chromium chloride and ammonium hydroxide give?
4. Chromium hydroxide and sodium peroxide give?
5. Sodium chromate and acetic acid give?
6. Sodium dichromate, barium chloride and ? give?

An orange-colored solution, which turns green on passing hydrogen sulphide into it, then gives a greenish precipitate with ammonium hydroxide. The greenish precipitate dissolves in water, upon the addition of sodium peroxide; but on acidifying with acetic acid a bluish or violet colored liquid results, which gives no precipitate with lead acetate. On boiling, however, a copious yellow precipitate is obtained. Account for the phenomena.

Zinc.

1. Zinc chloride and ammonium sulphide give?
2. Zinc sulphide and hydrochloric acid give?
3. Zinc chloride and sodium hydroxide give?
4. Zinc hydroxide and sodium hydroxide give?
5. Sodium zincate and acetic acid give?
6. Zinc acetate and hydrogen sulphide give?

7. Zinc sulphide and nitric acid give?

8. Zinc nitrate upon ignition gives?

Show by means of equations the action of sodium carbonate solution upon aluminium, chromium, and zinc salt solutions.

If we dissolve a mixture of manganese and zinc sulphides in hydrochloric acid and wish to separate the metals by means of sodium hydroxide, why is it necessary to first boil off the hydrogen sulphide?

Explain by means of the ionic theory and the law of mass action the fact that zinc sulphide is readily soluble in dilute hydrochloric acid, but not in acetic acid. Is zinc sulphide soluble in a mixture of equal volumes of dilute hydrochloric acid and saturated sodium acetate solution? Explain.

Why is it necessary to add sodium carbonate solution in the separation of the aluminium and iron groups, unless the alkali earth metals are known to be absent? Explain.

Explain the fact that zinc hydroxide will dissolve in either hydrochloric acid or sodium hydroxide. What are such hydroxides called? Is lead hydroxide soluble in ammonia? Is zinc hydroxide? Explain their different behavior in this respect.

B. THE IRON GROUP.

Manganese.

1. Manganese sulphate and ammonium sulphide give?

2. Manganese sulphide and hydrochloric acid give?

3. Manganese chloride and sodium hydroxide give?

4. Manganese hydroxide, sodium peroxide, and water give hydrated manganese dioxide, $MnO(OH)_2$, and ?

5. Manganese dioxide and hydrochloric acid give?

6. Manganese dioxide, hydrogen peroxide, and nitric acid give?

7. Manganese nitrate, nitric acid, and potassium chlorate give?

8. Hydrated manganese dioxide, nitric acid, and lead peroxide give?

Iron.

1. Ferric chloride and hydrogen sulphide give?
2. Ferrous chloride and ammonium sulphide give?
3. Ferrous sulphide and hydrochloric acid give?
4. Ferrous chloride and sodium hydroxide give?
5. Ferrous hydroxide, sodium peroxide, and water give?
6. Ferric hydroxide and nitric acid give?
7. Ferric nitrate and potassium ferrocyanide give?
8. Ferric chloride and potassium thiocyanate give?
9. Ferric chloride and ammonium acetate give?
10. Ferric acetate solution on boiling gives?
11. Ferrous sulphate and potassium ferrocyanide give?
12. Ferrous sulphate and potassium ferricyanide give?
13. Ferric chloride and potassium ferricyanide give?
14. Prussian blue and potassium hydroxide give?

Why is iron always in the ferrous condition when we get to the third group? Is ferrous ion precipitated by ammonium hydroxide in the presence of ammonium chloride and in the absence of air? (If you do not know, saturate a solution of ferric chloride with hydrogen sulphide, filter, boil to expel hydrogen sulphide, add an equal volume of concentrated ammonium chloride solution, made by dissolving the solid salt in freshly boiled water, and then at once add ammonium hydroxide.)

Cobalt.

1. Cobalt nitrate and ammonium sulphide give?
2. Cobalt sulphide and dilute hydrochloric acid give?

Account for the facts that cobalt and nickel sulphides are not precipitated by hydrogen sulphide from dilute hydrochloric acid solution, and yet they do not dissolve at all readily on treatment with dilute hydrochloric acid.

3. Cobalt sulphide and *aqua regia* give?
4. Cobalt chloride and potassium nitrite give?
5. Cobalt nitrite and potassium nitrite give?

6. Potassium cobaltonitrite, potassium nitrite, and acetic acid give?
7. Cobalt chloride and potassium cyanide give?
8. Cobalt cyanide and potassium cyanide give?
9. Potassium cobaltocyanide and bromine solution give?

Nickel.

1. Nickel nitrate and ammonium sulphide give?
2. Nickel sulphide and *aqua regia* give?
3. Nickel chloride and potassium cyanide give?
4. Nickel cyanide and potassium cyanide give?
5. Potassium nickelocyanide, potassium hydroxide, and bromine water give?
6. Nickel chloride and potassium nitrite give?
7. Nickel nitrite and potassium nitrite give?
8. Potassium nickel nitrite, potassium nitrite, and acetic acid give?

What is the action of ammonium hydroxide on the salts of each metal of Group III., in the presence of ammonium salts? In the absence of ammonium salts?

Explain according to the ionic theory and the law of mass action why magnesium is not precipitated by ammonium hydroxide and ammonium carbonate in the presence of ammonium chloride.

Show by means of equations the action of sodium carbonate solution upon manganese, iron, cobalt, and nickel salts.

GROUP IV.

Barium.

1. Barium chloride and ammonium carbonate give?
2. Barium carbonate and acetic acid give?
3. Barium acetate and calcium sulphate give?
4. Barium acetate, water and potassium dichromate give?
5. Barium chromate, hydrochloric acid and alcohol give on boiling?
6. Barium chloride and sulphuric acid give?

Strontium.

1–3. As with barium.

4. Strontium acetate and potassium dichromate.

5. Strontium acetate and ammonium carbonate give?

6. Strontium carbonate and acetic acid give?

7. Strontium acetate and calcium sulphate give?

8. Strontium acetate and ammonium sulphate give?

Calcium.

1–8. As with strontium.

9. Calcium sulphate and ammonium oxalate give?

What are the solubility relations of calcium, strontium, and barium salts?

GROUP V.

Magnesium.

1. Magnesium chloride, ammonium chloride, ammonia and sodium phosphate give?
2. Magnesium chloride and barium hydroxide give?

Lithium.

1. Flame color of lithium.
2. Spectrum of lithium and that of potassium.

Sodium.

1. Flame color of sodium.
2. Flame color of sodium and potassium.

Potassium.

1. Flame color of potassium.
2. Chloroplatinic acid and potassium chloride give?
3. Perchloric acid and potassium chloride give?
4. Sodium cobaltinitrite and potassium chloride give?

Ammonium.

1. Chloroplatinic acid and ammonium chloride give?
2. Effect of heat on ammonium salts.
3. Ammonium chloride and caustic soda give?
4. Sodium cobaltinitrite and ammonium chloride give?

QUESTIONS FOR REVIEW

1. Outline the analysis of Group I., giving equations for the final tests.

2. A solution contains $CrCl_3$, $MnCl_2$, $FeCl_2$, and $NiCl_2$. How may the four metals be separated?

3. Write reactions for the preparation of the following substances: Prussian blue; ammonium sulpho-arsenate; copper ferrocyanide; sodium stannite; ammonium sulphide.

4. Starting with a mixture of lead and chromium hydroxides, how may lead chromate be prepared? Write the reactions.

5. Outline the analysis of Group II., giving the reactions in the case of the final tests.

6. Tell exactly how arsenic and cadmium can be completely precipitated by H_2S, starting with a solution of cadmium arsenate in strong nitric acid.

7. What effect does sodium hydroxide solution have on each of the following ions? Which precipitates dissolve in an excess of the reagent, and what is formed in each case? Ag^+, Pb^{++}, Hg^{++}, Cd^{++}, Cu^{++}, Sn^{++}, Sn^{++++}, As^{+++}, Fe^{++}, Cr^{+++}, Al^{+++}, Mn^{++}, Zn^{++}, H^+.

8. Explain by means of the ionic theory and the law of mass action why zinc may be precipitated by H_2S from a hydrochloric acid solution, to which a large quantity of $NaC_2H_3O_2$ has been added.

9. Define oxidation. Reduction. Write equations for five reactions in which oxidation and reduction take place; underline the substances which are oxidized.

10. Name the group reagents and members of each group of metals. Write the formulas of the compounds precipitated in Group II. by the group reagent, and give the color of each.

11. Outline the analysis of Group III., giving equations in the case of the final tests. Give the colors of $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, CoS, NiS, MnS, ZnS, FeS.

12. A solution contains a copper salt. Write equations showing the successive changes through which the copper passes in the course of an analysis.

13. Same for each of the other metals.

14. How may pure silver be obtained from coin silver (which contains 10 per cent. of copper)? Write the reactions.

15. Starting with barium sulphate, how may barium chloride be prepared? Write the reactions.

16. When an alkaline solution is acidified with HCl, what substances may be precipitated? How would you analyze such a solution?

17. If, in the course of an analysis, on adding ammonium sulphide to the solution, in order to precipitate Group III., you should obtain a flocculent yellow precipitate, what could it be? To what error may its presence here be due?

18. Outline the analysis of Groups IV. and V. Name and give the formulas of the insoluble salts of ammonium and potassium.

19. Give a method for the detection of cadmium in a solution which also contains copper, and explain it. Write the reactions that take place.

20. What error may cause the filtrate from the ammonium sulphide precipitate (Group III.) to be dark in color? What is the procedure if this is the case?

21. Why is it necessary to add $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ to the filtrate from Group IV. before testing for the metals of Group V.?

22. Explain by means of the ionic theory and the law of mass action why the presence of ammonium chloride prevents the precipitation of magnesium by NH_4OH.

23. What is the effect of the presence of phosphates on the precipitation of Group III.? Explain your answer.

24. A solution contains $CdCl_2$, $ZnCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_2$, and $BaCl_2$. How may the six metals be separated? Write the reactions.

25. A solution containing the six salts mentioned in the preceding question also contains phosphoric acid. How may the six metals be separated?

26. In the separation of the aluminium and iron groups, why is it necessary to add Na_2CO_3 solution unless the alkali earth metals are known to be absent? Explain.

27. Arrange the sulphates of the metals of Group IV. in the order of their solubility. Also the oxalates and the chromates.

28. How may chromates be converted into dichromates; dichromates into chromates; dichromates into chromium salts; chromium salts into chromates? Illustrate each with an equation. Give the characteristic colors of chromates, dichromates, and chromium salts.

29. Name the members of each group of acids, and tell how the presence of each group may be detected.

30. Complete the following equations:

$$CrCl_3 + Na_2CO_3 + H_2O =$$
$$AlCl_3 + Na_2CO_3 + H_2O =$$
$$AlCl_3 + (NH_4)_2S + H_2O =$$

Explain in terms of the ionic theory how these reactions take place. Why does a solution of Na_2CO_3 in water react alkaline? Why does a solution of $FeCl_3$ in water react acid?

31. Explain in terms of the ionic theory the precipitation of $SrSO_4$ by $CaSO_4$ solution, and the absence of precipitation when the latter is added to a dilute solution of a soluble salt of calcium.

32. What are the tests for sulphuric, sulphurous, thiosulphuric, and hydrobromic acids? Write the reactions, starting with sodium salts.

33. How may the following transformations be effected? (Write the reactions.) Potassium ferrocyanide to potassium ferricyanide. Sodium sulphite to sodium sulphate. Nitrous acid to nitric acid. Nickelous hydroxide to nickelic hydroxide. Silica to hydrofluosilicic acid.

34. What salts, if any, of the following acids are insoluble: sulphuric, hydrochloric, acetic, nitric, and carbonic?

35. Describe the brown-ring test for nitric acid. Write the reactions, starting with $NaNO_3$.

36. How may phosphoric and arsenic acids be detected in the same solution?

37. How may chlorides, bromides, and iodides be detected in the same solution? Write the reactions, starting with sodium salts.

38. How may oxalic and carbonic acids be detected in the same unknown? Write the reactions, using calcium salts.

39. What acids form barium salts which are insoluble in water? What happens when $AgNO_3$ solution is added in excess to a cold solution of $Na_2S_2O_3$? Explain.

40. What inference do you draw from the fact that the chromates of calcium and strontium are not precipitated in presence of acetic acid, while $BaCrO_4$ is so precipitated? Explain in terms of the ionic theory the non-precipitation of $BaCrO_4$ in the presence of hydrochloric acid.

41. What indications may be derived from the preliminary test with conc. H_2SO_4 in regard to the acids present in an unknown substance?

42. Can As be precipitated from solution with Na_2CO_3? Why? Do any other members of the first four groups of metals (including Mg) resemble arsenic in this respect? What use is made of this fact in qualitative analysis? May Mg be precipitated from a solution containing NH_4Cl by boiling with Na_2CO_3? Explain your answer.

43. Explain the non-precipitation of Cd^{++} by H_2S if the solution is strongly acid with HCl. Would the result be different if much $NaC_2H_3O_2$ were added to the strongly acid solution? Explain. Why then do we not add $NaC_2H_3O_2$ solution in the precipitation of Group II.?

44. How may the presence of nitrate be detected in a substance known to contain chlorate? What is the purpose of the Na_2CO_3 used in this test?

45. Give tests for hydrofluoric, silicic, nitrous, and acetic acids.

46. How may we determine whether the H_2S precipitate (Group II.) contains only sulphides of the copper group, only those of the tin group, or both? If both are present, how may we know when we have completely separated them?

47. What ions are furnished by the salt $KFe(SO_4)_2.12H_2O$, when it is dissolved in water? By $(NH_4)_2Fe(SO_4)_2.6H_2O$? What is the class-name of such salts? How do they differ from salts like $Ag(NH_3)_2Cl$, $KAg(CN)_2$, $K_4Fe(CN)_6$, etc.? What is the class-name of these salts? Is there any sharp dividing line between these two classes of salts? Illustrate.

48. Upon warming Hg_2SO_4 with HCl, a gas with a suffocating odor is evolved; why? Copper sulphite, a brick red powder of the formula $CuSO_3$, is soluble in dilute HCl, but a white precipitate of Cu_2Cl_2 soon separates from the solution; account for this.

49. In testing a substance known to contain mercury for acetic acid, with conc. H_2SO_4 and alcohol, a disagreeable, suffocating odor was obtained, instead of the pleasant odor of ethyl acetate. Upon adding conc. H_2SO_4 to a little of the moistened substance in a watch glass, however, the odor of acetic acid was very distinct. Account for the failure of the first test.

50. What are the proper conditions for the precipitation of BiOCl in the confirmatory test for bismuth? Explain.

51. Explain why silver sulphide (which is less soluble in water than the chloride) is soluble in nitric acid, while the chloride is not.

PREPARATION OF REAGENTS.

Acetic acid: Sp. gr. 1.041 (30 per cent. $HC_2H_3O_2$); mix 1 liter of glacial acetic acid with 2.5 liters of water.

Ammonium acetate: Add 1000 c.c. NH_4OH (sp. gr. 0.90) to 900 c.c. glacial acetic acid and neutralize the mixture with more NH_4OH or $HC_2H_3O_2$. For a 50 per cent. solution, dilute to sp. gr. 1.092; for a 10 per cent. solution, dilute to sp. gr. 1.022.

Ammonium carbonate:

250 grams "am. carbonate"
100 c.c. NH_4OH (sp. gr. 0.90) Digest in a closed bottle.
1000 c.c. water.

Ammonium chloride: 1 :10.

Ammonium hydroxide: sp. gr. 0.96 (10 per cent. NH_3).

1 liter NH_4OH (sp. gr. 0.90)
2 liters water.

Ammonium molybdate: Mix 100 grams MoO_3 with 400 c.c. cold water and add 80 c.c. NH_4OH (sp. gr. 0.90). Filter, and pour the filtrate with constant stirring into a mixture of 300 c.c. HNO_3 (sp. gr. 1.42) and 700 c.c. water.

Ammonium oxalate: 1 :25. Use warm water.

Ammonium persulphide: Pass the gas evolved from the action of 200 c.c. conc. commercial H_2SO_4, properly diluted, upon an excess of FeS (calculated about 360 grams), into 1 liter NH_4OH (sp. gr. 0.96). Dissolve 25 grams of flowers of sulphur in each liter of solution.

Ammonium sulphate: 1 :4.

Barium chloride: 1 :40.

Barium hydroxide: 1 :20.

Bromine water: Saturated solution.

Calcium chloride: 1 :10.

Calcium hydroxide: Saturated (filtered) solution.

Calcium sulphate: Saturated (filtered) solution.

Chlorine water: Saturated solution. Keep in opaque glass-stoppered bottles.

Chloroplatinic acid: 1:50.

Cobalt nitrate: (1 c.c. contains 0.5 mg. metallic cobalt); 2.5 grams $Co(NO_3)_2.6H_2O$ in 1 liter.

Ferric chloride: 1:10.

Ferric sulphate: Take 200 grams $FeSO_4.7H_2O$, add 200 c.c. dil. H_2SO_4 and 12 c.c. conc. HNO_3. Heat rapidly to boiling and boil vigorously for some time to expel the nitric oxide. Dilute to 1 liter.

Ferrous sulphate:

400 grams $FeSO_4.7H_2O$.
200 grams $(NH_4)_2SO_4$.
100 c.c. conc. H_2SO_4.
1000 c.c. water.

The solution will keep well enough to use in tests for HNO_3 for several months. It should not be used in the test for hydrocyanic acid.

Hydrochloric acid (conc.): Sp. gr. 1.19 (37 per cent. HCl).

Hydrochloric acid (dil.): Sp. gr. 1.12 (24 per cent. HCl); mix 1 liter HCl (sp. gr. 1.19) with 700 c.c. water.

Hydrogen peroxide: 3 per cent. solution.

Lead acetate: 1:10.

Magnesia mixture: Dissolve 90 grams $MgCl_2.6H_2O$ and 240 grams NH_4Cl in 1 liter of water, and add 50 c.c. NH_4OH sp. gr. 0.90).

Mercuric chloride: 1:20.

Nitric acid (conc.): Sp. gr. 1.42 (70 per cent. HNO_3).

Nitric acid (dil.): Sp. gr. 1.20 (32 per cent. HNO_3); mix 1 liter HNO_3 (sp. gr. 1.42) with 1675 c.c. water.

Nessler's Solution: Dissolve 6 grams $HgCl_2$ in 50 c.c. ammonia-free water at 80° in a porcelain dish, add a solution of 7.4 grams KI in 50 c.c. ammonia-free water, cool, decant the liquid, and wash the precipitate by decantation with three separate 20 c.c. portions of cold water. Now add 5 grams solid KI, and enough water to dissolve the mixture, transfer the solution to a 100 c.c. measuring flask, add a solution of 20 grams NaOH in a little water, cool, and dilute the volume to 100 c.c. Allow the mixture to settle, siphon off the colorless liquid into a clean bottle and preserve it in the dark.

Perchloric acid: Sp. gr. 1.12 (20 per cent. $HClO_4$).

Potassium cyanide: 1 : 10.

Potassium pyrochromate: 1 : 10. Use hot water.

Potassium ferrocyanide: 30 grams $K_4Fe(CN)_6.3H_2O$ in 1 liter.

Potassium nitrite: 3 : 10.

Potassium thiocyanate: 1 : 10.

Silver nitrate: 1 : 40.

Silver sulphate: Saturated solution.

Sodium Acetate: Saturated solution.

Sodium carbonate: 100 grams of anhydrous salt in 1 liter.

Sodium hydroxide: 1 : 10.

Sodium phosphate: 1 : 10.

Sulphuric acid (conc.): Sp. gr., 1.84 (96 per cent. H_2SO_4).

Sulphuric acid (dil.): Sp. gr. 1.19 (26 per cent. H_2SO_4); mix 1 volume of conc. H_2SO_4 (sp. gr. 1.84) with 5 volumes of cold water, slowly adding the acid to the water with constant stirring.

Stannous chloride: Dissolve 125 grams $SnCl_2.2H_2O$ in 1 liter of water, with the addition of conc. HCl, and keep the solution in bottles containing granulated tin.

TABLE OF

	Arsenate.	Arsenite.	Chromate.	Sulphate.	Phosphate.	Borate.	Oxalate.	Fluoride.	Carbonate.	Silicate.	Chloride.
Silver........	HNO_3	HNO_3	HNO_3	W-A	HNO_3	HNO_3	HNO_3	W	HNO_3	......	I
Mercury (ous)..	HNO_3	HNO_3	HNO_3	W-A	HNO_3	......	HNO_3	HNO_3	HNO_3	......	HNO_3
Mercury (ic)...	HCl	HCl	W-A	W-A	HCl	......	HCl	HNO_3	HCl	......	W
Lead..........	HNO_3	HNO_3	A-I	A-I	HNO_3	HNO_3	HNO_3	HNO_3	HNO_3	HNO_3	W-A
Bismuth......	HCl	......	HCl	W-A	HCl	HCl	HCl	HNO_3	HCl	......	W-A
Copper........	HCl	HCl	W	W	HCl	HCl	HCl	HCl	HCl	HCl	W
Cadmium.....	HCl	......	HCl	W	HCl	W-A	HCl	W-A	HCl	HCl	W
Tin (ous)......	HCl	HCl	HCl	W	HCl	HCl	HCl	W	......	......	W
Tin (ic).......	HCl	......	......	......	HCl	......	W	W	......	......	W
Antimony.....	HCl	HCl	HCl	HCl	W-A	......	HCl	W	......	......	W-A
Iron (ous).....	HCl	HCl	......	W	HCl	HCl	HCl	W-A	HCl	HCl	W
Iron (ic)......	HCl	HCl	W	W	HCl	HCl	HCl	A-I	HCl	HCl	W
Aluminium....	HCl	......	......	W	HCl	HCl	HCl	A-I	......	A-I	W
Chromium.....	HCl	......	HCl	W or I	HCl	HCl	W-A	A-I	......	HCl	W or I
Cobalt........	HCl	HCl	HCl	W	HCl	HCl	HCl	W-A	HCl	HCl	W
Nickel........	HCl	HCl	HCl	W	HCl	HCl	HCl	W-A	HCl	HCl	W
Manganese....	HCl	HCl	W	W	HCl	HCl	W-A	W-A	HCl	HCl	W
Zinc..........	......	......	W	W	HCl	HCl	HCl	W-A	HCl	HCl	W
Barium.......	HCl	HCl	HCl	I	W&A	HCl	HCl	A-I	HCl	HCl	W
Strontium.....	HCl	HCl	W-A	I	W&A	HCl	HCl	A-I	HCl	HCl	W
Calcium.......	HCl	HCl	W-A	W-I	W&A	HCl	HCl	A-I	HCl	HCl	W
Magnesium....	HCl	HCl	W	W	HCl	W-A	HCl	A-I	HCl	HCl	W
Potassium.....	W	W	W	W	W	W	W	W	W	W	W
Sodium.......	W	W	W	W	W	W	W	W	W	W	W
Ammonium....	W	W	W	W	W	W	W	W	W	......	W

HNO_3. Soluble in HNO_3, in most cases insoluble, or slightly soluble in HCl.
HCl. Soluble in HCl, in many cases soluble in other acids, also.
W. Soluble in water.

SOLUBILITIES.

Bromide.	Iodide.	Cyanide.	Ferrocyanide.	Ferricyanide.	Sulphide.	Nitrate.	Chlorate.	Acetate.	Tartrate.	Citrate.	Oxide.	Hydroxide.	
I	I	I	I	I	HNO_3	W	W	W	HNO_3	HNO_3	HNO_3	......	Silver.
HNO_3	HNO_3	......	.....	.....	AqReg	W	W	W-A	W-A	HNO_3	HNO_3	......	Mercury(ous)
W	HNO_3	W	.....	.....	AqReg	W	W	W	HCl	W-A	HCl	......	Mercury (ic).
W-A	W-A	HNO_3	A	W-A	HNO_3	W	W	W	HNO_3	HNO_3	HNO_3	HNO_3	Lead.
W-A	HCl	......	.....	.....	HNO_3	W-A	W	W	HCl	......	HCl	HCl	Bismuth.
W	W	HCl	I	.....	HNO_3	W	W	W	W	W	HCl	HCl	Copper.
W	W	HCl	.....	.....	HNO_3	W	W	W	W-A	HCl	HCl	HCl	Cadmium.
......	W	......	.....	.....	HCl	.....	W	W	HCl	......	HCl	HCl	Tin (ous).
......	W	......	.....	.....	HCl	.....	..	W	......	......	A&I	HCl	Tin (ic).
W-A	W-A	......	.....	.....	HCl	.....	..	.....	W-A	......	HCl	HCl	Antimony.
W	W	A-I	I	I	HCl	W	W	W	W-A	W	HCl	HCl	Iron (ous).
W	W	......	I	W	AqReg	W	W	W	W	W	HCl	HCl	Iron (ic).
W	W	......	.....	.....	HCl	W	W	W	W	W	A&I	HCl	Aluminium.
W or I	W	HCl	.....	.....	A-I	W	W	W	W	W	A&I	HCl	Chromium.
W	W	A-I	I	I	HNO_3	W	W	W	W	W	HCl	HCl	Cobalt.
W	W	A-I	I	I	HNO_3	W	W	W	HCl	W	HCl	HCl	Nickel.
W	W	HCl	HCl	I	HCl	W	W	W	W-A	HCl	HCl	HCl	Manganese.
W	W	HCl	A-I	HCl	HNO_3	W	W	W	HCl	W-A	HCl	HCl	Zinc.
W	W	W-A	W-A	.....	W	W	W	W	HCl	HCl	W	W	Barium.
W	W	W	W	.....	W	W	W	W	HCl	HCl	W	W	Strontium.
W	W	W	W	W	W-A	W	W	W	HCl	W-A	W-A	W-A	Calcium.
W	W	W	W	W	HCl	W	W	W	W-A	W	HCl	HCl	Magnesium.
W	W	W	W	W	W	W	W	W	W	W	W	W	Potassium.
W	W	W	W	W	W	W	W	W	W	W	W	W	Sodium.
W	W	W	W	W	W	W	W	W	W	W	......	W	Ammonium.

W-A. Slightly soluble in water, soluble in acids.
A-I. Insoluble in water, slightly soluble in acids.
I. Insoluble in water and acids.