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# ELEMENTS

OF

QUALITATIVE AND QUANTITATIVE

# CHEMICAL ANALYSIS

BY

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AUTHOR OF AGRICULTURAL CHEMICAL ANALYSIS; MANUAL OF INTRODUCTORY  
CHEMICAL PRACTICE; MANUAL OF QUALITATIVE ANALYSIS.



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*SECOND EDITION, REVISED AND ENLARGED.*

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## PREFACE.

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In this work the author has brought together what has already been published, separately, in the "Manual of Qualitative Chemical Analysis," by himself and Dr. S. M. Babcock, and the "Notes on Chemical Analysis," by himself alone; he has added thereto much matter on qualitative analysis, all of Parts III and IV on quantitative analysis, and nearly all of Part V.

Of course no such work as this can be satisfactorily prepared without frequent reference to the standard treatises of Prescott and Johnson, and of Fresenius, in one of which the whole subject of qualitative analysis is very thoroughly treated, and in the other both qualitative and quantitative analysis. The author would acknowledge his indebtedness to these works, while claiming for himself at least some novelty in the arrangement of the matter, as well as in some of the matter itself, in this attempt to prepare a book that is much needed in his own laboratory.

Also, for valuable suggestions in the revision of the work for the second edition, he is indebted to Professor Dennis, and Instructors Chamot and Preswick, of the University.

Certain modifications in the spelling of chemical terms, adopted after careful consideration by the chemical section of the American Association for the Advancement of Science, are used in this second edition.



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- Tables showing per cent. of  $\text{NH}_3$ ,  $\text{SO}_3$ ,  $\text{HCl}$ ,  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$ , in solutions,  
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- Table of comparison of weights and measures.
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## INTRODUCTION.

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At Cornell University a large number of students in some of the technical courses are required to take an elementary course of practice in chemical analysis, including both qualitative and quantitative work, after having had the elements of general chemistry in this University or elsewhere.

There are many comprehensive and excellent works on chemical analysis in general, and on particular branches of chemical analysis, with which every special student of chemistry is acquainted; but these works are too large and expensive for any but the professional chemist. There are also numerous smaller works on the general subject. But in such of these as the author has met with no special chapters are devoted to the enlightenment of the student beginning this study, on the chemistry of the operations of qualitative and quantitative analysis in general; he must, therefore, be referred to the larger works for this important information.

Consequently either every beginner, whether his proposed course be thorough or elementary, must possess the works of Fresenius, or some other treatise of equal scope on the subject, or else copies of these works must be placed in the laboratory, for reading or reference,—many copies, if the number of students is large. Each plan has its manifest disadvantages.

In these considerations the author finds the reason for the publication of this little volume, for the convenience of his own students,—that they may have always at hand such full details as to the chemistry and manipulation of these operations that they are called upon to perform, many of which are entirely new to them, that they need never be at a loss as to what to do, or how to do it, or why they do it, if they will read with care what is here given. When the work laid out in this book is mastered, the student who wishes to go further in general or special directions will find himself prepared to use the general or special treatises on chemical analysis, for no one of which this introduction can be taken as a substitute.

Chemical analysis is studied usually because the student expects to make some application of it in his business or profession; in so far it is a practically useful study. But beyond this it has, as does the study of every branch of science, its special disciplinary value. It enforces the importance of attention to even small details in manipulation; the student learns, if he is capable of learning anything by experience, that the only sure way to success in any part of the work is by the closest following of the directions given him, at least till he has proved, by conclusive results of his own experiments or observations, that there is a better way; but this better way must in its turn be followed no less precisely.

No one of the analytical processes in use is absolutely perfect; it is this that makes accuracy and precision in the manipulation of so much the greater account. Such discipline as this practice affords of the hand, eye, and judgment is useful in many of the professions for which the first special training is given in the University.

Chemical analysis comprises two kinds:—

Qualitative analysis, by which we ascertain what chemical elements or compounds a substance contains.

Quantitative analysis, by which we ascertain how much of one or more of its constituents the substance contains.

The chemistry and manipulation common to both kinds of analysis is treated in Part I of this work. The systematic course of qualitative analysis follows in Part II. In Part III a description is given of some of the special operations of quantitative analysis, and in Part IV the special examples for practice comprised in this short course are described and explained. Finally, in Part V, lists of apparatus and reagents are given, with some instructions concerning their proper use, and several Tables for reference.



PART I.

THE PROCESSES OF ANALYTICAL CHEMISTRY,  
AND THE  
PRODUCTS OF ITS OPERATIONS.

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CHAPTER I.

SOLUTION AND SOLIDS FROM SOLUTION.

1. The getting of substances into solution, and getting them out of solution into the solid form, are fundamental operations of analytical chemistry with which the student has to deal more than with any others, especially in the earlier stages of his work. Some general acquaintance with the principles and methods of the solution of substances is essential at the very outset.

2. SOLUTION:—*The solvent agents used.* The more important solvent agents used in chemical analysis are, besides water, aqueous solutions of hydrochloric acid, nitric acid, and acetic acid, of the alkaline hydroxids, KOH, NaOH, or  $\text{NH}_4\text{OH}$ , of alkaline sulfids, especially ammonium sulfid, and alcohol, ether, and carbon disulfid.

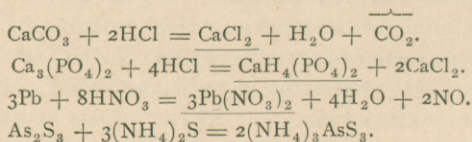
3. Since all these acids and alkaline solvents consist largely of water, a substance that is insoluble in water cannot, so long as it is the same chemical substance, be dissolved by any one of them. Therefore when a substance that is insoluble in water is dissolved with the aid of a solution of an acid, such as the hydrochloric acid of the laboratory, or of an alkaline hydroxid, or an alkaline salt, such as a sulfid or a chlorid, some chemical change must precede such solution. On these grounds two kinds of solution may be distinguished, *physical solution* and *chemical solution*.

4. *Physical solution* is the resultant solely of the mutual action of physical forces among the particles of the solid and of the liquid, the final result of which is the disappearance of the solid

as a separate substance, visibly distinct from the liquid; it becomes completely merged in the liquid, but suffers no chemical change; on removing the solvent, in any way that does not chemically affect the substance dissolved in it, as by evaporation, this substance reappears possessing the same chemical properties as before. This is the kind of solution that is commonly effected by water.

5. *Chemical solution* involves a chemical alteration of the substance dissolved, and the production of a new substance that is soluble. It may take place with water alone, when the substance is an oxid that can form a soluble hydroxid. CaO is probably insoluble in water, but Ca(OH)<sub>2</sub>, formed as soon as this oxid is brought in contact with water, is slightly soluble. We cannot say that we know whether K<sub>2</sub>O is soluble or insoluble in water; for in the instant of contact between the two KOH is formed, which is very soluble.

Most commonly, it is a more active agent than water, which serves to bring about the solution by chemical change, such as an acid or an alkaline solution; and if the excess of acid or alkali, remaining after the solution is completed, be wholly removed, leaving nothing but water, the solution still continues undisturbed, which is evidence that a new substance has been formed, soluble in water; and it has been formed by chemical changes affecting the solvent agent as well as the substance dissolved, as illustrated by the following equations:—



The substances whose formulas are underlined are new substances, which are soluble in water.

6. *Table of solubilities.* Some acquaintance with the solubility of the chemical compounds met with in the ordinary work of chemical analysis is very helpful to the student. In the following Table, *W* in the square corresponding to any salt indicates easy solubility in water, *w* sparing solubility, *wa* solubility in water only when at least slightly acidified, *A* insolubility in water but solution by moderately dilute mineral acids, and *I* insolubility in water or dilute acids. Slight trace of solubility in water or dilute acids, or solubility or insolubility in acetic

TABLE I.—SOLUBILITIES.

	Aluminum.	Ammonium.	Antimonous.	Barium.	Bismuth.	Cadmium.	Calcium.	Chromium.	Cobalt.	Copper.	Gold.	Ferrous.	Ferric.	Lead.	Magnesium.	Manganese.	Mercurous.	Mercuric.	Nickel.	Platinic.	Potassium.	Silver.	Sodium.	Stannous.	Stannic.	Strontium.	Zinc.
Acetate,	W	W	A	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Arsenate,	W	W	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Arsenite,	W	W	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Borate,	A	W	..	A	A	w	A	W	A	A	..	A	A	A	w	A	..	A	W	..	W	W	W	W	W	W	W
Bromid,	W	W	wa	W	wa	W	W	W	W	W	..	W	W	w	W	W	W	W	W	..	W	W	W	W	W	W	W
Carbonate,	W	W	..	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Chlorate,	W	W	..	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Chlorid,	W	W	wa	W	wa	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Chromate,	..	W	A	A	W	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Cyanid,	..	W	..	w	w	W	W	W	W	W	A	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Ferricyanid,	..	W	..	w	w	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Ferrocyanid,	..	W	..	w	w	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Fluorid,	A	W	W	W	W	w	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Hydroxid,	A	W	..	W	A	W	w	W	W	W	A	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Iodid,	..	W	wa	W	wa	W	W	W	W	W	A	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Nitrate,	W	W	..	W	wa	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Oxalate,	A	W	A	..	W	W	W	W	W	W	A	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Oxid,	A	W	A	..	W	W	W	W	W	W	A	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Phosphate,	A	W	A	A	A	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Sulfate,	W	W	wa	A	wa	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Sulfid,	W	W	I	W	I	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W
Sulfite,	W	W	A	W	A	W	W	W	W	W	..	W	W	W	W	W	W	W	W	..	W	W	W	W	W	W	W

acid is not taken account of, nor solubility or insolubility of other than *normal* salts (§ 15), except when, as in the case of many carbonates, for example, basic salts are those ordinarily met with.

An examination of this Table shows at once that all normal nitrates and acetates, and all the salts of the alkaline metals (potassium, sodium) are soluble. Other similar general conclusions can be deduced by the student himself, which, once familiarly learned, will be very useful in working out equations.

Of solubility in strong acids, but not in dilute, the following instances are specially important: nearly all insoluble sulfids are soluble in concentrated nitric acid; many insoluble silicates are decomposable by concentrated hydrochloric acid, with solution of the bases.

7. *Solution of metals.* As to the solubility of the commonly occurring metals, it is to be noticed that all are absolutely insoluble in pure water; that those of the aluminum and iron groups are soluble in hydrochloric or sulfuric acid, with evolution of hydrogen, and with the formation of chlorids or sulfates; they are soluble in nitric acid, with the formation of the usual products (§ 24 b); that the rest, except gold and platinum, are dissolved by nitric acid, forming solutions except in cases of antimony and tin, that gold and platinum are attacked by aqua regia or any mixture evolving free chlorin.

8. *Miscellaneous considerations.* a. *Solubility and temperature:* The solubility of salts is in most cases much greater in hot than in cold solvents.

b. *Solubility of salts in acids.* A salt that is perfectly soluble in water may be insoluble in strong acid: the salt, if separated out or precipitated in the acid, usually takes a somewhat crystalline form, often to the confusion of the young analyst; on the addition of sufficient water, solution takes place readily. For instance, barium chlorid, which is easily soluble in water, is not soluble in strong hydrochloric acid; hence, if barium carbonate is dissolved in too strong a solution of the acid, the chlorid is apt to appear as a crystalline deposit.

c. *Comparative range of solvent power of different solvents.* In the operations of chemical analysis, the solubility or insolubility of substances is utilized in, more particularly, water, alcohol, mineral acids, organic acids, and solutions of alkaline hydroxids or hydrates, or alkaline solutions as they are commonly called. Of these, water has by far the widest range of

solvent power; it may, in fact, be called *the* solvent upon which we depend in nearly all cases for solution of substances: a chemically active agent does not dissolve, but, as has been already shown, only makes new compounds that are soluble in water. For this preparatory work, hydrochloric and nitric acids have the widest range of action; comparing these two acids, it may be observed that while nitric acid will dissolve nearly all substances that are dissolved by hydrochloric acid, it will, in virtue of being an oxidizing agent (§ 20), dissolve many substances that hydrochloric acid will not dissolve, such as some metals and their sulfids.

d. *A saturated solution.* For each substance and each neutral solvent in which it is soluble, there is a definite limit to the amount of the substance that can be dissolved at a given temperature; when this limit is reached the solution is said to be saturated. When the temperature of such a solution falls, or, in a very few cases, is raised, or when any of the solvent is removed, a portion of the substance separates out in the solid form. When thus separated it is more or less crystalline. Therefore, when a crystalline deposit appears in a solution, for no other apparent reason than a possible change in one or both of these conditions mentioned above, it can be re-dissolved either by adding more of the solvent, usually only water being required, or by raising the temperature.

e. In the case of chemical solution, the quantity of the substance dissolved is dependent on the quantity of water present to dissolve the new substance formed, and also, in accordance with the laws of stoichiometry, on the quantity of the chemically active, solvent agent present. So far as this active agent is concerned, it is independent of the temperature, except that, as chemical action is stronger at high than at low temperatures, the solution will proceed more rapidly if the mixture of substance and solvent is heated.

g. *Solution of gases or of vapors.* Some of the reagents used in chemical analysis are solutions of gases or vapors in water, such as hydrochloric acid and ammonia; and some reactions that are made use of in the analytical work depend to some extent on such solution.

As in the solution of solids in water, there is a definite limit to the amount of the gas dissolved for any given temperature; but the amount dissolved increases, instead of diminishing, as the temperature falls, and increases also as the pressure of the

particular gas dissolved increases on the surface of the liquid, or, in other words, as the proportion of that gas increases in the air to which the dissolving liquid is exposed.

From what has been stated above, except when a solution of a gas is very dilute, that is, has but a very little of the gaseous substance in it, if the solution is warmed a portion of the substance will escape; or, if a strong solution is poured from a closed vessel into an open dish, or even if the stopper of the bottle containing it is left out, the gas will escape.

Other reagents in common use are solutions of substances that are volatile only at moderately elevated temperatures, or of vapors, such as bromin water. On heating such a solution the substance dissolved will escape in part, and the more rapidly the lower the temperature at which it assumes the vaporous form. In a solution containing a mixture of such substances, the more volatile one may be almost entirely expelled by heat, while a large portion of the other still remains; thus nitric acid or hydrochloric acid may be removed from a solution by heating it for a sufficient length of time with a large excess of sulfuric acid.

**10. SOLIDS FROM SOLUTION:**—There are many ways by which the reverse of solution of solids can be accomplished; some of these have been referred to in the preceding sections.

*The cooling of saturated solutions.* This is of little account in analytical work. In a few cases, when the cooling is slow, the crystalline form assumed by the solid may be a convenient means of identifying it or confirming results of other tests.

**11. The removal of the solvent agent.** This may be accomplished in three ways.

a. By its slow escape, as it passes into vapor by simple exposure to the air. This takes place readily with the chemically inactive solvents, water, alcohol, common ether, petroleum ether, and carbon disulfid. The process is of little use in analytical work, except when, as also in the case of slow cooling of saturated solutions referred to in the preceding section, the solid obtained may exhibit some characteristic crystalline form that will aid in its identification. Such an operation is best applied to a small quantity of the liquid in a watch glass, and it is usually necessary to examine the deposit with the microscope.

b. By the rapid removal of the solvent by the aid of heat. This is a very important analytical process, for it often becomes necessary to obtain the product of some operation, or series

of operations, in the solid form, expeditiously : see Evaporation, Chap. VI.

c. By the removal of an active solvent through neutralization. Many precipitates are soluble in acids, and some are soluble in solutions of alkaline hydroxids or salts, forming new, soluble compounds; on neutralizing the acid or the base, or decomposing the solvent salt by an acid, the original substance is precipitated again, in some cases; in other cases, another substance is formed, of the same qualitative composition, but different quantitative composition. The solution of ammonium magnesium phosphate in acid and the effect of the neutralization of the acid by ammonia, also the solution of aluminum hydroxid in sodium hydroxid and the result of the neutralization of the alkali by acid, are good illustrations of the first mentioned kind of action. See aluminum and magnesium in the aluminum and calcium groups, Chap. X. The precipitation by acids of the sulfids of arsenic, tin, and antimony from their solutions in ammonium sulfid, illustrates the second kind of action; see the tin group, Chap. X.

b. By the formation, through chemical action, of a new insoluble compound containing at least one of the constituents of the substance dissolved. This method of obtaining solids from solution, which is of fundamental importance in analytical chemistry, will be more fully considered in Chapter IV, on Metathesis.

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## CHAPTER II.

### ACIDS, BASES, SALTS.

12. A solution made in any of the ways described in Chap. I may contain *acids*, *bases*, or *salts*.

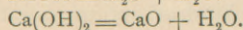
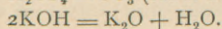
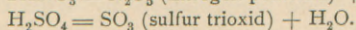
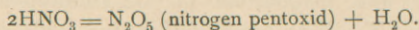
For our present purposes, an *acid* may be defined to be a body always containing (1) hydrogen, (2) a so-called electro-negative or acidigenic (acid-generating) element, such as chlorine, sulfur, phosphorus, and (3) sometimes oxygen; its hydrogen being replaceable by an electro-positive or basigenic (base-generating) element or compound, such as potassium, calcium, magnesium. An acid may, however, contain, in the place of one of the regular acidigenic elements, an element usually basigenic, as iron,

or manganese in manganic or permanganic acid. The presence of an acid in solution is indicated by the reddening of blue litmus paper.

13. A *base* is a body containing (1) a basigenic or base-forming element or compound, such as potassium, ammonium, calcium, or iron, and (2) the hypothetical hydroxyl, HO, this hydroxyl being replaceable by an acid minus its basic hydrogen. The presence of a base in solution is indicated by the blue color given to red litmus, or the brown color given to turmeric.

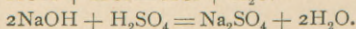
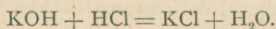
By the abstraction of the elements of water from one or two molecules of an acid or a base, the so-called *anhydrids* are produced: these anhydrids are also called oxids, with the prefixes *di, tri, tetra, pent*, used to indicate the number of atoms of oxygen, when more than one atom is present.

Thus:—



14. A salt is the body formed when the hydrogen of an acid replaceable by a basigenic element or compound, or the hydroxyl of a base replaceable by an acid minus its basic hydrogen, is so replaced.

Thus:—



It will be seen that in all cases where a salt is formed by the mutual action of a base and an acid, water is produced from the hydrogen of the hydroxyl and a part or all of the oxygen. Salts may also be formed by the direct union of acidigenic and basigenic oxids.

A most characteristic property of an acid and a base, respectively, is this tendency to react with each other, and, neutralizing each other's marked properties, to form a salt.

15. Of *salts* there are several kinds. A normal salt is one in which the basigenic element or compound is substituted for all the replaceable hydrogen of the acid; for example,  $\text{K}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ .

16. An acid salt is one of an acid having more than one replaceable atom of hydrogen, in which less than the whole number is replaced by a basigenic element; for example,  $\text{KHSO}_4$ ;  $\text{NaH}_2\text{PO}_4$ , compared with  $\text{Na}_3\text{PO}_4$ .



17. A basic salt is one, following the same line of definition, in which only a part of the hydroxyl of a base having more than one molecule thereof is replaced by an acid minus its hydrogen, or in which there is a smaller number of molecules of the acidigenic part of the salt, as compared with the basigenic part, than in the normal salt; for example,  $\text{PbOHNO}_3$ ,  $\text{Pb}_2\text{O}_2\text{OHNO}_3$ , compared with the normal salt  $\text{Pb}(\text{NO}_3)_2$ ;  $\text{Bi}(\text{OH})_2\text{NO}_3$ ,  $\text{BiOCl}$ , compared with the normal salt  $\text{Bi}(\text{NO}_3)_3$ .

Basic salts are often difficultly soluble, when normal salts of the same acid are soluble, and sometimes cause the analyst much trouble: thus, while solubility in water is an eminent characteristic of all normal nitrates, many basic nitrates are insoluble in water.

18. A double salt is defined as one containing with one acidigen two basigens, as  $\text{KNaSO}_4$ ,  $\text{KPtCl}_6$ .

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### CHAPTER III.

#### OXIDATION, CHLORINATION, REDUCTION.

19. These processes play an important part in the operations of chemical analysis, and a clear understanding of their nature, and of the conditions under which they take place, is essential to intelligent work.

Oxidation is the addition of oxygen to a substance, in chemical combination: chlorination is the addition of chlorin to a substance in chemical combination; the reverse of either of these operations is reduction.

20. *Conditions under which oxidation or chlorination may take place.*

a. The substance must be one capable of taking oxygen or chlorin into chemical combination. Such substances are all the basigenic elements, in the list in the Table, § 37, whether these elements are in the free state, or combined with sulfur as sulfids. In the latter case the sulfur is displaced by the oxygen or chlorin. Moreover, several of these elements are met with in ordinary analytical work in combination with more than

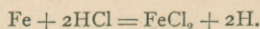
one proportion of oxygen or chlorin, as shown in the following table:—

FeO,	FeCl <sub>2</sub> ;	Fe <sub>2</sub> O <sub>3</sub> ,	FeCl <sub>3</sub>
NiO,	NiCl <sub>2</sub> ;	Ni <sub>2</sub> O <sub>3</sub> ,	NiCl <sub>3</sub>
CoO,	CoCl <sub>2</sub> ;	Co <sub>2</sub> O <sub>3</sub> ,	CoCl <sub>3</sub>
		Cr <sub>2</sub> O <sub>3</sub> ,	CrCl <sub>3</sub> ; CrO <sub>3</sub>
MnO,	MnCl <sub>2</sub> ;	Mn <sub>2</sub> O <sub>3</sub> ,	MnCl <sub>3</sub> ; MnO <sub>2</sub> ; MnO <sub>3</sub> ; Mn <sub>2</sub> O <sub>7</sub>
Cu <sub>2</sub> O,	CuCl;	CuO,	CuCl <sub>2</sub>
Hg <sub>2</sub> O,	HgCl;	HgO,	HgCl <sub>2</sub>
Au <sub>2</sub> O,	AuCl <sub>2</sub> ;	Au <sub>2</sub> O <sub>3</sub> ,	AuCl <sub>3</sub>
As <sub>2</sub> O <sub>3</sub> ,	AsCl <sub>3</sub> ;	As <sub>2</sub> O <sub>5</sub>	
Sb <sub>2</sub> O <sub>3</sub> ,	SbCl <sub>3</sub> ;	Sb <sub>2</sub> O <sub>5</sub> ,	SbCl <sub>5</sub>
SnO,	SnCl <sub>2</sub> ;	SnO <sub>2</sub> ,	SnCl <sub>4</sub>

Therefore any one of these elements, although already in combination with oxygen or chlorin, may possibly combine with an additional quantity.

Further, in our analytical work, we may meet with compounds of certain acidigenic elements with oxygen in different proportions. Such elements are nitrogen, sulfur, and carbon.

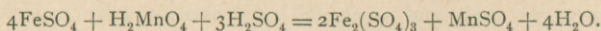
b. There must be an oxidizing or chlorinating agent. Such agents, as used in analytical work, are especially nitric acid and free chlorin. The free oxygen of the air, or the oxygen dissolved in water, may oxidize. Hydrochloric acid alone may act as a chlorinating agent on the metallic elements, but without ever carrying the chlorination higher than the first stage, if there be more than one with the metal in question; when this acid chlorinates, in this sense, its hydrogen is set free.



Also, when an oxid is dissolved in hydrochloric acid a chlorid is formed, but hydrogen is not set free.

In compounds of bromin and chlorin with oxygen, the union is a feeble one, and these compounds may serve as active oxidizing agents. Such are chlorates (KClO<sub>3</sub>), and hypobromites (NaBrO). See § 24, d and e, for examples.

Any element capable of combining with oxygen or chlorin in more than one proportion may yield compounds in these higher proportions, which themselves become oxidizing or chlorinating agents, when brought into contact, under the requisite conditions, with a substance capable of being oxidized or chlorinated.



Iron is changed from a ferrous to a ferric salt, and manganese is reduced from manganic acid to a manganous salt.

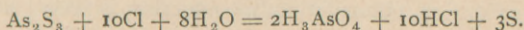
c. In case the oxidizing agent is the acid constituent of a salt, it must usually be set free by an excess of another and a stronger acid before action will take place in solution. Hence, a nitrate in solution in water, as sodium nitrate or silver nitrate, is not an oxidizing agent as free nitric acid is; further, nitric acid, as formed free in an aqueous solution, is usually too much diluted to act as an oxidizing agent. Potassium chlorate in solution does not oxidize till an excess of concentrated hydrochloric acid or other stronger acid is added. To get oxidizing action from potassium dichromate strong acid must be added in excess.

These substances may, however, act as oxidizing agents without such assistance, when fused.

d. Usually, heat favors oxidation or chlorination, as it does chemical action generally.

e. When an element can take more than one degree of oxidation or chlorination (see list in *a* of this section) the higher oxid or chlorid will commonly be formed (or a salt corresponding with the higher oxid), if the oxidizing or chlorinating agent be in excess to a considerable extent, and especially if its action be aided by heat. If the element itself is in excess, so that, as in the case of a solution of a metal by nitric acid, and especially if the acid be not very strong and the operation be conducted without heat, and a portion of the metal remains undissolved when the action of the acid has ceased, the lower oxid or chlorid is more likely to be formed. These rules as to chlorination apply, however, only to cases where the work is done by free chlorin, and have nothing to do with the simple solution of metals in hydrochloric acid.

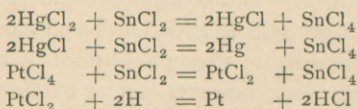
In cases where an element, or one of its compounds, is attacked by free chlorin in the presence of water, and the chlorid of this element cannot exist under the conditions of the attack, but the oxid or a compound of the oxid can exist, this oxygen compound may be formed, the oxygen being derived from the water present.



21. *Reduction.* This operation, the reverse of oxidation or chlorination, takes place under conditions the reverse of those required for oxidation or chlorination.

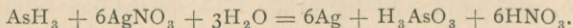
a. The compound must be one that is capable of giving up

oxygen or chlorin under the given conditions. Such compounds are any of those formed with oxygen or chlorin by the basigenic elements, and by certain acidigenic elements. And as an element may combine first with one quantity of oxygen or chlorin, and then with an additional quantity (§ 20 a), so in reduction under certain conditions, a part of the acidigenic element may be withdrawn, and under the same conditions continued in force, or under other more powerfully active conditions, another portion may be withdrawn.



b. There must be a reducing agent. This may be any element having under the given conditions a stronger attraction for the oxygen or chlorin in combination, than is exerted by the other element in the compound; or it may be a compound of one of these elements with oxygen or chlorin in a lower proportion, that is capable of combining with more than one proportion. (§ 20 a).

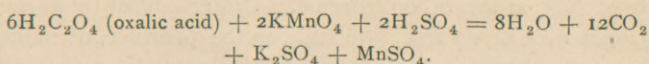
22. A reducing agent excelling all others in the scope and power of its action is *nascent* hydrogen, or hydrogen taken just at the moment when it is liberated from combination, as when zinc is dissolved in dilute sulfuric acid. Further, hydrogen compounds in which the hydrogen is rather loosely bound, and especially if associated with elements that are themselves capable of oxidation, are a strong reducing agent; sometimes the other element of the compound is set free.



Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , sulfurous acid,  $\text{H}_2\text{SO}_3$ , and hydrogen sulfid, often occur as agents of reduction in analytical work; carbon dioxid and water, sulfuric acid and water, and free sulfur being the products from the reducing agents in the several cases.

As to the hydrogen, it may be observed in general that whenever any oxidation, chlorination, or reduction is taking place, and there is any hydrogen in the substances engaged, it is very likely to appear in  $\text{H}_2\text{O}$  or  $\text{HCl}$  in the products of the action; the bond of union between hydrogen and oxygen, or between hydrogen and chlorin, is one of the strongest in chemistry; consequently the tendency to form one or the other of these

compounds, whenever there is any opportunity so do so, is very powerful.



Free hydrogen not nascent is a strong reducing agent when aided by heat. Also at higher temperatures, a red heat or above, carbon is a powerful reducing agent, carbon monoxid or carbon dioxid being the product.

23. Except when oxidation or chlorination is effected directly by free oxygen or chlorin, these processes and reduction go hand in hand; the simultaneous presence, and the co-operation, of both a substance capable of oxidation or chlorination, and a body capable of yielding oxygen or chlorin, are essential. Commonly, the existence together in a solution is impossible of a substance in the free state that is capable of acting as an oxidizing or a chlorinating agent under the existing conditions, and of a substance capable of taking up oxygen or chlorin.

Since, as is usually the case in analytical operations, oxidation or chlorination of one substance implies reduction of some other substance, the same general conditions that are favorable for one operation are favorable for the other.

24. *The reactions of oxidation and reduction.*

a. *With free oxygen.* When oxidation results from the action of free oxygen of the air, or the oxygen dissolved in water, as when moist and freshly precipitated ferrous sulfid is oxidized to the sulfate, the reaction needs no explanation.

b. *With nitric acid; products of the oxidation.* Water is always formed by the union of the hydrogen of the acid with a part of its oxygen.

When metals or their sulfids are treated, a nitrate of the metal is nearly always formed; in a very few cases, as with antimony and tin, for example, oxids that are insoluble in the excess of acid are produced. All such exceptions to the general rule that nitrates are formed are mentioned where they occur.

In the treatment of a sulfid the sulfur is either set free or oxidized to sulfuric acid (see sulfids, Chap. VII).

*Products of the reduction.* The nitrogen of the decomposed nitric acid may be evolved as ammonia,  $\text{NH}_3$ , free nitrogen, nitrogen monoxid or nitrous oxid,  $\text{N}_2\text{O}$ , nitric oxid or nitrogen dioxid,  $\text{N}_2\text{O}_2$ , or  $\text{NO}$ , nitrogen trioxid,  $\text{N}_2\text{O}_3$ , or nitrogen tetroxid,  $\text{N}_2\text{O}_4$ , or  $\text{NO}_2$ . If the nitric acid is in excess and a boiling heat

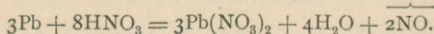
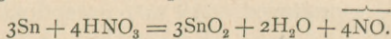
is used, the product is nearly all NO: but excess of reducing agent, a very dilute acid, and a low temperature favor the formation of NH<sub>3</sub> at the other extreme. Under certain conditions hydrogen may be set free, although, as the presence of nascent hydrogen and nitric acid together is incompatible, such conditions can occur but rarely. In general, NO, a colorless gas, is formed in analytical work, which in contact with the air takes up oxygen, forming N<sub>2</sub>O<sub>3</sub> and NO<sub>2</sub>, the latter appearing as brown fumes.

The following diagram illustrates the manner in which HNO<sub>3</sub> may be supposed to be broken up in the oxidation of substances, or in the production of nitrates of the metals, with NO as the product of the reduction:—

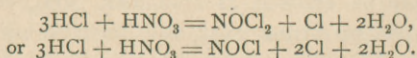


It will be seen that in simple oxidation 2 molecules of HNO<sub>3</sub> yield 3 atoms of oxygen: and that, in order to get the product H<sub>2</sub>O, which is always formed, the number of molecules of HNO<sub>3</sub> taken must always be 2 or some multiple thereof; and that the number of atoms of oxygen used for the oxidation must always be 3 or some multiple thereof. Observe, also, that just half of the oxygen of the HNO<sub>3</sub> consumed goes to oxidize the metal, and the other half appears in the H<sub>2</sub>O and NO.

It is also shown that in the formation of nitrates, 4 molecules of HNO<sub>3</sub> yield 3 molecules of the hypothetical NO<sub>3</sub>; and that, in order to get the product H<sub>2</sub>O, the number of molecules of HNO<sub>3</sub> used must be 4 or some multiple thereof, and the number of molecules of NO<sub>3</sub> used directly in the production of, and appearing in, the nitrate in the right hand member of the equation must be 3 or some multiple thereof.



c. *With aqua regia* (3 parts conc. HCl, 1 part conc. HNO<sub>3</sub>). These acids react with each other as follows:—

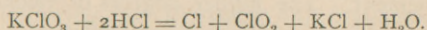


The products vary according to the existing conditions.

The reaction is aided by heat, and takes place only very slowly between moderately dilute acids. These compounds of nitrogen, oxygen, and chlorine, or nitrosyl chlorids, are gaseous and very unstable; they are dissolved by that part of the acid still undecomposed: when the solution is saturated their production ceases. If a metal is put into this solution, action (chlorination) takes place, these compounds being decomposed and supplying chlorine, while oxids of nitrogen escape; the solution being then no longer saturated with these gases a fresh quantity is formed: thus the operation goes on, as long as these chlorinating products are consumed by a body capable of chlorination. It is especially the production of this abundance of free and nascent chlorine that makes aqua regia such a powerful chlorinating agent.

The products of the action of aqua regia are, therefore, a chlorid of the metal attacked, and water, and, for the reduction, lower oxids of nitrogen, probably nitric oxid for the most part.

d. *Potassium chlorate and hydrochloric acid.* This mixture gives when heated a greenish yellow gas, a mixture of chlorine and chlorine dioxid.

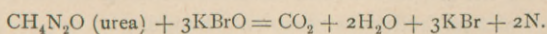


The chlorine dioxid is very unstable, giving nascent chlorine and oxygen by its decomposition. The mixture is, therefore, a very efficient chlorinating agent: in the presence of water it may act also as a strong oxidizing agent.

The products of the action of this mixture on substances capable of oxidation or chlorination are oxids and chlorids of the basigenic element.

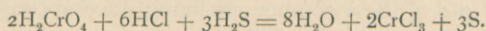
e. *Bromine.* This acts as an oxidizing agent in the presence of water, by reason of its strong attraction for hydrogen, and the generally greater stability of the oxids than of the bromids. Being much more soluble in concentrated hydrochloric acid than in water, this acid solution is often used in preference to an aqueous solution. Hydrobromic acid and oxygen are the products of the reaction with water, in the presence of a substance capable of oxidation.

Dissolved in solutions of potassium or sodium hydroxid it yields a mixture of hypobromite,  $\text{KBrO}$  or  $\text{NaBrO}$ , and bromite,  $\text{KBrO}_2$  or  $\text{NaBrO}_2$ , powerfully oxidizing substances: a bromid of the alkaline metal is the product of the reduction.



f. *Chromic acid.* In a solution of a chromate containing free acid, the chromic acid is liberated from its base, and acts as an oxidizing agent, or chlorinating in the presence of hydrochloric acid.

Salts containing chromium as a basigenic constituent are the products of the reduction.



g. *Sulfuric acid.* This when concentrated and hot may act as an oxidizing agent, sulfurous acid being the product of the reduction, and a sulfate of the metal oxidized. As under *e* above, the carbon and hydrogen of organic substances may be oxidized in this way, but the nitrogen nearly always appears in the form of ammonia. Kjeldahl's exceedingly useful method of determining nitrogen in organic compounds is based on this reaction.

25. *Changes in valence accompanying oxidation or chlorination, or their reverse.* Thus far, these operations have been regarded only as involving the addition or removal of oxygen and chlorine: other important changes, as in valence, may, however, take place simultaneously, supposing that more than one valence be allowed to the same element. The higher degrees of valence are found in the higher grades of oxidation or chlorination. Illustrations will be found in the Table, § 37, where the same element is given in more than one group. The student should notice the very marked changes in chemical properties that sometimes accompany such changes in valence.

## CHAPTER IV.

### METATHESIS.

26. Constant use is made in chemical analysis of the kind of chemical change designated as metathesis, from the Greek, meaning to set over.

*Conditions under which metathesis takes place.*

a. Metathesis takes place as a rule only between substances that are liquefied either by solution or fusion. Only under such conditions is there that closeness of contact, and freedom of motion among the particles of the substances acting on one another, which permits or facilitates chemical change.



In the case of exceptions to this rule, which are to be found in the course of the qualitative work, it will be noticed that at least one of the substances engaged is in solution, while the other is often freshly precipitated and moist, when it may reasonably be supposed to exist in a much more porous condition, exposing a larger surface to attack by the dissolved reagent, than when even in the finest powder of the previously dried substance.

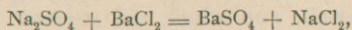
*W* or *wa* in the Table of Solubilities, § 6, may be taken as indicating sufficient solubility for a precipitating reaction; and such a reaction will be given, provided that the reagent used is capable of giving it in any solution of the substance.

b. That one and the same elementary or compound substance exhibits unequal attraction for different elementary or compound substances is an important fundamental principle of chemistry, which the student learns very early in his study of the science. But the formation or decomposition of chemical compounds, or, in other words, the kind of metathesis that takes place, is sometimes powerfully modified by conditions quite independent of the relative forces of attraction that make or break these compounds.

27. The following law illustrates this statement, and at the same time bears a very important relation to the operations of analytical chemistry.

On bringing together a substance from the acidigen column, Table, § 37, and one from the basigen column, if a substance can be formed by their union that is insoluble in the medium of contact, or one that is gaseous at the temperature of contact, such union will take place; or such changes will take place in the arrangement of the constituents of compounds containing these substances as may be necessary to produce the new insoluble or gaseous compound.

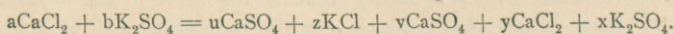
It is above all upon the unfailing operation of this law that the success of the work of the analytical chemist depends; if, for instance, he could not rest assured beyond all doubt of the certainty of the reaction expressed by the following equation:—



or, that in a solution prepared in a certain definite manner a barium salt would always react with a sulfate, yielding a precipitate of barium sulfate, and at least almost completely removing the sulfuric acid from the solution, no dependence could be placed on the reliability of his qualitative or quantitative results,

where the detection or quantitative estimation of either barium or sulfuric acid is concerned.

28. In cases where insoluble compounds cannot be formed by interchange of the constituent parts of the substances brought together, it may be supposed that new compounds are nevertheless formed, even though there may be no visible changes. If, for instance, the substances brought together in solution were, instead of those in the above equation, sodium sulfate and ferric chlorid, a part of the chlorine may go to the sodium and a part of the sulfuric acid to the iron, so that four salts,  $\text{Na}_2\text{SO}_4$ ,  $\text{FeCl}_3$ ,  $\text{NaCl}$ ,  $\text{Fe}_2(\text{SO}_4)_3$  exist in the solution instead of the two original ones, or instead of only one salt, as in the second member of that equation. Evidence of such change is found in certain color reactions, as, for instance, the deep red color which results from the reaction between a ferric salt and a sulfocyanate, (§ 92): no insoluble substance is formed, but there must be, nevertheless, a partial interchange of acids and bases. Moreover, when a new compound can be formed by interchange of the constituents, or by metathesis, that is partially or slightly soluble in the medium of interchange, a portion of the new compound will be precipitated, while the rest may remain in solution as such, and we will have also some of the original, undecomposed salts; thus, with the first letters of the alphabet, used as coefficients, representing known quantities and the last letters unknown quantities:—

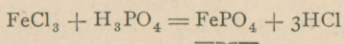


Calcium sulfate is slightly soluble in water, and while one portion is precipitated, another will remain in solution, together with a portion of the original calcium salt.

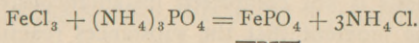
Such will be the result, as may now be readily understood, if the conditions under which a complete precipitation is to be made are not carefully fulfilled: errors may follow, which may be especially serious in quantitative work, and often in qualitative analysis as well, and which the student is too prone to attribute to the fallibility of the reaction instead of his own want of care.

29. If, as a result of the metathesis, one of the new substances produced be an acid, or any other solvent agent that will dissolve the other possible product of the metathesis, of course the conditions are not fulfilled, according to the law stated above,

for the production of that substance, and there may be no visible evidence of its production.



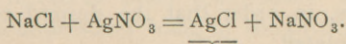
may not be a correct representation, since  $\text{FePO}_4$ , though insoluble in water, is soluble in hydrochloric acid; but the following is correct:—



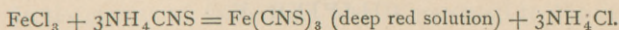
A precipitate may be formed in the first case, however, since the small quantity of  $\text{HCl}$  set free can make only a very dilute acid liquid, perhaps insufficient to keep the phosphate from separating out.

30. Several kinds of metathesis are made use of in analytical work. *Between two salts* giving:—

a. An insoluble new salt;



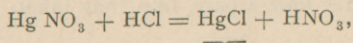
b. No insoluble salt, but at least a partial exchange of acids and bases, and some evidence of the exchange visible to the senses;



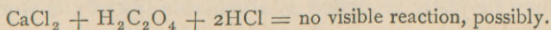
A more nearly correct equation would, however, be similar to that in § 28, but without any precipitation at all.

*Between an acid and a salt* giving:—

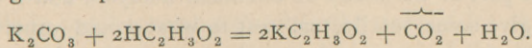
c. An insoluble salt, insoluble in water, but possibly not in the new acid produced, unless very dilute;



But

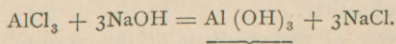


d. A gaseous product.

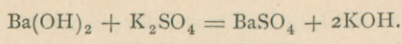


*Between an hydroxid and a salt* giving:—

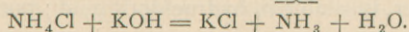
e. Metallic hydrates or hydroxids, insoluble:—



f. Insoluble salts into which the basigenic element of the hydroxid enters:—



g. A gaseous product:—



31. Metathesis is not completed instantaneously, although it may set in the moment that the substances reacting upon one another are brought together. If a slightly soluble salt is the product, this slight solubility may retard the completeness of the separation, or prevent it altogether; but if time is allowed, the separation may be carried much further than at the beginning of contact, and it may in the end be quite complete. Instances in illustration of these points will be met with in the course of the analytical work that follows, where directions are given to allow the mixture of reagent and solution of substance to stand for several hours, in order that the desired reaction may be obtained or completed.

## CHAPTER V.

### WRITING EQUATIONS.

32. All the chemical changes that take place in the operations of chemical analysis, and upon which these operations are based, are comprised under these three heads of (1) solution, (2) oxidation and reduction, and allied processes in which chlorine, bromine, iodine or sulfur may take a part, like that taken by oxygen, and (3) metathesis.

The working out of chemical equations explaining these changes may be justly regarded as a valuable test of the student's insight into their chemistry; the writing of these equations is an important part of his study of chemical analysis, and it may be made to give some intellectual zest to what would otherwise be little more than mere machine work.

33. The correct writing of an equation requires:—

a. A knowledge of the formulas of the substances originally acting upon each other.

b. A knowledge of the products of this action.

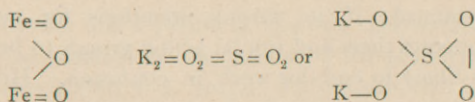
c. A balancing of the equation so that its two members shall be equal in respect to kind and number of atoms, without including any substances, elementary or compound, whose presence is impossible or unreasonable under the existing conditions, and in which every simple or compound hypothetical body included shall have its supposed combining power or valence satisfied.

The information under *a* is given in the text-books, or often on the labels of the bottles; that under *b* is usually partly given in the description of the reaction; what is not thus explained must be worked out under the general rules to be found in this text-book or in other works.

The law stated in § 27 can be usefully applied, in combination with the study of the table of solubilities, in the working out of this part of the problem, where it becomes necessary to decide whether any reaction will take place.

The work under *c* is accomplished by the application of principles laid down in this or other text-books. Under this head it is important to understand some of the principles upon which formulas are constructed.

34. *Structural or graphical formulas of compounds.* The ordinary formula of a compound shows only the relative and most reasonable number of atoms of each of the elements composing it. In the structural formula an idea is presented to the eye of the manner in which the component elements may reasonably be supposed to be grouped together, as illustrated by the following examples:—



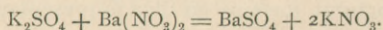
In these formulas each element is supposed to have a certain combining power, measured in terms of a monovalent atom, which is called its valence; this is shown in the formula by the number of dashes connected with its symbol, or by Roman numerals in small type above and to the right of it; the valence of each of the elements in the second plan of the formula of potassium sulfate is indicated with perfect clearness by the method first stated.

35. The true valence of many of the metallic elements is not yet settled: and this whole matter of valence should be strictly

regarded as merely a working theory, and one which can be made useful in the study of chemical equations.

In the following Table the apparent valence is assigned, in such unsettled cases, that corresponds with the most generally adopted formulas of the compounds of these elements. To silver the valence one is assigned, which is apparent in the formulas  $\text{AgCl}$ ,  $\text{AgNO}_3$ ,  $\text{Ag}_2\text{SO}_4$ , etc., although there are reasons for regarding it as a dyad metal with a valence of two. Lead is probably a tetrad element, but the formulas of all its common salts can be and are constructed on a dyad basis: the same may be said of barium, strontium, etc. Iron is regarded by many as dyad in ferrous compounds and tetrad in ferric compounds, while others regard it as tetrad in both. Again, more recent researches tend to show that it is triad in the ferric compounds, instead of tetrad; although the question is, perhaps, not yet fully settled, the simpler formulas on the triad basis are given in the case of iron, and of some other elements also, in regard to which the same view is at least permissible.

36. In the equations of the more simple forms of metathesis certain groups of elements are invariably transferred from one member of the equation to the other, apparently without being broken up in the actual course of the changes involved in the reaction; thus, in the equation



$\text{SO}_4$  and  $\text{NO}_3$  changes places; in the structural formula for  $\text{K}_2\text{SO}_4$  (§ 34), it is seen that the group  $\text{SO}_4$  is dyad; so in the structural formula for sodium nitrate  $\text{Na}-\text{O}-\text{N}\equiv\text{O}_2$ , the group  $-\text{O}-\text{N}\equiv\text{O}_2$  is monad; if, in writing equations for metathesis the student supposes these and similar acidic groups to be broken up he is very likely to end his work in confusion. Hence, for his purposes in equation writing, the most practical course is to regard these groups as actually transferred from one basigen to another, and as bearing the valence indicated by the composition of the compounds containing them. But he must not forget that they are purely hypothetical groups which have not been isolated, or proved to exist as such in any chemical compound apparently containing them.

37. For assistance in explaining by equations the reactions that take place in the course of ordinary qualitative analysis, the following classification is given of elements, and of certain hypothetical compounds of which examples were mentioned in the preceding section.

In any product of the ordinary metatheses of chemical analysis there will be at least one *basigen* and one *acidigen*, but not necessarily only one *atom* or *molecule* of each: very rarely will there be more than one acidigen (see basic salts § 17); more often there will be more than one basigen, provided that the acidigen is more than monovalent (see acid salts § 16), as illustrated in the following formula of sodium ammonium phosphate:  $\text{Na NH}_4\text{HPO}_4$ .

*Basigens (base-forming).*

*Acidigens (acid-forming).*

MONAD.

H, K, Na,  $\text{NH}_4$ , Ag, Hg(ous),  
Cu.

Cl, I, Br, F, OH,  $\text{NO}_3$ ,  $\text{ClO}_3$ , Cy,  
(or CN), CyS (or CNS),  $\text{C}_2\text{H}_3\text{O}_2$ .

DYAD.

Ba, Sr, Ca, Mg, Zn, Mn, Fe(ous),  
Ni, Co, Pt, Hg(ic), Cd, Cu, Pb.

O, S,  $\text{SO}_3$ ,  $\text{SO}_4$ ,  $\text{CO}_3$ ,  $\text{C}_2\text{O}_4$ ,  $\text{CrO}_4$ ,  
 $\text{SiO}_3$ ,  $\text{SnO}_3$ ,  $\text{C}_4\text{H}_4\text{O}_6$ .

TRIAD.

Au, Bi, Fe.

$\text{PO}_4$ ,  $\text{AsO}_3$ ,  $\text{AsO}_4$ ,  $\text{SbO}_4$ ,  $\text{C}_6\text{H}_5\text{O}_7$ ,  
 $\text{Fe}(\text{CN})_6$  (in ferricyanid).

TETRAD.

$\text{FeCy}_6$  (or  $\text{Fe}(\text{CN})_6$ ) (in ferrocyanid).

DYAD OR TETRAD.

Sn, Pt.

TRIAD OR PENTAD.

Sb, As.

38. In order that a chemical equation shall exhibit at a glance as much as possible of the nature of the products formed, the sign  $\underbrace{\quad}$  is always to be put underneath the formula of an insoluble compound precipitated, and the sign  $\overbrace{\quad}$  over the formula of any gaseous product evolved. In the case of the solution of a substance originally insoluble in water, effected by any active solvent agent, by which a new compound soluble in water is formed, the special, new, soluble product of the solution is to be indicated by a straight line under its formula. See equations, § 5.

39. In writing equations it must be remembered that water is always present when the reactions are obtained in the wet way, that is in solutions, and that water can always be incorporated into the equation if necessary for reasonable results.

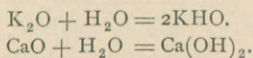
Also, when solution is made by an acid, an excess of the acid is always supposed to be present, and the possible effect of such excess must be regarded, such, for instance, as its tendency to form salts with oxides (§ 40 c).

Also, that any soluble salt of an acid will give the same reaction as will the acid itself, but will not, of course, act as a solvent, like the free acid. Thus NaCl and HCl give the same characteristic product with silver salts.

40. *Providing against some of the common errors in writing equations.* a. An equation written is to be regarded as representing some chemical change of which there is sensible proof, such as the disappearance of a solid as it passes into solution by an acid, a case of oxidation or an allied process, or of reduction, a precipitate formed, or a gas evolved, or a change of color of the liquid. Metatheses may take place, and doubtless do when there is no plain evidence of it presented to the senses (§ 28): but they are not such as are expressed by the ordinary equations explaining the operations of chemical analysis. The student must be able to give one of the above reasons for every equation that he writes. Failure to meet this requirement is a very common source of error.

b. As a result of the metatheses made use of in analytical work, in the wet way, it is not common that the metals themselves appear as precipitates; they of course never exist as such in a solution, for they are not soluble; it is only their compounds that are soluble. Therefore an equation that leaves a metal in a free state, and at the same time unprecipitated, cannot be a correct one.

c. The oxids of the metals do not exist as such, in a free state, in a solution, since every oxid which is capable of forming a base soluble in water, immediately on contact therewith forms such a base.



Nor do the oxids, whether in solution or insoluble, exist as such in the presence of an excess of a free acid, provided that they are capable of yielding soluble salts with that acid; any explanation of a metathesis which results in this condition of things must therefore be incorrect.

d. It is more common to meet with the acidigenic elements in the elementary form, as the products of metathesis or other operations of analytical work; they may be in solution, as in the



case of bromin or chlorin, or precipitated, as iodin or sulfur, or gaseous, as chlorin.

e. The anhydrids of the acids, such as  $N_2O_5$ ,  $SO_3$ , corresponding to the oxids of the bases, cannot exist in a free state, in an excess of water, provided that they are capable, as is the fact in most cases, of forming a soluble acid: for such an acid will be immediately formed on contact with the water, and will go into solution.

f. Of course an acid and a base cannot exist free in the same solution; whichever is in excess, or present in quantity more than sufficient to combine with all of the other, will take it all up to form a salt, no matter whether the salt so formed be soluble or insoluble. In this connection it is to be remembered that a hydroxid or hydrate (Chap. VIII) answers to the definition of a base (§ 13).

g. In writing equations a reagent added is always to be considered, as in the actual use of it, in excess, more or less above what is required of it for the actual work of precipitation or solution: and in completing an equation the possible effect of such excess must be taken into account; as, for example, when the reagent is a strong base, like KOH or NaOH, and an acid is one of the products of the reaction. Other illustrations of this principle occur in some of the equations given out.

41. Students are too ready to extricate themselves from some difficulty in completing an equation, by indicating some chemical element which they cannot dispose of readily in any other way, as left in the free state; and usually, as the element so left free is often a very active one, as oxygen, chlorin, hydrogen, etc., this is done in direct violation of well established chemical laws. Some common errors of this kind are noticed in the preceding paragraphs with reference to some of the elements and to some compounds. A few other elements need mention in this connection.

a. *Oxygen.* Except by the action of the electric current this element is left in the free state only when liberated from compounds containing it loosely held in combination, such as nitrates, chlorates or other compounds containing both chlorin and oxygen, and many of the metallic oxids, especially higher oxids where more than one is formed with the same metal—and *in the absence* of any substance with which it can combine at the temperature of liberation, such as metals especially of the potassium, calcium, aluminum, and iron groups, and some lower

oxids where more than one is formed with the same metal (§ 20), or any of the reducing agents mentioned in § 22, to which might be added hydrogen sulfid.

This liberation of oxygen very rarely takes place except by heating the dry substance or mixture of substances, the temperature required for such liberation being in nearly all cases above the boiling point of water or of any aqueous solution. Free oxygen is therefore so very rarely a product of metatheses taking place in solution, that such a result would always be specially stated in the description of the metathesis.

This statement as to the liberation of oxygen from its compounds does not refer to cases where it is withdrawn from oxidizing agents, that readily yield it at temperatures within the boiling point of solutions, when bodies are presented that are capable of combining with it under such conditions: no free oxygen appears, however; the element simply passes, so far as our observation extends, from one compound into another.

b. *Chlorin*. This element is set free:—

1. By heating, in the dry condition, certain chlorids of metals of the copper and tin groups.

2. When a substance containing chlorin and one containing loosely bound oxygen are brought together; and in case the chlorin is in the form of a stable salt, the coöperation of a strong acid is necessary. The common method of making chlorin, with  $MnO_2$  and  $HCl$  illustrates the principle. For other illustrations see § 24 c, d, and f.

But chlorin cannot appear in the free state simultaneously with any body that will readily combine with it, like a metal, or hydrogen, or a compound containing hydrogen loosely bound, as hydrogen sulfid, or in the presence of any other sulfid, of which it at once takes the metal, or in the presence of water and an easily oxidizable substance, such as a sulfite or any organic substance.

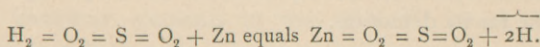
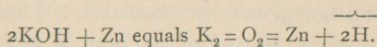
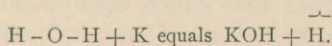
c. *Hydrogen*. When this element appears in the free state, as the result of a chemical reaction, and evolved from a liquid, it is the product:—

1. Of the action of certain metals of the first and second groups on water, these metals having such an exceedingly strong attraction for oxygen as to be able to take it from this most stable compound.

2. Of the action of certain metals, as zinc, aluminum, or tin, on an aqueous solution of an alkali ( $KOH$ ,  $NaOH$ ), the metal displacing the hydrogen.

3. By the substitution, in a solution of an acid, of a metal for the hydrogen. The common method of preparing hydrogen by means of zinc and  $H_2SO_4$  is a familiar illustration of this principle.

It will be seen that a common reaction characterizes all these methods: regarding water as a compound of the hypothetical substance hydroxyl, HO, with hydrogen ( $HO + H = H - O - H$ ) the hydrogen which appears may be always considered as this second atom of the element, as shown in the following equations, illustrating each mode of production above mentioned:—



It must not be forgotten that hydrogen in the moment when it is set free is in its nascent state and possessed of powerful reducing properties; and that, therefore, it cannot appear in the second member of the equation if there is present at the same time any oxidizing or chlorinating agent, or any of the substances in the list in § 20 a, that readily give up oxygen or chlorine (or bromine or iodine).

d. *Nitrogen*. Although this is not, like the elements already considered, powerfully active, and eager to enter into chemical combination, still it is set free from solutions only under certain conditions, occurring so rarely in ordinary analytical work, as always to receive special mention in the account of the reaction yielding it.

e. *Bromine* and *Iodine*. The same may be said as to the appearance of these elements in the free state that was said of chlorine.

f. *Sulfur* is very often set free in the reactions of sulfides, appearing as a very fine powder, or turbidity: its appearance in the right-hand side of the equation is therefore allowable, and in this respect it differs strikingly from the other elements noticed above.

42. Good practice is obtained in writing equations, as well as a better acquaintance with the chemistry of the analytical work, by writing out, in equations, the history of each substance in its passage through the special course in which it is tested for. Taking, for example, calcium in the scheme for the

calcium group, the solution brought there contains all its basigenes in the form of their chlorids, as a consideration of the preceding schemes will show. The first reagent added that affects the calcium is  $(\text{NH}_4)_2\text{CO}_3$ , by which the carbonate is precipitated; this, then, would be the first step in the history, to be shown by an equation.

These carbonates are next dissolved in  $\text{HC}_2\text{H}_3\text{O}_2$ , and the next equation would show the action of this acid on calcium carbonate.  $\text{K}_2\text{CrO}_4$  has no action on the calcium in this solution, and therefore the next step to be shown is the precipitation again by  $(\text{NH}_4)_2\text{CO}_3$ ; next comes the solution of this precipitate in  $\text{HCl}$ , then the action of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  on the salt of calcium in this solution, giving the final test. Thus it takes five equations to express the history of calcium, in its passage through the course for its detection.

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## CHAPTER VI.

### THE MANIPULATIONS OF ANALYTICAL CHEMISTRY.

43. *Making Solutions.* The suitable preparation of a solution for analytical purposes is not so unimportant a matter as on first thought it might appear to be. There is a certain degree of strength, or concentration of the solution that is most suitable for the work to be done with it, which may be different in different cases.

Of substances soluble in water, there are few that will not dissolve in ten times their weight of the solvent. A solution of such concentration is not unsuitable, as a general thing, either for reagents, or as a solution of a substance to be analyzed. As to reagents, however, it is better that some should be much more dilute, and others stronger; for such cases directions will be given where they are needed.

A substance to be analyzed in the wet way, that is by treatment with the reagents in solution, must first be brought into solution itself. For this purpose, only three reagents are in common use: distilled water, hydrochloric acid, and nitric acid, the acids being either dilute or concentrated. In general the presence of strong acid in a solution to be analyzed is to be avoided, as liable to

interfere with the success of subsequent operations; the young analyst needs especially to bear this in mind. If strong acid is required for the actual solution of the substance, the excess of it must usually be removed by evaporation nearly to dryness; water is then added to the residue in such quantity as to make a solution of about the right strength. For the details of the operation of getting the substance into solution for analysis, see the directions given in Chapter VIII.

44. *Fluxing.* Some substances can be brought into solution only after a metathesis has been produced between them and certain reagents in a state of fusion. Sodium and potassium carbonates are used for such reagents. A soluble salt of the acid of the insoluble substance and the alkali metal is formed, while the carbon dioxide either escapes, or forms carbonates of the basigenic elements in the insoluble substance, or is disposed of in both ways. None of these new compounds being insoluble in acids, the original substance can by this means be brought entirely into solution for analysis; with this exception, however: in the silicates we have a large class of insoluble substances; when the flux obtained with these compounds is treated with water and acid to dissolve it, a portion of the silica immediately appears in an insoluble form; but it is entirely separated from the basigenic elements with which it was originally combined, and the condition of insolubility of the substance is broken up.

In order that this operation of fluxing shall be entirely successful, three conditions must be fulfilled:—

The insoluble substance must be very finely pulverized in an agate mortar, till the powder does not feel gritty under the pestle; this proper pulverization requires much patience. The powder must be most carefully mixed with a large proportion of the reagent, not less than three or four times its own volume. This mixture must be kept in a state of fusion for not less than fifteen to thirty minutes. The fusion is best performed in a platinum vessel of some kind; porcelain might itself be attacked by the flux; the heat of a blast lamp is necessary.

45. *Evaporation.* This operation comes into use very often in analytical work, to make a solution more concentrated, or to free it from some ingredient that would interfere with operations to follow, or to get a solid from the substance held in solution.

Evidently, the larger the surface exposed for the escape of

vapor, in proportion to the mass of the liquid, the greater the rapidity of the evaporation; and since the rate of evaporation is more rapid, the less there is of the vapor of the solvent in the air over the surface of the liquid, the more frequently this air, more or less laden with the vapor, is replaced by fresh air, the faster the evaporation will proceed. The porcelain evaporator is the utensil most frequently employed for this purpose; in such a shallow dish the surface is large, and the vapor-laden air is readily removed by air currents passing over. A flask or a nearly covered beaker is most unsuitable for evaporation, for plain reasons; if the flask is laid over on its side evaporation will proceed more rapidly than if it is upright; or, if, while upright, a continuous current of air is forced into it, the evaporation will proceed quite satisfactorily.

46. In all quantitative work there must be no loss of substance. From the surface of a boiling liquid, even if the boiling is very quiet, minute particles of the solution are constantly projected upward and obliquely, some of which will fall outside of the dish, unless the surface of the liquid is much below its rim; therefore, in all work of this kind evaporation must be conducted without boiling the liquid, unless it is in a deep beaker, or in a flask laid on its side; in this last case the projected particles strike the upper side of the flask, and are soon washed back again by the condensed vapor flowing down.

As the evaporation nears the end, and some of the solid matter is deposited, the sputtering of the thickened liquid may become so violent that small masses of the substance may be projected out even from a deep beaker. Even in qualitative analysis, where the loss by the boiling of the liquid may be disregarded, this closing part of the operation must be conducted with care; more loss may be suffered than can be afforded; and, moreover, particles of the substance thrown out may fall into solutions near by, and thus do serious damage to other work.

47. *Ignition.* A residue left by evaporation, or a precipitate, must sometimes be subjected to a stronger heat than is attainable in a solution, that is it must be ignited. This operation must be performed in a crucible, or, if the quantity is small, on a platinum foil. It cannot be done in an evaporator without risk of breakage. Therefore, when the residue from an evaporation is to be ignited, with a spatula transfer it to the crucible while it is still in a pasty condition, dry it over a direct, low flame, and then proceed with the ignition, gently or strongly, as may be directed.

48. *Acidification, alkalization, neutralization, adding a reagent in excess.* It is often directed that a solution shall be made acid, alkaline, or neutral before proceeding further. With reference to acidification, this does not mean that the liquid shall be made strongly acid, unless specially so stated, but rather that, if alkaline or neutral, acid shall be added slowly, and with constant stirring, or mixing in some other way, only till the reaction is clearly acid to the test paper; and the same is true as to making a solution alkaline. The proper mode of procedure, therefore, is to add the reagent in small portions at a time, carefully mixing each portion as added, and frequently applying a drop of liquid to the test paper; when the reaction indicates an excess of the reagent, a little more may safely be added, in order to be sure of enough. The mode of procedure is similar for making a liquid alkaline. Since ammonia is the reagent commonly used for this purpose, the careful mixing is all the more essential, as it is lighter than water or any solution of salts or acids, and will tend to float on the surface of such a solution; on dipping the test paper into the liquid, or taking a drop out on a glass rod and touching it to the paper, the reaction might be strongly alkaline, even with a strongly acid liquid in the lower part of the tube. When this reagent is used to neutralize acidity, as soon as the liquid smells strongly of it, after the thorough mixture has been made, one can be sure that the liquid is alkaline. When a solution made alkaline by an excess of an alkaline carbonate,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , or  $(\text{NH}_4)_2\text{CO}_3$ , is to be made acid, as soon as the addition of the acid does not cause decided effervescence, due to the escape of carbon dioxide, the same precautions being taken as to the careful mixing in of each portion of acid added, the condition of acidity is probably reached; but in any case the final test with litmus paper should never be omitted. One can never afford any uncertainty in regard to the matter.

When the liquid to be treated is in a test tube, the mixing can be most easily done simply by pouring it back and forth from one tube to another.

*Addition of a reagent in excess.* Directions are often given to add a reagent in excess; but unless the desired excess is specially stated to be large, which is rarely the case, it is not meant that a great quantity of it is to be added. If it is an acid or an alkali that is added, it should be known, by the use of test papers, when it is first in slightest excess, as directed above; then the further addition of a quantity of the reagent equal to about one-

tenth of the volume of the solution, will usually suffice. If it is a precipitating reagent that is added, then it should be known when the precipitation is first complete; then a further addition of one-tenth, as above described, will be sufficient.

49. *Precipitation.* This operation, the eduction of a solid substance from solutions, as the result of some metathesis, is the most important one in analytical chemistry. The reagent used is commonly called the precipitant.

Qualitative analysis consists almost entirely in the production of precipitates for one purpose or another, and generally under certain prescribed conditions. In order that the result sought for shall always be obtained, the conditions prescribed in each case must be fulfilled—such as neutrality, or acidity, or alkalinity of the solution, precipitation with heat or without, with time given for the reaction to be completed or not. Especially in quantitative analysis, the conditions under which the precipitation is to be made, are usually very precisely indicated, since in that kind of work the completeness in the reaction is of the utmost importance.

But this matter of completeness of precipitation is in many cases of no less importance in qualitative analysis, as in the separation of groups of substances from one another, or of removing one substance from the solution that may interfere with the detection of another. Therefore, in the very beginning of his work, whether such beginning is made in qualitative or quantitative analysis, the student has to learn to be careful in the preparation of his solutions for precipitation, and in the management of the precipitation itself.

50. *Description of precipitates.* Precipitates are distinguished as having this or that color, or, as to structure, as being crystalline, pulverulent, or flocculent.

A *crystalline* precipitate is usually characterized by the property of sinking rapidly to the bottom and leaving a comparatively clear supernatant liquid. Sometimes a precipitate is so finely crystalline as to show only a glistening shimmer when present in very small quantity in a liquid that is gently disturbed. Precipitates that take the crystalline form will usually appear sooner if the liquid is strongly agitated; sometimes such agitation is almost necessary to start their formation, as in precipitation of morphia by ammonia.

A *pulverulent* precipitate is very fine, usually not settling quickly nor leaving a clear, supernatant liquid. One that is



pulverulent, if produced quickly and in large quantity, may be plainly crystalline if formed slowly and in small quantity, as may be seen sometimes in the formation of the precipitate of ammonium magnesium phosphate. The more insoluble a precipitate is in the liquid in which it is produced, the more it inclines to the pulverulent rather than crystalline character; but even some of the most insoluble precipitates, as barium sulfate, will, if produced only in traces, exhibit the glistening appearance above mentioned, as indicating crystalline structure.

51. A *flocculent* or *flaky* precipitate, sometimes defined as woolly-looking, never presents this glistening appearance, however slowly formed. It settles slowly, and occupies much more space than a crystalline or pulverulent precipitate. It is often separated from the liquid by filtration only with difficulty. It is sometimes translucent, so that, if at the same time colorless, it is almost invisible till gathered together in masses; of this character the precipitate of aluminum hydroxid is an example.

Precipitates will usually collect together and settle to the bottom more quickly, and be more easily filtered out, if the liquid containing them is hot.

52. According as a precipitation is made simply for the detection of a substance in a solution, by the appearance under the prescribed conditions, of a precipitate of a certain form or color, or is made for the separation of one or more substances from others, the manner of making it differs. In the former case, the first appearance of the precipitate suffices, and any further addition of the reagent is useless, except when there is necessity for getting a large quantity of the product for confirmatory tests. But in the other case, the addition of the reagent must be continued as long as a precipitate is formed; and this cessation of further precipitation must be determined beyond all doubt by adding a few drops of the precipitant, either to the supernatant liquid clarified by standing for the precipitate to settle, or to a portion of the liquid filtered from the precipitate; sometimes it is necessary to give time for the completion of the reaction, even after no further precipitation is shown by testing as above.

53. *Digestion.* In order that a chemical reaction, and especially an operation of solution or precipitation, shall be complete, it is often necessary to leave the substance and reagent in contact for a time. This is commonly called digestion. Usually heat is applied, but not always; in this case we speak of

digestion in the cold. Digestion at a boiling temperature is sometimes specified ; but this is too often incorrectly construed as vigorous boiling, while it means only that the liquid shall be kept just at the boiling temperature.

**54. Boiling.** Rapid boiling of liquids is required only when they are to be quickly evaporated, or some product is to be distilled off. It is very rarely necessary in qualitative work, and is to be avoided unless specially called for.

A clear liquid can usually be boiled without any trouble, in a beaker, flask, or evaporator ; but in a test tube, especially if half full or more, the vapor does not escape in a continuous stream of small bubbles, but in very large ones, often, which are formed suddenly, and are very likely to propel a part of the liquid before them in their escape.

When any solid matter is mixed with the liquid, and especially if the liquid is strongly alkaline, boiling without spurting is still more impracticable in a test-tube, and should never be attempted ; even in a flask, beaker, or evaporator it is not easily managed, and must be carefully watched, particularly when the quantity of liquid is small as compared with that of the solid ; by holding the lamp in the hand, and, with the flame very low, moving it in and out under the dish, without the intervention of a sand bath, thus keeping the mixture just at the simmering point, the whole object of the operation may be accomplished without danger. When there must be actual boiling for a time, as in the treatment of the precipitated chlorids of the silver group with water to dissolve out the lead chlorid, it is advisable to hold the flask by the test-tube holder and keep its contents in rapid motion by a movement of the hand in a small circle.

**55. Filtration.** It is usually necessary, after having made a precipitate, to separate it from the liquid, in order to perform some further operation with it. For this purpose, paper filters already cut are now supplied in every laboratory. To fit a filter in the proper manner, first fold it over so as to form a semicircle, and then again, forming a quadrant ; then open this quadrant in such a way that when it is pressed down into a funnel there is a continuous lining of the paper on the sides of the funnel of three thicknesses half way round and one thickness on the other half. The filter should always be about half or a third of a centimeter smaller than the funnel when thus fitted into it. In preparing for the filtration, push the filter, opened as above described, down till its apex is in the throat of the funnel, and

hold it there with the finger while wetting it with a jet of water from the wash-bottle; then by gentle pressure with the finger fit it snugly to the walls of the funnel throughout. Time should be taken to carefully adjust the filter in this manner *for every filtration*.

56. *Decantation before filtration.* Filtration can often be made more quickly if the liquid is first digested at a gentle heat till the precipitate has settled, and the supernatant liquid is then carefully decanted off before putting the mass of the precipitate on the filter. If the work is qualitative and nothing further is to be done with the liquid, the decantation can be made at once into the sink; otherwise it should be made into the filter.

57. *Washing precipitates.* It is usually important to completely free a precipitate from the substances in solution in the liquid from which it has been filtered, and with which its pores are filled.

This washing may sometimes be partially done with advantage, by repeating the above described process of decantation, two or three times, pouring boiling water over the precipitate, stirring it up well and decanting again after a little time, and so on, and finally washing once or twice after the precipitate has been put on the filter. When, however, it is crystalline pulverulent, and filters quickly, it may as well be thrown on the filter at once and washed there. In all cases use hot water, unless otherwise directed, for with this the washing is sooner finished; and use only distilled water.

In qualitative work the washings need not be saved; but they often must be preserved in quantitative work.

The completion of the washing may be tested for in two ways: first, by evaporating a drop of the washings to dryness on a watch glass, at a gentle heat; no residue, or in qualitative work only a slight one, should be left on the spot where the drop was: second, by testing about a cubic centimeter of the washings for some substance which one may know to be in the solution, and for which there is some very delicate test. Such a substance is a chlorid, which is usually present in qualitative solutions, from the hydrochloric acid that has been added in some previous operation; the silver test for chlorin, after acidification of the liquid with nitric acid is exceedingly delicate.

58. *Dissolving precipitates.* This often necessary operation, especially in qualitative work, may be done simply by dropping the solvent over the precipitate in the filter, when heat or

digestion is not required; when two or three cubic centimeters of the solvent have run through, this may be again poured through the filter, if the solution is not complete, thus avoiding the use of a large excess of acid. If the precipitate must be removed from the filter, take the latter from the funnel by slipping the spatula under it, open it on the piece of window glass that is in the set of apparatus, and scrape the precipitate off with the spatula.

59. *Cleanliness in the laboratory.* Reasonable cleanliness of apparatus and work table is much more conducive to good results than the extreme slovenliness that is often seen. Every piece of apparatus must be clean within before a liquid is put into it that is under treatment for analysis; if not clean, then the constituents of the dirt that was on the walls of the vessel are liable to be added to the solution, and to be reported as a part of the substance analyzed. Unless a piece of glassware is clean on the outside, it cannot be known whether it is clean on the inside. The cleaning is never more easy than immediately after the apparatus has been used; and it is liable to be more difficult if put off for days.

Therefore, the student should never leave the laboratory for the day without having first cleansed every soiled piece of apparatus that is not in actual use, finishing the operation by rinsing each piece off with a little distilled water. By the use of a little strong hydrochloric or nitric acid, pouring the same portion from one piece to another, intractable dirt may often be dissolved. While the student is at work his table should be kept neat, everything spilled by accident or otherwise being at once washed off with a sponge and an abundance of water.

If acid comes in contact with the clothing, the spot should as soon as possible be saturated with a few drops of ammonia. Strong nitric acid on woolen cloth makes a permanent yellow stain unless immediately neutralized; sulfuric acid if not neutralized, even if dilute at first, becomes more and more concentrated by the slow evaporation of the water, and finally the cloth is corroded; hydrochloric acid leaves only a red stain, easily removed by ammonia.

60. *Rapidity of work.* Much time will be spent in accomplishing little work, unless the student is always careful to keep as many operations in progress as he can manage without making mistakes. Early in his course of practice he should seek in this way to make the best possible use of his time in the laboratory.

The teacher's estimate of the proficiency of the student must be based on the amount of good work accomplished in the amount of time that is given to the practice. Therefore, there should never be any idle waiting for a precipitation, tedious filtration, or any other slow operation to be completed; some other operation should be started. If the work is qualitative, two substances can be carried along at once; or, the constituents being separated into groups if the analysis is one covering the entire course, two or more groups can be worked along together. In many ways the student who is really in earnest, meaning to do the best that he can with his time, can get over much more ground without slighting any part of his work, than he will if he gives this matter of rapid work no serious thought. If every stage of the work is properly labeled, trusting nothing to the memory, none of the mistakes need be made that might seriously lessen the gain in progress.

PART II.

THE SYSTEMATIC COURSE OF QUALITATIVE  
ANALYSIS.

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CHAPTER VII.

THE MODE OF PROCEDURE IN GENERAL.

61. *Introduction.* This course in qualitative analysis is, in many respects, similar to that of Fresenius. The same grouping of substances is followed, although under different names; the name of a familiar member of each group applied to it is more easily remembered, and conveys somewhat more of meaning than a mere number. Usually the methods of separating the members of each group from each other, and of detecting them, are the same as those given by Fresenius. But the work is much abridged, in order that it may be completed in a reasonably satisfactory manner in the short time that can be allowed for the study in some of the University courses, and to make it possible for the student in these courses to devote a little attention to quantitative analysis, some knowledge of which may be of more importance to him than a fuller acquaintance with qualitative methods. To the student who intends to make a special study of chemistry, the full course given in Fresenius, or in Prescott and Johnson, is none too extended; and for guidance in the more difficult parts of the analysis, he must refer to these comprehensive works.

Whatever is peculiar to the course of analysis given here, has been thoroughly tested by practical use for many years in the chemical laboratory of Cornell University. This experience has shown that with strict following of the directions laid down, the careful student will from the beginning commit but few errors, and will readily learn how to make a correct analysis of any mixture containing the more commonly occurring elements.

62. *The grouping of the substances tested for.* The substances that are tested for in all ordinary schemes of qualitative analysis are of two classes, the acidigenic and the basigenic elements or groups, or, as they are called in other works, the acids and bases. Of the acidigens, or acids, a small number can be associated together by their common property of being precipitated in a neutral solution, as barium salts; and another group consists of those that give a precipitate with silver nitrate in a solution acidified with nitric acid. In other words, the barium salts of the members of the group first mentioned are insoluble in water, and the silver salts of the members of the other group are insoluble in dilute nitric acid.

But this grouping has no such significance as there is in the grouping of the basigens, as the student will understand much more clearly after he has completed his qualitative work; neither the barium nor the silver group of acidigens is separated out by itself, in any scheme of analysis, for the purpose of testing for each member of the group in the precipitate thus obtained. The analysis for the acids consists mostly of a succession of independent tests applied to the original substance, or to a solution of the substance prepared by boiling with sodium carbonate, so as to have only sodium salts in the solution to be worked with. The only use of this grouping is to determine by a single brief test whether any acid of one or the other group is present, thus making it possible in some cases to omit the whole series of the tests required to prove the presence or absence of the several members of one or both groups. On the other hand, a very important part of the analysis for the bases consists in their separation into six groups: the members of each one of these groups being allied in so far as they possess at least one common property, as to insolubility of certain of their compounds in water or in acids of different degrees of dilution, by which they may be thus brought out together. Each group is then, perhaps, subdivided, sometimes by difference in respect to solubility in some other active agent than an acid; and, finally, each member of the group is so far isolated as may be necessary to make a final confirmatory test for its presence or absence.

The substances thus brought out of the solution in company are often not at all chemically allied; consequently the analytical grouping is in some cases not so sharply defined as to avoid all overlapping of groups. While this measure of unlikeness may facilitate the sub-grouping of elements, on the other hand, when

members of the same group are closely allied, their separation and identification may be very difficult; of this, nickel and cobalt, in the iron group, furnish a striking example.

The whole course of the analysis is thus divided into eight principal stages, of which the examination for the acidigens or acids is the first. See Table at end of this chapter.

With reference to the basigens we have three classes of compounds that are commonly made use of for grouping purposes, namely, chlorids, sulfids, and carbonates. Of these the sulfids are so important in analytical work as to be worthy of the special consideration of their more important properties.

#### THE SULFIDS.

63. These may be produced by fusion of metals with sulfur, or by the action of hydrogen sulfid or of solutions of soluble sulfids on metallic salts in solution.

They are distinguished:—

a. For their different degrees of solubility in (1) water, (2) acids, (3) other solvent liquids.

b. For their different degrees of susceptibility to oxidation.

c. For their variety of color.

64. *Solubility of the sulfids.* Most of the sulfids of the basigens are insoluble in water, only those of the potassium and calcium groups being soluble.

The sulfids of the iron group of metals differ much in solubility in dilute acids, as the behavior of nickel, cobalt, and zinc sulfids shows, in the course of the separation of the members of this group from one another.

The sulfids of the metals of the aluminum group are in their nascent state decomposed by water, forming hydroxids and hydrogen sulfid.

All the remaining sulfids are insoluble, not only in water but in at least moderately strong mineral acids; some of them are insoluble even in strong acid, and the metal contained in them can be brought into solution only through attack by strong oxidizing agents.

Thus, it is seen, we have every grade, from easy solubility of the alkaline sulfids in water, to insolubility in the strongest acid of sulfids of some metals of the copper and tin groups. Hence, in part, the great importance of the sulfids in analytical chemistry.

65. Certain elements (tin group) are capable of forming with



oxygen a lower oxid that is basigenic and a higher oxid that is acidigenic. Similar compounds are formed in which sulfur takes the place of oxygen; and, as nearly all salts of the alkaline metals are soluble, we may have soluble alkaline salts of these metals in which all the oxygen is replaced by sulfur, as, for instance,  $(\text{NH}_4)_3\text{AsO}_3$ , ammonium arsenite, and  $(\text{NH}_4)_3\text{AsS}_3$ , ammonium sulfarsenite. Remembering that the formulas of the oxygen salts of the acids formed from these elements are as follows, it is easy to see the relation of the sulfo-salts of the tin group to them:  $\text{M}_3\text{AsO}_3$ ;  $\text{M}_3\text{AsO}_4$ ;  $\text{M}_3\text{SbO}_4$ ;  $\text{M}_2\text{SnO}_3$ .  $M$  in these formulas stands for any monad basigen.

These sulfo-salts are readily formed by simple treatment of the solutions of compounds of these elements, or their freshly precipitated sulfids, by solutions of alkaline sulfids, especially such as have an excess of sulfur, as  $(\text{NH}_4)_2\text{S}_x$ , for example. Hence, the easy and nearly complete separation by means of ammonium sulfid of the tin group elements from those of the copper group.

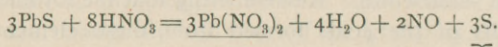
It is worthy of notice that, in this treatment, the action of the  $(\text{NH}_4)_2\text{S}_x$  on the antimonous and stannous sulfids corresponds in its character to one of oxidation; for, from these "ous" sulfids there is formed the sulfo-salt corresponding to the antimoniate or the stannate, and the sulfid precipitated by acid from the solution of the sulfo-salt is antimon $\acute{e}$ ic or stann $\acute{e}$ ic sulfid.

66. *Oxidation of the sulfids.* In the sulfids we have two elements both of which are capable of combining with oxygen, but the metal usually more eagerly than the sulfur. In nearly all cases a nitrate of the metal is formed, if nitric acid is used as the oxidizing agent; if the nitrate is not formed it is either because of the production of a higher oxide of the metal not basigenic, or because, the sulfate of the metal being insoluble, that is formed, to the entire or partial exclusion of the nitrate.

If the metal is capable of forming more than one oxid and series of salts, whether it be the lower or the higher oxid depends upon the conditions of the oxidation; if the sulfid is in excess and no heat is employed, a nitrate of the lower oxid may be the product; ordinarily an excess of acid and heat are employed, yielding a salt of the higher oxid. Nickel and cobalt sulfids are exceptions, giving only the lower oxid salts.

The sulfur of the sulfids is mostly set free as a precipitate, which in a hot liquid is liable to fuse together in small globules that resist oxidation with much obstinacy. Even when the sulfate of the metal is soluble, some of the sulfur is oxidized to sul-

furic acid, and some of this sulfate is formed together with the nitrate which is the chief product. However, it is usual in writing the equations for these reactions to assume, unless it is otherwise stated, that all the sulfur is set free, and only nitrate of the metal formed, at least in the first part of the reaction, as illustrated in the following equation:—



Occasionally a sulfid is so susceptible to oxidation as to suffer change by simple exposure to the oxygen of the air, or to the free oxygen dissolved in the water used to wash the precipitate.

67. *Chlorination of the sulfids.* When a sulfid is attacked in the presence of water by reagents setting chlorin free, oxidation may be the result by oxygen from decomposed water; but, especially if the chlorin be in excess and heat is applied, chlorination may also take place; and if the metal forms more than one chlorid the higher one is produced. Most of the sulfids are converted into chlorids by simple treatment with more or less concentrated hydrochloric acid, with evolution of hydrogen sulfids; but this is metathesis rather than chlorination; in the latter case, as in oxidation, sulfur is set free.

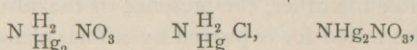
68. *Reduction of sulfids.* Just as oxids may be reduced by nascent hydrogen, which takes the oxygen to form water, so sulfids, subjected to the same treatment (with zinc and sulfuric acid), may be reduced,  $\text{H}_2\text{S}$  being formed instead of  $\text{H}_2\text{O}$ , and set free. Thus some sulfids may be decomposed that are with difficulty broken up in other ways.

#### THE HYDROXIDS (OR HYDRATES).

69. By the action of solutions of hydroxids on salts of other metals in solution, a class of reactions is produced of great importance in analytical work: the *normal* product of the reaction is a hydroxid of the metal acted upon.

Regarding this action as *normal* in all cases where with all three of the alkaline hydroxids,  $\text{KOH}$ ,  $\text{NaOH}$ , and  $\text{NH}_4\text{OH}$ , insoluble hydroxids are produced of normal composition, such as  $\text{Fe}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ , it is strictly normal with the metals of the aluminum group, and those of the iron group except cobalt, which yields a basic salt; with some metals of the copper and tin groups the result is more or less irregular; only with bismuth, cadmium, copper, and tin (ous) is it fully normal, but in

the case of copper only when the reagent is added just to saturation: with lead and the *fixed* hydroxids, KOH, NaOH, it is regular, but  $\text{NH}_4\text{OH}$  yields basic salts,  $\text{PbOCl}_2$ , or  $\text{Pb}_3\text{O}_2\text{OHNO}_3$ , according to the acid of the lead salt. With silver,  $\text{Ag}_2\text{O}$  is precipitated, and with salts of mercury and the fixed alkalies in excess,  $\text{Hg}_2\text{O}$  or  $\text{HgO}$ : with  $\text{NH}_4\text{OH}$ , compounds are produced in which a part or all of the hydrogen of the  $\text{NH}_4$  is replaced by mercury: these new compounds play the part of a basigenic body, like the ammonium, and remain in combination with the acid of the mercury salt. Example,



according as Hg is monad (mercurous) or dyad (mercuric).

With arsenic compounds, soluble salts of the alkaline metals are formed, arsenites and arsenates, and of course no precipitates; with antimonous compounds,  $\text{Sb}_2\text{O}_3$  is precipitated; with antimonic compounds, soluble antimonates are formed, or an insoluble antimonate,  $\text{NaSbO}_3$ : with stannic salts (stannates), stannic acid,  $\text{H}_2\text{SnO}_3$ , is precipitated. With gold only  $\text{NH}_4\text{OH}$  gives a precipitate, and that has a peculiar composition,  $(\text{NH}_3)_2\text{Au}_2\text{O}_3$ . Platinum in the form of chlorid gives with KOH and  $\text{NH}_4\text{OH}$  insoluble double chlorids, of great value in the quantitative estimation of potassium and ammonium,  $2\text{KCl.PtCl}_4$  and  $2\text{NH}_4\text{Cl.PtCl}_4$ : NaOH gives a precipitate of  $\text{Na}_2\text{PtO}_3$ .

The reactions with the hydroxids are seen to be more and more varied as we pass up to the tin group, where the elements tend to yield acidigenic oxides even in their lower degrees of oxidation; and the reaction in such cases has little analytical value.

*70. Solubility of the hydroxids.* All the normal hydroxids are insoluble in water, except those of the potassium group, and of barium, strontium, and calcium of the calcium group; all are soluble in dilute acids, forming salts of the acids used.

Most of them when freshly precipitated are soluble in solutions of either KOH, NaOH, or  $\text{NH}_4\text{OH}$ ; but only one,  $\text{Zn}(\text{OH})_2$ , is soluble in both a fixed and a volatile hydroxid, meaning by the latter ammonium hydroxid. New compounds are produced by this solution, differing so widely in form for different metals, that no general formula can be given for them; some of these formulas are given later.

Owing to this property of the hydroxids, we may have

two metatheses produced by one reagent, an insoluble product being formed first, which is afterward dissolved by an excess of the precipitant, with the formation of a second new compound that is soluble in water.

71. *Behavior when heated.* All the hydroxids, except those of the potassium group, are decomposed by heat, with the formation of an oxid of the metal, and water. In some cases this decomposition takes place even in boiling water.

#### THE FINAL TESTS.

72. One after the other, the presence or the absence of each substance to be tested for is proved by a final characteristic test, after it has been, if present, more or less completely isolated. Some of the reactions of these tests are so unique that they can be made in the presence of all the other members of the group, or even in the original solution, without regard to anything else that may be present: this is the case with many of the tests for the acids after they have been separated from all the bases except the alkalis by the transposition with sodium carbonate. The final tests for gold, platinum, copper, and iron are excellent illustrations of such as are not interfered with by the presence of other members of the groups to which they severally belong.

73. In these final tests we have two general classes of reactions:—

a. Color reactions, among which are some of the most delicate, marked, and unmistakable in use. Often nothing can interfere with their production. We may get them in:—

- (1) solution products;
- (2) precipitates from solution;
- (3) fusion products, on the foil or in the borax bead;
- (4) flame tests.

b. Precipitates without any marked color, usually white. The main safeguard against error, in the interpretation of results in such cases, is to have the conditions under which the precipitates are obtained, precisely as laid down in the directions for obtaining them.

#### THE COURSE OF ANALYSIS.

74. *Order of the arrangement of the work.* Beginning with the acidigen group, Chap. IX, the student reads over the description of the reactions of the first acid taken up, and writes out the equations explaining those reactions; he then tries the reaction or

reactions given in italics ; that is, to a small quantity, one or two cubic centimeters, of a solution containing a salt of the acid under consideration, in a test tube, he adds a small quantity of the reagent, precisely in the manner described in the account of the reaction, and compares the results obtained with the description of the result that should be obtained ; only in this way can he become so acquainted with the reactions described, that he will surely recognize them when he may meet with them again in the actual analysis of an unknown substance. The italicized reactions are those specially characteristic of each substance, made use of each time that it is tested for ; a thorough, personal acquaintance with them is therefore of great importance. The other reactions come into use only in the separation of substances from one another, or as occasional confirmatory tests in doubtful cases.

This work having been carefully performed with every substance in the group, the student then makes a mixture containing all the substances of which he has tried the characteristic reactions, and proceeds to analyze it according to the directions for the analysis for acids, § 85.

To simplify this part of the work with respect to the large group of the acids, by reducing the number of tests to be made in one solution, a mixture containing salts of only the barium group may be analyzed by itself, then a mixture containing only the silver group, with nitric acid added, and finally a mixture of the organic acids.

In doing this work he should get, clearly and unmistakably, the final, characteristic, reaction of every substance ; if he does not, he should repeat so much of the work as may be required to bring out this reaction ; evidently he is not prepared to take up the analysis of a substance whose composition is unknown to him, if there is any possible constituent of it which he should find, but cannot even when he has put it in himself and knows that it is present.

The student should then study carefully the explanation of the chemistry of the work on the acidigens in § 84. He is not fully prepared to do the best that is possible for him, in the analysis of an unknown substance, till he has learned the reasons for all the steps of the work, and is fully posted as to the special precautions that may be necessary to avoid errors.

Being then ready for the actual analysis of an unknown substance, this work is first done for the acidigens only ; when

the required proficiency has been attained, the student passes on to the first group of the basigens or metals, those precipitable by silver nitrate from a solution acidified with nitric acid, going through with the same series of preliminary operations and study, before analyzing the unknown substances containing the members of this group, and so on through all the groups in succession. Here, however, the work with his own solution begins with sub-section *b* of the section headed, "Preparation and Analysis of the Silver Group Precipitate," and follows this and sub-section *c*, headed "Analysis of the Silver Group Precipitate," with its table, to the end. Then comes the study of sub-section *a* of the same section on the chemistry of the analysis. The same course is followed with each of the other groups following. Finally comes the test of the thoroughness with which the several groups have been studied, in the analysis of substances in which the presence or absence of all the members of all the groups has to be proved. The following tabular view of the complete course of analysis of a substance may be useful as a general guide in this part of the work.

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## CHAPTER VIII.

### THE PREPARATION OF THE SOLUTION OF THE SUBSTANCE.

76. As nearly all the work of the analysis, for both acidigens and basigens is done with solutions<sup>§</sup>, the matter of the suitable preparation of these solutions is a very important one.

#### The solutions for the acidigens.

*a.* To 1 gm. of the *original substance*, finely powdered, add 15 c.c. of a concentrated solution of  $\text{Na}_2\text{CO}_3$  and boil ten minutes, replacing the water as it evaporates, dilute to 30 c.c. and filter if a residue remains.

This solution or filtrate contains all the acids of the substance except possibly phosphoric, hydrofluoric and silicic acids; mark it **A**, and test separate portions for the other acids as directed in § 85.

*b.* Acidify a small portion of **A** with  $\text{H}_2\text{SO}_4$ . The formation of a yellow or orange ppt. shows the presence of metals of the

TABLE II.  
75. General View of the Full Course of Analysis of a Substance.

1.—The original substance is:		4. Non-metallic.		9.—Prepare the solution for the rest of the analysis, as directed in Chap. VIII.	
2.—Metallic.		5.—Test for $H_2S$ , as directed in the acid group, Chap. IX.		8.—Test for $NH_4$ , as directed in the potassium group, Chap. X.	
3.—There need be no tests for acids, nor for metals of the potassium group, nor for metals of the calcium group, except Mg. Prepare a solution for analysis (as directed in Chap. VIII) and pass on to 10, below.		6.—Test for $CO_2$ , HF and $H_3PO_4$ , as directed in Chap. IX.		7.—Boil with conc. solution of $Na_2CO_3$ , filter and test the filtrate for the remaining acids, as directed in Chap. IX.	
10.—To the solution of the substance, whether metallic or non-metallic, add HCl, if not already present, and filter.					
11.—Precipitate.		12.—Filtrate: add $H_2S$ and filter.		16.—Filtrate: add $(NH_4)_2CO_3$ and filter.	
Sider group. All white. $PbCl_2$ . $AgCl$ . $HgCl$ .		13. Precipitate.		17. Precipitate.	
(a). Sulfids of the <i>tin</i> group, soluble in $(NH_4)_2S_x$ . $SnS$ , brown. $Sb_2S_3$ , yellow. $Sb_2S_3$ , orange. $As_2S_3$ , yellow. $Au_2S_3$ , $Au_2S_3$ , black or brown. $PtS_2$ , black.		(a). Sulfids of the <i>iron</i> group, insoluble in cold HCl. $CoS$ , black. $NiS$ , "		18.—Filtrate: divide in two portions.	
(b). Sulfids of the <i>copper</i> group, insoluble in $(NH_4)_2S_x$ , soluble in $HNO_3$ . $PbS$ , black. $CuS$ , " $Bi_2S_3$ , " $CdS$ , yellow. $HgS$ , black, insoluble in $HNO_3$ .		Ditto, soluble in cold HCl. $FeS$ , black. $MnS$ , flesh colored. $ZnS$ , white.  (b). Hydroxids of the <i>aluminum</i> group soluble in cold, HCl. $Al(OH)_3$ , white. $Cr(OH)_3$ , green.		19.—Portion 1. Add $Na_2HPO_4$ . Precipitate, $MgNH_4PO_4$ , white.	
		Carbonates of the <i>calcium</i> group, except Mg, all white. $CaCO_3$ . $BaCO_3$ . $SrCO_3$ .		20.—Portion 2. Soluble salts of the <i>potassium</i> group. $KCl$ . $NaCl$ .	

Sn group; in such case acidify a large portion of **A** with  $\text{H}_2\text{SO}_4$ ; filter, and boil the filtrate in a beaker or an Erlenmeyer flask until  $\text{H}_2\text{S}$  is entirely removed, which may be determined by holding a piece of moistened lead-paper in the escaping vapor at the mouth of the flask. Mark this solution **B**, and reserve also for § 85.

### 77. The solutions for the basigens.

#### The substance is metallic.

To about half a gram add 2 c.c. of  $\text{HNO}_3^*$  and warm until the substance is entirely dissolved or until no further change is observed, even when more  $\text{HNO}_3$  is added.

*a.* The substance is *entirely dissolved*, either at once or upon addition of water and boiling.

Gold, platinum, tin, and antimony are absent, except when present in alloys with very large proportions of soluble metals, when some of these metals may be completely dissolved. Take the solution to § 87 b.

*b.* *The substance is not completely dissolved*, a white residue remaining even when boiled with water. Sn, Sb and As may be present, the residue consisting of  $\text{SnO}_2$  or  $\text{Sb}_2\text{O}_4$  and  $\text{Sb}_2\text{O}_5$ , and possibly  $\text{As}_2\text{O}_5$ .

Dilute with water and filter. Heat the *insoluble residue* with  $\text{HCl}^*$ ; if it is not all dissolved decant the liquid carefully through a filter, after adding about its volume of water to it, so that the strong acid shall not cut through the paper, boil the residue with water, decant this off into the same filter, and repeat the treatment with  $\text{HCl}$ . Test the united solutions, thus obtained, for As, Sb and Sn, after removal of the excess of strong acid as directed in 32 § 89, c, then taking the solution to 37, b.

Evaporate a drop or two of the filtrate from the treatment with  $\text{HNO}_3$  in *a* above (the first filtration mentioned in *b*) on a watch glass; if a residue remains, showing that the liquid holds something in solution, take it to § 87, b, testing, in the following course for the Sn group, only for those members of the group not found in the above residue.

*c.* *A metallic residue* remains in *a*, undissolved. Treat it

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\* When the formula of an acid is given in this heavy type, concentrated acid is indicated, otherwise dilute acid.



with aqua regia (§ 24, c,) and test the solution for Au and Pt, as in 36 § 89, c.

Treat the *filtrate* from this residue, as directed for the filtrate under **b**, above.

### The substance is non-metallic.

78. *a.* Make a preliminary test, with about one-fifth gm. of the substance, as follows: add 2 c.c. of water and heat to boiling; if a residue remains, add to the contents of the tube a few drops of **HCl** and heat again; if a residue still remains allow it to settle, pour off the clear liquid and add to the residue 1 c.c. of **HCl** and warm. If a solution is not obtained in this way, repeat the experiment with another portion of the substance, using **HNO<sub>3</sub>** instead of **HCl**. If neither of these methods gives a clear solution, treat a third portion with aqua regia (a mixture of one part of **HNO<sub>3</sub>** and three parts of **HCl**). In a few cases, where the addition of acid causes a ppt., it is necessary to remove the portion soluble in water before treatment with acids. If a solution is obtained by any of the above methods, treat about 1 gm. of the substance by the same method, and take the solution to § 87, b.

If in the above tests, there is an insoluble residue which is white and gelatinous, and remains for some time suspended in the liquid, it will probably consist of **SiO<sub>2</sub>** from silicates that have been decomposed by acids; in this case evaporate the solution, with the residue, to *complete dryness*, moisten with a few drops of **HNO<sub>3</sub>**, add 10 c.c. of water, boil and filter; this residue, if white and gritty, consists of **SiO<sub>2</sub>**. Take the filtrate to § 87, b.

*b.* A reaction obtained in the aluminum group for Al might be misleading unless in every case of the solution of a *mineral* by acid, the silica possibly present is not removed by this evaporation to dryness before proceeding with the analysis: an error might also be made in the test for **P<sub>2</sub>O<sub>5</sub>**. Therefore, in important cases the silica should be removed here.

*c.* If **H<sub>2</sub>S** was found in the tests for acids, a residue of sulfur may remain; this will be yellow, will float on the liquid and when heated on a crucible cover will first melt, then burn with a blue flame emitting the odor of **SO<sub>2</sub>**.

*d.* If the substance is not affected by the above treatment, it must be treated as directed in § 79 for insoluble substances;

or if a residue remains that is not white and gelatinous ( $\text{SiO}_2$ ) and is not sulfur, this residue must be so treated.

**79. The substance is non-metallic, and wholly or partially insoluble.**

*a.* The only substances of ordinary occurrence that are not dissolved by the treatment described in § 78, are C, S, AgCl, AgBr, AgI (possibly  $\text{PtCl}_2$ , and  $\text{PbI}_2$ ),  $\text{PbSO}_4$ ,  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $[\text{CaSO}_4]$ ,  $\text{SiO}_2$ , many silicates and a few oxids and fluorids. *If in the tests for acids no HI, HBr, HCl, HF, or  $\text{H}_2\text{SO}_4$  is found,* the insoluble substance is generally either a silicate or an oxid [or chrome iron]. In this case pass to *c.*

*If either of the above mentioned acids is found* add to the residue obtained in § 78, or to the original substance if wholly insoluble, 5 c. c. of a mixture of equal parts of **HCl** and water, and a piece of Zn and warm gently; if the Zn or the residue is blackened after a few minutes,  $\text{PbSO}_4$ , or a salt of silver may be present; let the action continue till no further change is observed and decant the liquid, rejecting it, wash the residue by decantation, add **HNO<sub>3</sub>**, heat as long as any action appears to take place, as indicated by the evolution of reddish fumes, and filter, if solution is not complete.

*b. Filtrate.* Test for Ag and Pb as in § 87, b.

*c. Residue.* Mix the dry and very finely powdered residue (See § 44) obtained above, or the residue referred to in § 78, *d*, or a portion of the original substance, if it was wholly insoluble, and contains no lead or silver salts, with 4 or 5 parts of a flux composed of about 4 parts of  $\text{Na}_2\text{CO}_3$  and 1 part of  $\text{KNO}_3$ , and fuse on platinum foil, in several separate portions; heat gently at first over an ordinary burner, and then with full flame, so managing the operation as to lose no substance by boiling over; then heat over the blast lamp for about ten minutes, or till bubbles of gas are no longer set free; the mass should fuse to a liquid; if not, more flux should be added and the heating over the blast lamp be repeated. Put the foil in an evaporator with water, and digest (§ 53) till the fused mass is completely disintegrated; fuse the second portion of the mixture of substance and flux, and so on, digesting all the fused masses in the same portion of water; finally, filter.

*d. Filtrate.* Acidify with **HCl** and evaporate in the hood to complete dryness, moisten the residue with a few drops of **HCl**,

evaporate to dryness again, and moisten again with  $\text{HCl}$ , add 20–25 c. c. of water, and heat. A white residue, gritty under the glass rod indicates  $\text{SiO}_2$ .

Filter, reject the residue, and take the filtrate to § 87, b. See also filtrate from *e*, below.

*e. Residue from filtration at end of c.* Wash thoroughly with hot water, add about 5 c. c. of  $\text{HCl}$ , and evaporate in the hood to *complete dryness*; moisten the residue with  $\text{HCl}$ , add 20–25 c. c. of water, heat and filter, rejecting the residue if *white*. This filtrate may be put with the filtrate from *d*, if no ppt. appears on mixing small portions of them together. Take the mixture, or the two solutions separately if they cannot be mixed, to § 87, b.

*f.* If the residue from the above filtration is black, and therefore appears to be unaffected by the fluxing, fuse it with 7–8 parts of  $\text{KHSO}_4$  (potassium bisulfate), to which a little borax may be added; the fused mass thus obtained is to be treated as directed for the fused product in *c* above.

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## CHAPTER IX (A).

### THE ACIDIGENS OR ACIDS.

#### DESCRIPTION.

80. *The barium group: Solubility of compounds, and reactions.*

CARBON DIOXID;  $\text{CO}_2$ :—An odorless gas, slightly soluble in water, forming probably carbonic acid,  $\text{H}_2\text{CO}_3$ .

All normal carbonates except those of metals of the potassium group are insoluble in water.

All carbonates are decomposed by dilute acids,  $\text{CO}_2$  being set free with strong effervescence.

*Reaction:—When  $\text{Ca}(\text{OH})_2$  in solution (lime water) is exposed to  $\text{CO}_2$  gas, the solution is made turbid by the formation of  $\text{CaCO}_3$ ; on longer exposure the turbidity may disappear, owing to the solution of the carbonate in the excess of  $\text{CO}_2$ .*

SULFURIC ACID;  $\text{H}_2\text{SO}_4$ :—All sulfates except  $\text{PbSO}_4$ ,  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ , and  $\text{CaSO}_4$ , are readily soluble in water;  $\text{CaSO}_4$  is soluble in about 400 parts of water, and in  $\text{HCl}$ ; the other three are nearly insoluble in all acids.

$PbSO_4$  is decomposed by Zn and HCl, Pb being set free; all of these insoluble sulfates are transposed by fusion with  $Na_2CO_3$ , carbonates of the metals and  $Na_2SO_4$  being formed. All sulfates except the native barium sulfate (heavy spar) are similarly transposed by boiling with a conc. solution of  $Na_2CO_3$ .

*Reaction*:— $BaCl_2$  ppts. immediately from solutions containing  $H_2SO_4$ , or sulfates, barium sulfate,  $BaSO_4$  pulverulent, white, heavy and very insoluble. Traces or even more than traces may not be precipitated from a solution containing ammonium nitrate or normal citrates, as well as from solutions acid with free HCl or  $HNO_3$ .

SULFUROUS ACID;  $H_2SO_3$ :— $SO_2$ , sulfur dioxide is a gas possessing a suffocating odor, and soluble in water.

Sulfites except of the potassium group are mostly insoluble in water.

They are transposed by boiling with conc. solution of  $Na_2CO_3$ ,  $Na_2SO_3$  and carbonate of the base being formed.

*Reaction*:— $SO_2$  reduces ferric to ferrous salts, and therefore causes a blue ppt. in a mixture of  $FeCl_3$  and  $K_3FeCy_6$ , since ferric salts give no ppt. with  $K_3FeCy_6$ , while ferrous salts do.

OXALIC ACID;  $H_2C_2O_4$ :—Oxalates except those of metals of the potassium group are mostly insoluble in water; all are soluble in dilute mineral acids.

Oxalates except of the aluminum and iron groups are readily transposed by boiling with conc. solution of  $Na_2CO_3$ ; they are decomposed by ignition, but without blackening.

*Reactions*:— $Pb(C_2H_3O_2)_2$  ppts. from solutions of oxalates  $PbC_2O_4$  white, pulverulent, insoluble in  $HC_2H_3O_2$ , and in  $NH_4OH$ , soluble in  $HNO_3$ .

$CaSO_4$  ppts. from neutral or acetic solutions of oxalates, calcium oxalate,  $CaC_2O_4$ , pulverulent, white, soluble in HCl or  $HNO_3$ , insoluble in  $HC_2H_3O_2$ .

CHROMIC ACID;  $H_2CrO_4$ :—Chromates, except those of the potassium group, are mostly insoluble. Solutions of normal chromates are yellow, of acid chromates yellowish-red. All chromates are colored.

*Reactions*:—When a solution of a chromate is acidified with HCl and boiled after the addition of alcohol, aldehyd,  $C_2H_4O$ , and a green solution of  $CrCl_3$  are obtained; this solution with  $NH_4OH$  gives  $Cr(OH)_3$ , greenish ppt. provided that, as just directed, the alcohol was added after the HCl.

If to a solution of a chromate, acidified with HCl, and containing no other oxidizing agent than the chromate, KI is added, iodine is set free, which colors  $CS_2$  violet, if this reagent is shaken up with the liquid. This reaction is exceedingly delicate.

*If a solution of a chromate is added to a mixture of lead acetate and ammonium acetate acidified with acetic acid, a yellow ppt.  $PbCrO_4$ , appears, at once, or after standing a short time if the chromate solution was very dilute; the ppt. is insoluble in acetic acid, slowly soluble in  $HNO_3$ , soluble in NaOH: no other acids present as normal salts interfere with the test.*

BORIC ACID ;  $H_3BO_3$  :—Borates except those of metals of the potassium group are insoluble in water, but soluble in acids.

Borates are decomposed by  $H_2SO_4$ , with liberation of the acid, and are transposed by boiling with  $Na_2CO_3$ .

*Reaction :—Boric acid liberated by a stronger acid, such as  $H_2SO_4$ , imparts a green color to the flame of burning alcohol, particularly when the alcohol is nearly burned away.*

HYDROFLUORIC ACID ; HF :—Fluorids except of the metals of the potassium group are mostly insoluble or difficultly soluble in water.

Any fluorid in solution will quickly corrode the surface of glass with which it comes in contact.

*Reaction :— $H_2SO_4$  liberates from a fluorid HF, a gas which corrodes glass.*

PHOSPHORIC ACID ;  $H_3PO_4$  :—All normal phosphates, except those of the potassium group, are insoluble in water, but are readily soluble in dilute mineral acid.

*Reaction :— $(NH_4)_2MoO_4$  ppts. immediately or in a very short time from solutions containing  $H_3PO_4$  or phosphates, and  $HNO_3$ , ammonium phospho-molybdate, pulverulent, partly adhering strongly to the sides of the tube, lemon-yellow, readily soluble in  $NH_4OH$ .*

SILICIC ACID ;  $H_2SiO_3$  :—Silicates, except those of the potassium group containing an excess of alkali, are insoluble in water or acids.

Silicates are transposed by fusion with  $Na_2CO_3$ , and some are decomposed by strong acids with the liberation of the silica in a gelatinous form.

*Reaction :—When a solution containing silicic acid or a silicate is evaporated to dryness with HCl, the silicate is decomposed, and  $SiO_2$  remains as an insoluble gritty powder.*

**81.** *The silver group: solubility of compounds, and reactions.*

HYDROSULFURIC ACID;  $H_2S$ :—An ill-smelling gas, slightly soluble in water.

All sulfids except those of metals of potassium and calcium groups are insoluble in water.  $FeS$ ,  $MnS$ , and  $ZnS$  are soluble in cold  $HCl$ , with evolution of  $H_2S$ .  $NiS$ ,  $CoS$ ,  $CdS$ ,  $Bi_2S_3$ ,  $CuS$ ,  $PbS$ , and  $Ag_2S$  are soluble in hot  $HNO_3$ , nitrates of the metals being formed and the sulfur partially oxidized to  $H_2SO_4$  and partly set free, and giving in the case of  $PbS$  insoluble, white  $PbSO_4$ . Sulfids of arsenic, tin and antimony are decomposed by hot  $HNO_3$ , oxids of the metals,  $H_2SO_4$  and  $S$  being formed. The sulfids of mercury are not decomposed by  $HNO_3$ .

Most of the sulfids that are not attacked by dilute acid are decomposed by such acid in the presence of metallic zinc.

*Reaction*:— $H_2S$  gas, liberated by  $HCl$  or  $H_2SO_4$ , with the aid of  $Zn$  if necessary, blackens paper moistened with  $Pb(C_2H_3O_2)_2$ .

HYDRIODIC ACID;  $HI$ :—The iodids closely resemble the chlorids in solubility (see below under hydrochloric acid).

Iodids are transposed by boiling with a conc. solution of  $Na_2CO_3$ .

*Reactions*:— $AgNO_3$  ppt. immediately from solutions of iodids acidified with  $HNO_3$ , silver iodid,  $AgI$ , flocculent, yellow, insoluble in  $NH_4OH$  and in  $(NH_4)_2CO_3$ , and decomposed by  $Zn$  and  $H_2SO_4$ ; it is not decomposed by ignition to low redness.

*In a solution of an iodid containing free acid the addition of a little  $K_2CrO_4$  causes the liberation of free iodin.* Chlorin causes the same liberation.

$CS_2$  in a solution containing free iodin will dissolve the iodin if the mixture is well shaken, and be colored violet.

HYDROBROMIC ACID;  $HBr$ :—Bromids closely resemble chlorids in solubility (see below under hydrochloric acid).

Bromids are transposed by boiling with  $Na_2CO_3$ , and are decomposed by chlorin with liberation of  $Br$ .

*Reactions*:— $AgNO_3$  ppt. immediately from solutions of bromids acidified with  $HNO_3$ , silver bromid,  $AgBr$ , flocculent, yellowish-white, soon darkening in the light, slightly soluble in  $NH_4OH$ , and insoluble in  $(NH_4)_2CO_3$ ; it is decomposed by  $Zn$  and  $H_2SO_4$ , the metal being set free, but is not decomposed by ignition to low redness.

$CS_2$  added to a solution containing free  $Br$  will dissolve it if the mixture is well shaken, and take a yellow or orange color.

HYDROCYANIC ACID ;  $\text{HCy}$ :—Simple cyanids of metals of the copper and iron groups, except  $\text{HgCy}_2$  are insoluble, of the potassium, calcium and aluminum groups, are soluble in water.

Soluble cyanids are readily decomposed by dilute acids,  $\text{HCy}$ , a colorless and *very poisonous* gas being liberated. Cyanids are transposed by boiling with  $\text{Na}_2\text{CO}_3$ .

*Reactions*:— $\text{AgNO}_3$  ppt. immediately from solutions of cyanids acidified with  $\text{HNO}_3$  silver cyanid,  $\text{AgCy}$ , flocculent, white, soluble with decomposition in boiling  $\text{HNO}_3$ , and soluble in  $\text{NH}_4\text{OH}$  and in  $(\text{NH}_4)_2\text{CO}_3$ . It is decomposed by Zn and  $\text{H}_2\text{SO}_4$ , and also by ignition to low redness, metallic silver remaining.

$(\text{NH}_4)_2\text{S}_x$  exposed to  $\text{HCy}$  gas for a few minutes gives, in solution, ammonium sulfocyanate,  $\text{NH}_4\text{CyS}$ ; if the drop of solution is evaporated to dryness and the residue moistened with  $\text{FeCl}_3$ ,  $\text{Fe}(\text{CyS})_3$ , deep red, will be formed.

HYDROFERROCYANIC ACID ;  $\text{H}_4\text{FeCy}_6$ :—Ferrocyanids, except those of metals of the potassium and calcium groups, are mostly insoluble in water, and in acids.

Ferrocyanids are transposed by boiling with  $\text{Na}_2\text{CO}_3$ .

*Reactions*:— $\text{FeSO}_4$  gives immediately with acid solutions of potassium ferrocyanid, potassium ferrous ferrocyanid  $\text{K}_2\text{FeFeCy}_6$ , flocculent, light blue, which, on exposure to air or treatment by  $\text{HNO}_3$ , becomes by oxidation ferric ferrocyanid (Prussian blue),  $\text{Fe}_4(\text{FeCy}_6)_3$ , dark blue, insoluble, and decomposed by  $\text{NaOH}$  with the formation of ferric hydrate,  $\text{Fe}(\text{OH})_3$ , reddish brown.

$\text{FeCl}_3$  gives in solution of ferrocyanids,  $\text{Fe}_4(\text{FeCy}_6)_3$

HYDROFERRICYANIC ACID ;  $\text{H}_6(\text{FeCy}_6)_2$  or  $\text{H}_3\text{FeCy}_6$ :—In solubility the ferricyanids are similar to the ferrocyanids.

Ferricyanids are transposed by boiling with conc. solution of  $\text{Na}_2\text{CO}_3$ .

*Reactions*:— $\text{FeSO}_4$  gives immediately, in acid solutions of ferricyanids, ferrous ferricyanid,  $\text{Fe}_3(\text{FeCy}_6)_2$  flocculent, dark blue, decomposed by  $\text{NaOH}$ , as above, giving ferrous hydrate.

$\text{FeCl}_3$  gives no ppt. with ferricyanids, but a darkening of the liquid.

HYDROCHLORIC ACID ;  $\text{HCl}$ :—Chlorids, except  $\text{AgCl}$ ,  $\text{HgCl}$  and  $\text{PbCl}_2$ , are soluble in water.  $\text{PbCl}_2$  is slightly soluble in cold water, and readily soluble in hot water ;  $\text{AgCl}$  and  $\text{HgCl}$  are insoluble in dilute acids.

Chlorids are transposed by boiling with conc. solution of  $\text{Na}_2\text{CO}_3$ .

*Reaction*:— $\text{AgNO}_3$  ppt. immediately from solutions of chlorids acidified with  $\text{HNO}_3$  silver chlorid,  $\text{AgCl}$ , flocculent, white, soon darkening in the light, soluble in  $\text{NH}_4\text{OH}$  and in  $(\text{NH}_4)_2\text{CO}_3$ ; it is decomposed by contact with  $\text{Zn}$  and  $\text{H}_2\text{SO}_4$ ,  $\text{Ag}$  being deposited, but is not decomposed by ignition to low redness.

**82.** *The oxidizing acids, solubility of compounds, and reactions.*

**NITRIC ACID**;  $\text{HNO}_3$ :—All normal nitrates are soluble in water.

Nitrates are decomposed, with liberation of the nitric acid, by sulfuric acid, and are transposed by boiling with a conc. solution of  $\text{Na}_2\text{CO}_3$ .

*Reactions*:—In presence of  $\text{H}_2\text{SO}_4$  and a reducing agent the liberated  $\text{HNO}_3$  is decomposed, with the formation of nitric oxide,  $\text{NO}$ ; if the reducing agent is  $\text{FeSO}_4$  and the liquid is cold,  $(\text{FeSO}_4)_2\text{NO}$  is formed, giving a blackish-brown solution.  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_3\text{FeCy}_6$ ,  $\text{H}_4\text{FeCy}_6$  and  $\text{H}_2\text{CrO}_4$  interfere.

If a drop of phenyl-sulfuric acid is put on a dry nitrate and after a few minutes two or three drops of strong  $\text{NH}_4\text{OH}$  are added, a bright yellow color appears, ammonium nitro-phenylate. The reaction is exceedingly delicate. Chromates interfere.

**CHLORIC ACID**;  $\text{HClO}_3$ :—All chlorates are soluble in water.

Chlorates are decomposed by ignition, with liberation of their oxygen, and by  $\text{H}_2\text{SO}_4$  and are transposed in boiling  $\text{Na}_2\text{CO}_3$  solution.

*Reactions*:— $\text{Na}_2\text{SO}_4$  in an acidified solution of a chlorate, by taking up a part of the oxygen of the chloric acid sets free chlorine or some compound thereof, bleaching indigo solution.

With  $\text{H}_2\text{SO}_4$  a chlorate gives off an offensive greenish-yellow product,  $\text{ClO}_2$ , which partly dissolves in the acid, coloring it greenish-yellow. The experiment should be performed in a watch-glass with a very small quantity of the substance.

**83.** *The organic acids (except oxalic), solubility of compounds, and reactions.*

**ACETIC ACID**;  $\text{HC}_2\text{H}_3\text{O}_2$ :—All acetates are soluble. On ignition the dry salts are decomposed and blackened by separation of carbon with evolution of odorous products.

*Reactions*:—When heated with  $\text{H}_2\text{SO}_4$  and a little  $\text{C}_2\text{H}_6\text{O}$ , acetic ether,  $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$ , very volatile, is formed, possessing a peculiar, pleasant odor.



When a neutral acetate and  $FeCl_3$  are mixed together the solution assumes a deep red color, not removed by  $HgCl_2$ , but it disappears when the liquid is boiled after much dilution.

TARTARIC ACID ;  $H_2C_4H_4O_6$  :—Tartrates of the alkali metals are soluble, but only sparingly so in the case of some acid tartrates ; other tartrates are partly soluble and partly insoluble in water, those of metals of the aluminum and iron groups being mostly quite soluble.

Tartrates are transposed by boiling with  $Na_2CO_3$  and are decomposed on ignition, turning black and giving off the odor of burnt sugar.

Reactions :—With  $Pb(C_2H_3O_2)_2$  tartrates give  $PbC_4H_4O_6$ , white, soluble in  $NH_4OH$  free from carbonate. With  $KC_2H_3O_2$ , acidified with  $HC_2H_3O_2$ , concentrated neutral solutions of tartrates give hydrogen potassium tartrate,  $KHC_4H_4O_6$ , white, crystalline, insoluble in alcohol. Boric acid interferes with this test.

CITRIC ACID ;  $H_3C_6H_5O_7$  :—Citricates of the alkali metals are readily soluble in water, those of the calcium group metals are insoluble, the others are mostly soluble.

All citricates are decomposed on ignition, with separation of black carbon, and evolution of odorous products of the decomposition.

Reaction :— $Pb(C_2H_3O_2)_2$  in solutions of citrates ppt. lead citrate,  $Pb_3(C_6H_5O_7)_2$ , white, amorphous, soluble in  $NH_4OH$  free from carbonate ; on digestion for several hours with water or  $HC_2H_3O_2$  it becomes crystalline.

## CHAPTER IX B.

### THE ANALYSIS FOR THE ACIDIGENS.

#### 84. Notes on the chemistry of the analysis.

With regard to the course for the detection of the acids so much of the work consists in the mere application of final tests, which are sufficiently explained under the description of the reactions for the acids, or elsewhere, that little remains to be made clear.

The transposition in  $\alpha$  § 76 with  $Na_2CO_3$  is made in order to

remove from the solution all bases except those of the alkaline metals: these, giving only soluble salts with all the acids, will themselves give no precipitates or reactions with any of the reagents used, that might confuse or mislead the analyst, or interfere with his work.

The tin group metals if present in the alkaline solution that was prepared in (*a*) would be precipitated on acidification in **12** and cause difficulty.

It must not be overlooked in making this group test, in **1** following, that the liquid while containing an excess of  $\text{Ba}(\text{OH})_2$  may slowly become turbid by absorption of carbon dioxid from the air.

Since the treatment with acid in **1**, in the course of analysis following, expels the carbon dioxid of the original substance, as well as of the  $\text{Na}_2\text{CO}_3$  used for the transposition of the acids into sodium salts, this acid must be tested for in every case, whether a ppt. is obtained for the barium group or not.

$\text{H}_2\text{S}$  is also a reducing agent: by metathesis with the lead acetate it gives insoluble  $\text{PbS}$ , and is thus removed, in **4**.

Chlorates and ferricyanids are, like chromates, oxidizing agents in the presence of free acid; hence the iodine test cannot be used as confirmatory of the lead test, in the presence of those compounds, in the test for chromic acid in **7**.

This precipitate for  $\text{P}_2\text{O}_5$  in **10**, by molybdate, is more insoluble in a liquid containing  $\text{HNO}_3$ , if it is not too strong, than in other acids.

It is soluble to some extent in solutions of phosphates; hence the method of making the test which secures always an excess of the reagent, in **10 a**.

Compounds of arsenic and phosphorus are much alike, and both arsenic and phosphoric acids give lemon-yellow precipitates with molybdate; hence the removal of members of the tin group in **10 b**.

Ferrocyanid and molybdate react, giving a flocculent brown precipitate, which might mask the yellow phospho-molybdate, if only a little of it were precipitated. Zinc ferrocyanid is insoluble in dilute  $\text{HNO}_3$  while the phosphate is soluble, and the former is thus removed in **10 c**.

Sulfites also give  $\text{H}_2\text{S}$  with zinc and free acid; hence they must be removed before making the test for  $\text{H}_2\text{S}$  with these reagents, as in **13**.

In the reaction in **14** the  $\text{HI}$  produced from the iodide by the

stronger  $\text{HNO}_3$  becomes a reducing agent, its hydrogen reducing the chromic acid of the chromate, while its iodine is set free.

Solution **A** must be used in the test for HCy in **16** because HCy was expelled from **B** by the  $\text{H}_2\text{SO}_4$  added. The  $(\text{NH}_4)_2\text{S}$ , which would give a black precipitate with the  $\text{FeCl}_3$ , added later, is decomposed by the evaporation to dryness; in this evaporation, if the dry residue be heated too strongly the sulfocyanate itself will also be decomposed.

The laboratory solution of ammonium carbonate contains free  $\text{NH}_4\text{OH}$ , which, according to the required conditions of this operation, should not be present: hence the treatment with  $\text{CO}_2$ , in the separation of  $\text{AgCl}$  from  $\text{AgBr}$  in **19 b**.

While the fused residue of  $\text{AgCl}$ ,  $\text{AgI}$ , and  $\text{AgBr}$  is acted upon by  $\text{Zn}$  and  $\text{H}_2\text{SO}_4$  in the same manner that these salts are acted upon when freshly precipitated, it is not so acted upon by  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$ ; hence the freshly precipitated salts must be prepared again, after this decomposition of the salts in the fused products, as directed in **19 c**.

The tests for citric and tartaric acids are satisfactory only when very carefully performed, and even then are not easily obtained unless the solution contains at least a moderate quantity.

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### 85. *The course of analysis:—*

*The Barium group:—Preliminary test for this group.*

1. To 3 c. c. of **A** from § 76, in a small beaker or flask, add  $\text{HCl}$  very slowly and with constant stirring, till there is no further effervescence, and the solution is *slightly* acid; boil thoroughly, cool, and add  $\text{Ba}(\text{OH})_2$  till the liquid is slightly alkaline, and with care to expose to the air as little as possible.

The liquid remains clear; none of the Ba group of acids need be tested for except  $\text{CO}_2$ . A slight turbidity, remaining after the acidification of the liquid (§ 48), may be due to traces of sulfuric acid, sulfates being very commonly present as impurities in many ordinary chemicals.

2. CARBONIC ACID:—To a portion of the *original substance* add  $\text{HCl}$ . If solution with effervescence takes place, test the gas evolved with a drop of lime water in the open end of a small tube.

If no other acids of the barium group are present to **14**.

3. SULFURIC ACID:—To 2 c. c. of **A** (§ 77) add  $\text{HCl}$  till acid and then  $\text{BaCl}_2$  in excess.

4. SULFUROUS ACID:—Acidify a portion of **A** with HCl, warm and immediately expose to the gas in the tube in the open end of a small tube, a drop of mixture of  $\text{FeCl}_3$  and  $\text{K}_3\text{FeCy}_6$ . If  $\text{H}_2\text{S}$  is present a little  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  should be added to **A** before acidifying with HCl.

5. *Preliminary test for the presence of either of the three organic acids, acetic, tartaric, or citric:*—Carefully ignite about 0.5 gm. of the original substance on a crucible lid, heating only for a moment at a time, at first gently, then more strongly, removing the test repeatedly from the flame to observe the odor, and any appearance of smoky products of combustion, or formation of a carbonaceous residue; if none of these results are perceived, these acids are absent, except at the most in very small quantities.

6. OXALIC ACID:—(a) *No indication of organic acids was observed in 5*—Acidify a portion of **A** with acetic acid, and add  $\text{CaSO}_4$ .

(b) *Organic acids are present.*—Acidify 3 c.c. of **A** with dilute  $\text{HC}_2\text{H}_3\text{O}_2$  (1 of acid to 4 of water), add 8–10 c.c. of neutral  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , filter, wash the ppt. with dilute alcohol (equal parts of 95 per cent. alcohol and water), transfer to a small beaker and add about 8 c.c. of  $\text{NH}_4\text{OH}$ , mix well and filter, saving the filtrate for 23.

Wash the contents of the filter with dilute  $\text{NH}_4\text{OH}$ , treat it in a beaker with 1–2 c.c. of  $\text{HNO}_3$ , pass  $\text{H}_2\text{S}$  through the liquid and filter. Neutralize the filtrate with  $\text{NaOH}$ , acidify with  $\text{HC}_2\text{H}_3\text{O}_2$  and add  $\text{CaSO}_4$ .

7. CHROMIC ACID:—Acidify a portion of **A** with  $\text{HC}_2\text{H}_3\text{O}_2$  and add to it about 2 c.c. of the lead and ammonium acetate mixture.

8. BORIC ACID:—Evaporate 2 c.c. of **A** to dryness, moisten the residue with  $\text{H}_2\text{SO}_4$ , add 2 c.c. of alcohol, set the mixture on fire, and stir it, while burning, with a glass rod. If copper is absent, as indicated by the absence of any greenish or blue color in the original solution, the original substance may be used directly for this test.

9. HYDROFLUORIC ACID:—To the finely pulverized substance, in a small platinum or leaden cup, add enough  $\text{H}_2\text{SO}_4$  to make a thin paste, and cover the dish with a piece of Bohemian glass coated with wax except where the coating has been removed by writing through it down to the glass with a pointed wooden

pencil; heat the dish *gently* for an hour, warm the glass till the wax is melted, and rub it off with filter paper. The etched lines to be looked for may need to be brought out by breathing on the clean glass; they should reappear after the glass has been rinsed off, dried, wiped, and breathed upon again.

**10. PHOSPHORIC ACID** :—Dissolve a small portion of the original substance in  $\text{HNO}_3$  with the aid of heat, add its volume of water to the liquid. Filter if solution is not complete, evaporate the solution nearly to dryness, and dissolve the residue in a little water.

(a) *No members of the Sn group of metals were found in (77 b), and no  $\text{H}_4\text{FeCy}_6$  is present*; add 0.5 c.c. of this solution to 4 c.c. of  $(\text{NH}_4)_2\text{MoO}_4$ .

(b) *Members of the Sn group of metals were found, but no  $\text{H}_4\text{FeCy}_6$  is present*; remove these metals by heating the solution and passing  $\text{H}_2\text{S}$  through it till no further precipitation is produced by the reagent, boil to remove all  $\text{H}_2\text{S}$ , and test the cooled solution with  $(\text{NH}_4)_2\text{MoO}_4$ , as above directed. Or the test for this acid may be deferred till the work in § 89 c has been completed, when, if no As has been found, the test for  $\text{H}_3\text{PO}_4$  may be made as above, with the original solution; if As is found in § 89, c, a portion of the filtrate from the group precipitation by  $\text{H}_2\text{S}$  may be used for the test, after first heating it with a few drops of  $\text{HNO}_3$ .

(c)  *$\text{H}_4\text{FeCy}_6$  is present*: add  $\text{ZnSO}_4$  to the solution, freed from Sn group metals if originally present, as long as any further precipitation takes place, filter and test the filtrate as above with  $(\text{NH}_4)_2\text{MoO}_4$ .

**11. SILICIC ACID** :—Evaporate a portion of **A** to complete dryness, after acidification with  $\text{HCl}$ , and dry thoroughly at a gentle heat; moisten the residue with  $\text{HCl}$ , and after a little time add  $\text{HCl}$  and digest for a short time. For the detection of  $\text{SiO}_2$ , in an insoluble substance, see § 79.

**12. Preliminary test for the silver group of acids** :—Acidify a small portion of **B** (or of **A** if there is no **B**) with  $\text{HNO}_3$ , and add  $\text{AgNO}_3$ . The formation of a white or whitish precipitate indicates the presence of either  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{H}_4\text{FeCy}_6$  or  $\text{HCy}$ . In ordinary cases a mere turbidity may be taken as indicating traces of  $\text{HCl}$  only, and the other acids precipitated by silver nitrate may be regarded as absent, unless there be special reasons for searching for any of them. A colored precipitate

may contain also  $\text{H}_3\text{FeCy}_6$  or  $\text{H}_2\text{CrO}_4$ . A black precipitate will be due to the presence of  $\text{H}_2\text{S}$ . If no precipitate appears all these acids are absent from this solution.  $\text{H}_2\text{S}$  may be present in the original substance, in sulfids that were not transposed in § 76. Pass on to 13.

**13. HYDROSULFURIC ACID:**—To a portion of the *original substance* in a test tube add  $\text{HCl}$  and warm gently. If solution with effervescence takes place, test the gas evolved with moistened lead paper. If a *colored* residue remains after this treatment, it may contain sulfids, although no reaction for  $\text{H}_2\text{S}$  was obtained as above; in such case, warm the contents of the tube until all action ceases, to insure removal of  $\text{SO}_2$  that may be present, add a piece of zinc, and repeat the test with lead paper. Should no reaction for  $\text{H}_2\text{S}$  be now obtained, and a residue still remain, remove the  $\text{Zn}$  and wash the residue several times with water, to remove soluble sulfates, add to it  $\text{HNO}_3$  and warm till red fumes are no longer set free, dilute with 5 or 6 parts of water, filter if not clear, and add  $\text{BaCl}_2$  to the filtrate. A white ppt.,  $\text{BaSO}_4$ , shows that a sulfid or free sulfur was present in the substance. If the other members of the  $\text{Ag}$  group are absent, pass on to 20.

**14. HYDRIODIC ACID:**—To 2 c.c. of **B** (or of **A** if there is no **B**) add 2 c.c. of  $\text{HNO}_3$ , 3 drops of  $\text{K}_2\text{CrO}_4$  and 1 c.c. of  $\text{CS}_2$ ; bring the last mentioned reagent into contact with every part of the solution by thorough shaking; if ferrocyanid or ferricyanid is present (see below), this shaking should be gentle, in order not to flour the liquid.

**15. HYDROBROMIC ACID:**—(a) *HI was not found in the preceding test*; to the same test add 0.5 c.c. of moderately strong chlorin water, and mix thoroughly by shaking. Too much chlorin may itself color the  $\text{CS}_2$ .

(b) *HI was found in the preceding test*; filter out the colored  $\text{CS}_2$  through a wet filter, add 2 c.c. of the chlorin water, mix well, add 0.5 c.c. of  $\text{CS}_2$  and mix again thoroughly by shaking.

**16. HYDROCYANIC ACID:**—To a small portion of **A** add  $\text{H}_2\text{SO}_4$  till acid, and in the open end of a small glass tube expose a drop of  $(\text{NH}_4)_2\text{S}_x$  to the gas evolved; the tube may be supported by means of a perforated cork that rests in the top of the test tube. After exposure for 15 minutes, evaporate the drop of  $(\text{NH}_4)_2\text{S}_x$  to dryness, on a crucible cover, by a very gentle heat, and moisten the residue with  $\text{FeCl}_3$ .

17. HYDROFERROCYANIC ACID:—Acidify a portion of **B** (or of **A** if there is no **B**) with  $H_2SO_4$  and add a drop of  $FeCl_3$ . In case HI is present the same reaction will, however, be obtained from  $H_3FeCy_6$ . HI acting as a reducing agent would change  $FeCl_3$  to  $FeCl_2$ ; but in any ordinary analysis an iodid and a ferricyanid would rarely be found together.

18. HYDROFERRICYANIC ACID:—Dissolve 1 gm. of iron filings in  $H_2SO_4$ , thus preparing a fresh solution of a ferrous salt, and add a drop of the solution to a portion of **B** (or of **A** if there is no **B**) that has been made acid with  $H_2SO_4$ . It must be observed that even in the absence of ferricyanid a light blue ppt. will be formed if  $H_4FeCy_6$  was found in 17, which will be changed to dark blue on addition of a few drops of  $HNO_3$ . The ferrous solution must be used at once, as it oxidizes rapidly in the air, becoming unfit for use.

For the more difficult separation and identification of ferro- and ferricyanid, when occurring together, see Prescott and Johnson, or Fresenius.

19. HYDROCHLORIC ACID:—If no HI, HBr,  $H_4FeCy_6$  or HCy has been found, and a *white* precipitate was obtained in 12, it can be due to HCl only, and no further test need be made for this acid; the precipitate may be black, owing to the presence of  $H_2S$ , and still contain HCl: in this case treat it with ammonia, filter, and acidify the filtrate with  $HNO_3$ ; a white precipitate indicates HCl.

If HI, HBr,  $H_4FeCy_6$  or HCy has been found make a portion of **B** (or of **A** if there is no **B**) acid with  $HNO_3$ , add  $AgNO_3$ , shake well, decant the liquid, and wash the ppt. twice with water by decantation, and test it as follows:—

(a) *HI only was found.*—Digest the ppt. for a few minutes with  $NH_4OH$ , filter and acidify the filtrate with  $HNO_3$ . A white ppt. shows HCl.

(b) *HBr is present and HCy is absent.*—Add to the ppt. 2 c.c. of  $(NH_4)_2CO_3$ , pass  $CO_2$  through the mixture for a short time and digest, shaking occasionally, for fifteen minutes, filter, and acidify the filtrate with  $HNO_3$ . A white ppt. shows HCl.

(c) *HCy,  $H_4FeCy_6$  or  $H_3FeCy_6$  is present.*—Put the ppt. into a porcelain crucible, dry by gentle heat, ignite to low redness and allow to cool; put a piece of Zn in the crucible in contact with the ppt., add a little  $H_2SO_4$  and allow the action to continue an hour; pour off the liquid, add to it  $AgNO_3$ , and test

the ppt., as directed in (*a*) or (*b*), remembering that in the absence of HI and HBr the formation of a *white* ppt. with  $\text{AgNO}_3$  is a sufficient test for HCl.

**20. NITRIC ACID** :—If **A** contains no chromate, evaporate a drop of it to dryness on a crucible lid, at a very gentle heat, cover the residue with a drop of phenyl-sulfuric acid, warm gently, and allow the action of the reagent to continue five minutes, special care being taken, by tipping the lid this way and that, that every part of the residue is brought into complete contact with the reagent; then add two or three drops of  $\text{NH}_4\text{OH}$ . The yellow color to be looked for may be transient, but more  $\text{NH}_4\text{OH}$  will make it permanent.

If **A** does contain chromate, nearly but not quite neutralize it with HCl, add  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  in slight excess, that is till precipitation is quite complete, filter, evaporate a drop of the filtrate on a crucible lid, then another drop on this residue, wet the last residue with a drop of water, and test with phenyl-sulfuric acid as above. If the solution to be tested is a very dilute one, as a sample of water, several drops may be evaporated one after the other on the same spot.

**21. CHLORIC ACID** :—To the solution colored light blue with indigo solution add a little  $\text{H}_2\text{SO}_4$ , and then, dropwise,  $\text{Na}_2\text{SO}_3$ ; observe whether the color is discharged. The  $\text{H}_2\text{SO}_4$  test should be made, to confirm this result, if affirmative.

No reaction was obtained for organic acids in **5**. Pass on to the silver group, § 87.

**22. ACETIC ACID** :—To a small portion of the aqueous extract of the original substance, or of **A** after neutralization with dilute acid, add 1 c.c. of  $\text{H}_2\text{SO}_4$  and a little alcohol, warm the mixture for a moment, then cool it in a stream of cold water, and observe the odor while shaking the tube gently; to be sure of the reaction, and of not mistaking it for the odor of nitric ether if  $\text{HNO}_3$  should be present, a comparison test should always be made at the same time, with sodium acetate,  $\text{H}_2\text{SO}_4$  and  $\text{C}_2\text{H}_6\text{O}$ , in another tube.

If HCy is present, this test might be dangerous, and only the  $\text{FeCl}_3$  test should be used.

**23. TARTARIC ACID** :—Pass  $\text{H}_2\text{S}$  through the filtrate saved in **6 b**, heat the liquid gently to remove  $\text{NH}_4\text{OH}$ , filter, add about 1 c.c. of strong  $\text{HC}_2\text{H}_3\text{O}_2$ , a volume of  $\text{KC}_2\text{H}_3\text{O}_2$  solution about equal to the volume of the liquid, and a volume of alcohol



about equal to twice the whole, shake well, and allow to stand an hour.

**24. CITRIC ACID:**—Evaporate the filtrate from the final ppt. obtained in **23**, till the  $C_2H_6O$  is removed, and add  $Pb(C_2H_3O_2)_2$ ; if a ppt. appears test its solubility in  $NH_4OH$ .

## CHAPTER X.

### BASIGENS, OR METALS

#### 86. THE SILVER GROUP: *forms of occurrence and reactions.*

SILVER; Ag:—May be met with as metal, alone or in alloys, or as silver salts.

*Reactions:*— $HCl$  ppts. immediately from neutral or acid solutions of silver salts, silver chlorid,  $AgCl$ , flocculent, white, soon darkening in the light, insoluble in hot as well as in cold water, insoluble in dilute acids, soluble in  $NH_4OH$ , as  $(NH_3)_3AgCl$ , from which it is re-precipitated by acids. This ppt. is often so fine that unless flocculated by strong agitation it passes easily through the filter.

$H_2S$  ppts. immediately from all solutions, silver sulfid,  $Ag_2S$ , flocculent, black, insoluble in  $(NH_4)_2S_x$  and dilute acids, soluble in moderately dilute  $HNO_3$ .

LEAD; Pb:—May be met with as metal, alone or in alloys, as insoluble oxids or as lead salts.

*Reactions:*— $HCl$  ppts. from not too dilute, cold solutions of lead salts, lead chlorid,  $PbCl_2$ , pulverulent or crystalline, white, soluble in boiling water, and separating, crystalline, from this solution, on cooling.

$K_2CrO_4$  ppts. from neutral solutions,  $PbCrO_4$ , yellow, slightly soluble in acetic acid, very slightly soluble in  $HNO_3$ , easily soluble in solution of  $KOH$  or  $NaOH$ .

$H_2S$  ppts. immediately from all solutions lead sulfid,  $PbS$ , flocculent, black, insoluble in  $(NH_4)_2S_x$  and in cold dilute acids, soluble in hot moderately dilute  $HNO_3$ ; insoluble, white  $PbSO_4$  is formed if  $HNO_3$  is used to dissolve it.

$H_2SO_4$  ppts. in a short time, and immediately if its volume of

alcohol is added to the liquid, lead sulfate,  $PbSO_4$ , pulverulent, white, less soluble in  $H_2SO_4$  than in pure water.

MERCURY ; Hg :—As mercurous salts.

Reactions :— $HCl$  ppts. immediately from solutions of mercurous salts, mercurous chlorid,  $HgCl$ , pulverulent, white, insoluble in hot as in cold water, and in cold acids, not dissolved by  $NH_4OH$ , but blackened,  $NH_2Hg_2Cl$  being formed.

$H_2S$  ppts. immediately mercurous sulfid,  $Hg_2S$ , flocculent, first white if  $HgNO_3$  was in the solution, then, after long continued action of the  $H_2S$ , black ; this black sulfid is insoluble except in aqua regia, forming then  $HgCl_2$ .

### 87. Preparation and analysis of the silver group precipitate.

#### a. The chemistry of the work on this group.

The members of this group are precipitated as chlorids from a solution made somewhat acid by  $HNO_3$  ; the lead chlorid is separated from the others by making use of its solubility in hot water, and the silver chlorid is then obtained by itself, by means of its solubility in  $NH_4OH$ .

As the grouping work of the course begins thus with the precipitation of its members as chlorids by  $HCl$ , it is evident that if the solution was originally made with this acid it is therefore present in the clear liquid, and no members of the group can also be present unless the acid was concentrated and no water has been added.

Many substances (Prescott and Johnson § 547), are held in solution by an alkaline liquid, the free alkali or the alkaline salt, to which the alkaline reaction of the liquid is due, acting as a chemical solvent (§ 5). New soluble salts are formed, by the production, generally, of feeble acids, in which the metal of the compound dissolved acts as an acidigen, yielding soluble salts with the alkaline base : such salts are decomposed by stronger acids with the reprecipitation of the substance dissolved, which is sometimes redissolved by an excess of the acid, and sometimes not. Hence, by the addition of  $HCl$  to a solution having an alkaline reaction, compounds of elements belonging to other groups may be precipitated together with the chlorids of this group, which, besides perhaps being in the way here, might be

missed where they should be tested for; therefore this test for alkalinity must be made as in 26. Nitric acid will also precipitate these compounds not properly belonging in the HCl precipitate, but only one member of this group, the other two remaining undisturbed, to be thrown down by HCl in the proper manner: the one possibly precipitated, silver, will be found in its place on following out the course of treatment laid down in 26, a.

Since, as above stated, some of the foreign compounds precipitated are redissolved on the addition of acid beyond the point of neutralization, leaving the solution clear and in a proper condition for the HCl precipitation, there should be certainty that enough acid has been added for this purpose, while at the same time any great excess is avoided.

The products of this group precipitation may contain a little antimony oxychloride (§ 89), if much antimony is present; this will not, however, interfere with the examination of the precipitate for this group, nor will this element be missed in Table III, since this precipitation is only partial.

The weak points in the work of this group, which the student should bear in mind, are the imperfect insolubility of the  $\text{PbCl}_2$  in cold water, its rather sparing solubility in hot water, and the slight solubility of  $\text{AgCl}$  in strong HCl or solution of alkaline chlorids.

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*b. Preparation of the silver group precipitate.*

25. If HCl was used in making the solution, and it is clear when cold, or HCl was used, and the solution remains clear when diluted with two or three times its volume of cold water, pass on to § 87 b.

If not clear when cold, as when hot, or after such dilution, proceed as in case a ppt. is obtained in 26 b, below.

26. If the substance is already in solution when received, or is made with water only, test it with litmus paper; if found to be alkaline pass to (a); if acid or neutral, to (b).

(a) *The solution is alkaline.* Add  $\text{HNO}_3$  till acid; if no ppt. forms pass to (b); if a ppt. is formed and does not dissolve on adding more acid, filter, examine the ppt. by § 78, and examine the filtrate as directed in (b).

(b) *The solution is acid or neutral.* Add a few drops of HCl; if no ppt. appears pass to § 89, **b**. If a ppt. is formed continue to add HCl till it no longer increases, shake vigorously, allow the ppt. to settle and decant the liquid through a filter. If much Sb is present in the original substance this ppt. may possibly contain a little  $\text{Sb}_4\text{O}_5\text{Cl}_2$  (see above.) Reserve the *filtrate* for the tin and following groups, § 89, **b**.

**c. Analysis of the Silver Group Precipitate.**

TABLE III.

TABLE III.	
<p><b>27.</b> Wash the precipitate with cold water, by decantation, till the wash water is no longer acid, then boil it with about 10 or 20 c.c. of water, and filter while still boiling hot.</p>	
<b>28. Filtrate.</b>	<b>29. Residue.</b>
<p>To a portion add <math>\text{K}_2\text{CrO}_4</math>. A yellow ppt. or turbidity indicates Pb.</p>	<p>Add about 5 c.c. of <math>\text{NH}_4\text{OH}</math>, shake thoroughly and filter if solution is not complete.</p>
	<b>30. Filtrate.</b>
<p>Acidify with <math>\text{HNO}_3</math>. A white ppt. indicates Ag.</p>	<p>This, if there is any of it, is blackened by the treatment with <math>\text{NH}_4\text{OH}</math>. Hg, as mercurous salt, is indicated.</p>

88. THE TIN GROUP: *forms of occurrence, properties, and reactions.*

GOLD; Au:—To be met with as pure metal or in alloys, and as soluble chlorid.

*Reactions*:—Gold is soluble in aqua regia, forming yellow  $\text{AuCl}_3$ .

$\text{H}_2\text{S}$  ppts. from cold acid solution  $\text{Au}_2\text{S}_3$ , black, from hot solutions  $\text{Au}_2\text{S}$ , brown; both sulfids are slowly soluble in  $(\text{NH}_4)_2\text{S}_x$  as  $(\text{NH}_4)_3\text{AuS}_3$  and repptd. from this solution by acids as  $\text{Au}_2\text{S}_3$ .

$\text{H}_2\text{C}_2\text{O}_4$  especially in presence of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  ppts. from not too acid solutions of gold, metallic gold, brown to violet, very fine powder, which rubbed with a knife on a hard surface shows the color and lustre of gold.

$\text{SnCl}_2$ , to which a little chlorin water has been added to convert a small portion of the stannous to stannic salt, gives in solutions of gold a purple red ppt. or coloration, or sometimes violet or brownish-red (purple of Cassius), insoluble in  $\text{HCl}$ .

PLATINUM; Pt.:—To be met with as metal, alone or in alloys, and as soluble chlorid.

*Reactions*:—Platinum is soluble in aqua regia, forming soluble  $\text{PtCl}_4$ .  $\text{H}_2\text{S}$  ppts. from acid solutions of platinum salts, slowly unless the solution is hot,  $\text{PtS}_2$ , blackish-brown, soluble slowly and with difficulty in  $(\text{NH}_4)_2\text{S}_x$ , and repptd. from this solution by acids.

$\text{SnCl}_2$  reduces platonic salts to platinous salts, which dissolve in  $\text{HCl}$ , giving a deep red color.

ARSENIC; As:—To be met with as, (1) arsenous oxid,  $\text{As}_2\text{O}_3$ , slightly soluble; (2) as sulfids,  $\text{As}_2\text{S}_2$  realgar,  $\text{As}_2\text{S}_3$ , orpiment, or  $\text{As}_2\text{S}_5$ , all insoluble; or (3) in arsenites,  $\text{M}^*_3\text{AsO}_3$  or arsenates  $\text{M}_3\text{AsO}_4$ , both mostly insoluble; or (4) as a gaseous compound with hydrogen,  $\text{AsH}_3$  very poisonous.

*Reactions*:— $\text{H}_2\text{S}$  ppts. from acid solutions immediately arsenous sulfid,  $\text{As}_2\text{S}_3$ , flocculent, light yellow, soluble in  $(\text{NH}_4)_2\text{S}_x$  forming  $(\text{NH}_4)_3\text{AsS}_3$  (variable), and repptd. from this solution by acids as  $\text{As}_2\text{S}_3$ , insoluble in  $\text{HCl}$ , but dissolved by digestion with fully concentrated hydrochloric acid and  $\text{KClO}_3$  (potassium chlorate) forming  $\text{H}_3\text{AsO}_4$ .

With  $\text{Zn}$  and  $\text{H}_2\text{SO}_4$  solutions containing  $\text{As}$  yield arsenous hydride,  $\text{AsH}_3$ , a colorless gas, which conducted into a solution of

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\* M stands for any monad basigen.

$AgNO_3$  causes the separation of *Ag*, black ppt., while the *As* remains in solution as  $H_3AsO_3$ .  $HNO_3$  is also formed, but no  $NO$  as when  $HNO_3$  is itself the oxidizing agent. The oxygen for this oxidation appears to come from the water present.

To make this test, a hydrogen generator is required, consisting of a small flask provided with a two-hole rubber stopper; through one of these holes a funnel-tube passes, and extends nearly to the bottom of the flask; a short tube in the other hole, bent at a right angle, is connected by a rubber tube with the glass delivery tube that conducts the gas evolved in the flask into the solution of  $AgNO_3$ . Put two or three small pieces of granulated zinc into the flask, while holding it in an inclined position, so that the zinc will glide down the side, and not fall directly on the thin bottom, perhaps breaking it; put in also a piece of clean platinum foil, add about 10 c.c. of  $H_2SO_4$ , or so much that the mouth of the funnel tube will be immersed, carry the delivery tube into about 10 c.c. of  $AgNO_3$ , in a test tube, and then add the solution containing the arsenic, or to be tested for arsenic, very slowly. The gas from the generator should never be allowed to escape except through the silver solution, if there is any possibility that arsenic is present.

*Compounds of arsenic, and especially the sulfid, when heated in a bulb of hard glass with a perfectly dry mixture of sodium carbonate and potassium cyanid, are reduced, and the arsenic is volatilized and deposited as a black, lustrous ring on the cooler part of the tube. To make this test, proceed as follows: put a small quantity of the perfectly dry substance in the bulb of the tube, and cover it with a mixture of equal parts of dry  $Na_2CO_3$  and  $KCy$ ; the bulb should be so large, or the quantity of substance taken so small, that the bulb will not be more than half filled. Heat the bulb gently, and with a twisted piece of filter paper wipe out any moisture that may collect on the inner walls of the tube; this drying must be very thoroughly done; now heat the bulb strongly, and for some time if no black deposit appears at once.*

**ANTIMONY; Sb**:—May be met with (1) as metal, alone or in alloys; (2) as insoluble sulfids,  $Sb_2S_3$ , and  $Sb_2S_5$ ; (3) as oxids,  $Sb_4O_6$  and  $Sb_2O_4$ , insoluble, acting feebly acidigenic or basigenic, and  $Sb_2O_5$ , acting only acidigenic and forming mostly insoluble compounds; (4) in combination with  $Cl$  as  $SbCl_3$ , or  $SbCl_5$ ; or (5) in a gaseous compound with hydrogen,  $SbH_3$ .

*Reactions*:—Metallic antimony is oxidized by  $HNO_3$  to

$Sb_2O_4$  and  $Sb_2O_5$ , white, soluble in **HCl** and, when freshly precipitated, in tartaric acid.

$H_2S$  ppts. immediately, from acid solutions containing antimony, antimonous sulfid,  $Sb_2S_3$ , flocculent, orange yellow, soluble in  $(NH_4)_2S_x$  forming  $(NH_4)_3SbS_4$ , and reprecipitated by acids from solution as  $Sb_2S_5$ . Both sulfids are soluble in hot **HCl** forming  $SbCl_3$ .

$H_2O$  added in large quantity to a solution containing  $SbCl_3$  ppts. basic salt or oxychlorid, variable, but mostly  $Sb_4O_5Cl_2$ , pulverulent, soluble in tartaric acid, and converted into antimonous sulfid by  $H_2S$  passed through water in which it is suspended.

*With Zn and  $H_2SO_4$ , in the hydrogen generator, solutions containing antimony yield metallic antimony, deposited as an adherent black coating on platinum foil kept in contact with the zinc; this deposit is insoluble in **HCl**, soluble in  $HNO_3$ ; at the same time that this deposit is formed a part of the antimony yields antimonous hydrid,  $SbH_3$  a colorless gas, which in a solution of  $AgNO_3$  gives  $SbAg_3$  black ppt. The more rapid the evolution of hydrogen, the more Sb is liable to be carried off as  $SbH_3$ .*

**TIN**; **Sn**:—May be met with (1) as metal, alone or in alloys, (2) as insoluble oxids,  $SnO$  or  $SnO_2$ , one acting basigenic, the other basigenic or acidigenic, (3) as insoluble sulfids,  $SnS$  or  $SnS_2$ , and (4) as soluble chlorids,  $SnCl_2$  or  $SnCl_4$ .

*Reactions*:—**HNO<sub>3</sub>** oxidizes tin to  $SnO_2$ , white, which at once forms with the water metastannic acid,  $H_{10}Sn_5O_{15}$ , variable, insoluble in acids. **HCl** dissolves tin as  $SnCl_2$ , soluble.

$H_2S$  ppts. immediately from not too strongly acid solutions containing stannous salts, stannous sulfid,  $SnS$ , flocculent, dark brown, soluble in  $(NH_4)_2S_x$  forming  $(NH_4)_2SnS_3$ , and reprecipitated by acids as  $SnS_2$ . From solutions of stannic salts  $H_2S$  ppts. stannic sulfid  $SnS_2$ , flocculent, white at first, while the stannic salt is in excess, then yellow, soluble in  $(NH_4)_2S_x$  with formation of the same compound as in the solution of  $SnS$ .  $SnS$  and  $SnS_2$  are soluble in hot **HCl**, forming  $SnCl_2$  and  $SnCl_4$ , respectively.

*With Zn and  $H_2SO_4$  solutions containing tin give Sn, gray ppt. deposited mostly on the zinc, and not adhering either to this or to the platinum foil if deposited thereon.*

*$HgCl_2$  gives with solutions of stannous salts, mercurous chlorid,  $HgCl$ , pulverulent, white first and becoming grayish with excess of stannous salt.*

89. *The preparation and analysis of the tin group precipitate.*

a. *The chemistry of the work on this group.*

For the separation of the members of this group from those that follow, use is made of the insolubility of their sulfids in moderately strong hydrochloric acid. Since the sulfids of the metals of the copper group are equally insoluble in acids, both groups are precipitated together by this reagent. The two groups are then separated by means of the solubility of the sulfids of the tin group in  $(\text{NH}_4)_2\text{S}_x$  (ammonium sulfid with excess of sulfur). When this solution is treated with excess of dilute acid, the metals of the tin group are again precipitated as sulfids. Separate and special tests being made in the original solution for gold and platinum, only arsenic, antimony and tin remain to be tested for in this second precipitate. For the separation of these elements use is made of their different behavior with nascent hydrogen, especially in the presence of metallic platinum; the first passes off as a gaseous compound,  $\text{AsH}_3$ , and is taken up by a silver solution; the second is mostly precipitated as an adherent coating on the platinum; the third is precipitated as a loose metallic deposit, or loosely adhering to the zinc; both the second and the third therefore remain in the generator.

In this Table the grouping by sulfids first comes into effect, and so far as it takes place here depends upon the solubility in dilute acid of sulfids of metals to be tested for in the iron and aluminum groups, and the insolubility of those to be precipitated here. But a study of the properties of these sulfids will show that they are more or less soluble in strong mineral acids when hot, and in *aqua regia*; hence, especially as the precipitation must be made in a hot liquid, the directions for the careful preparation of the solution as to its acidity.

Furthermore, since these sulfids are soluble in solutions of the fixed alkaline hydroxids by the formation of oxygen salts of these bases, such as  $\text{K}_3\text{AsO}_3$ , and in solutions of alkaline sulfids forming soluble sulfo-salts (§ 65), and since, if the solution contained free alkali at the start, the first portions of  $\text{H}_2\text{S}$  added would be taken up to form these sulfids of the alkaline metals, acidity in the beginning is also an essential condition. Also, some of these sulfids are not readily precipitated in a neutral solution, as will appear on writing the equation for the precipitation of arsenic or antimony from neutral solutions of salts of the alkaline metals in which they take the part of acidigens.

The fact that  $\text{Sb}_4\text{O}_5\text{Cl}_2$  and  $\text{BiOCl}$ , if precipitated in the course



of the preparation of the solution, may be left undissolved is an interesting illustration of the principle (§ 26 a) that metathesis may sometimes take place between substances when one of them is in the solid condition; that these oxychlorids cannot be allowed to remain as such in the later work of the course will become evident on careful study of the steps that follow, which result in confining antimony to this course and sending bismuth to the next, and comparison of the solubility of these oxychlorids and of the four corresponding sulfids.

The tests for gold and platinum in **36**, Table IV, exhibit a nice distinction between the power of different reducing agents; oxalic acid reduces only the former, while  $\text{SnCl}_2$  reduces both.

In order that the color of the reduced gold may not interfere with the sharpness of the other reaction, it must first be removed. Concentrated HCl serves to dissolve any platinum that might be precipitated in the test for gold, in the presence of the ammonium salt added, as  $2\text{NH}_4\text{Cl.PtCl}_4$ .

The group precipitation must be made in a hot solution as in **33** below, chiefly on account of the possible presence of arsenic salts. Under the reactions of arsenic it will be seen that only  $\text{As}_2\text{S}_3$  is precipitated by  $\text{H}_2\text{S}$  from any solutions containing this element; therefore, if the arsenic is not already in the form of arsenous salts, reduction must take place before precipitation; such reduction by  $\text{H}_2\text{S}$  requires the aid of heat, about  $70^\circ$ , and considerable time, even perhaps twelve to twenty-four hours; previous treatment with a more active reducing agent, as  $\text{H}_2\text{SO}_3$ , greatly shortens the time required for complete precipitation.

Under the reactions for mercuric salts, considered in connection with the first step in sub-grouping taken in § 91 c, will be found another reason for keeping the solution under the influence of  $\text{H}_2\text{S}$  for a considerable time.

The use of yellow ammonium sulfid,  $(\text{NH}_4)_2\text{S}_x$ , in **34**, which is necessary for the separation of members of this group on account of the difficult solubility of tin and antimony sulfids in the normal, colorless  $(\text{NH}_4)_2\text{S}$ , has this disadvantage, that the  $\text{CuS}$  which should pass over to § 91 c, is soluble in it; but this sulfid is almost completely precipitated again on boiling the solution.

The constitution of the compounds formed in this solution of the sulfids is explained in § 65.

In the re-solution by concentrated acid of the sulfids precipitated from the  $(\text{NH}_4)_2\text{S}_x$  solution, as in **37a**, the use of the

strong oxidizing agent,  $\text{KClO}_3$  in presence of  $\text{HCl}$ , is likely to carry at least a portion of the elements combined with the sulfur up to their highest degree of chlorination; this makes more striking the illustration furnished here of the reducing power of nascent hydrogen, all the antimony, tin and arsenic being reduced to the elementary form; then, by further action in the same direction, all of the arsenic and a part of the antimony are carried off as gaseous products in combination with hydrogen.

The sharp separation of arsenic and antimony is a difficult matter; any one of several methods will give satisfactory results, as will this one, as given in **37b**, if carefully executed, but otherwise failure is likely to be encountered. In this method arsenic may possibly remain in its reduced form in the generating flask, or by misfortune in the opposite direction all the antimony may be carried as  $\text{SbH}_3$  out of the generator. By the slower production of hydrogen in the first part of the operation, the deposition of a certain portion of the antimony on the platinum foil is secured, when it will be safely fixed, having passed the nascent state; a subsequent more rapid evolution of gas secures the transfer of at least the largest part of the arsenic to the test-tube.

Tin cannot leave the generator under any conditions.

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*b. Preparation of the group precipitate.*

**32.** Before proceeding further with the analysis the solution must be so prepared that it will be moderately acid with  $\text{HCl}$ , and it is better that it should not contain free  $\text{HNO}_3$  or strong acid of any kind; if the solution was made with water and then acidified with  $\text{HCl}$ , or made with dilute  $\text{HCl}$ , it is already in this condition; pass to **33**. If  $\text{HCl}$  was used for the solution, 6 or 7 parts of water may be added, then pass to **33**. If  $\text{HNO}_3$  was used in preparing the solution, evaporate the liquid nearly to dryness, in the hood, add to the residue 1 c. c. of  $\text{HCl}$  and 10 c. c. of water; if a white ppt. forms on addition of water it probably consists of  $\text{Sb}_4\text{O}_5\text{Cl}_2$  or  $\text{BiOCl}$  (see § 89 *a*).

**33.** Reserve about 5 c. c. of the solution for the tests for gold and platinum, and through the rest of it pass a slow current of

H<sub>2</sub>S for at least 15 minutes, or till no further precipitation is produced by the reagent, or no further change appears in the color of the ppt. For this important group precipitation the liquid must be hot in the beginning; and if the operation requires much time for its completion the liquid should be heated as often as may be necessary to keep it hot; finally, on filtering, the first portions of the filtrate should be heated nearly to boiling, and tested with H<sub>2</sub>S for complete precipitation.

If no ppt. is formed, or only one that is white, very fine and plainly only sulfur, pass on to the iron group, § 93, **b** (see Table II).

If a colored ppt. is formed, filter and wash thoroughly with hot water till a drop of the washings received in a little AgNO<sub>3</sub> in a test tube gives at the most only a slight turbidity. Reserve the *filtrate* for following groups, beginning with the iron group, § 93 **b**. See also Table II.

**34. PRECIPITATE.** Digest a *small* portion in an evaporator with (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>: *if it dissolves completely*, only metals of the Sn group are present in this ppt., and the remainder of it may be used in the analysis for these metals, as directed below (**37 a**); if a residue remains undissolved, metals of the Cu group are also present: in this case pour off the (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> and test it with HCl as in **35**; if no metals of the Sn group are shown to be present, take the remainder of the ppt. to § 91, **b**, for the analysis of the Cu group. If metals of both groups are present, the whole of the ppt. must be treated as above, with (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> and the mixture boiled and filtered. Reserve the insoluble residue for the Cu group.

**35. FILTRATE.** Dilute with 3 or 4 parts of water and acidify with HCl; *if only a fine, white, or faintly yellowish ppt. appears* that remains suspended in the liquid it consists of sulfur from the (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>, and As, Sn, and Sb are absent; pass on to the Cu group. *A colored ppt. that is flocculent*, or becomes so on warming, may contain the sulfids of these metals: filter, rejecting the filtrate, and take the precipitate to Table IV, following.

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*c. Analysis of the Tin Group Precipitate.*

TABLE IV.

**36.** Filter a small portion of the solution, reserved in **33** for this purpose, if not clear, and add to the filtrate 1 c.c. of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and of  $\text{H}_2\text{C}_2\text{O}_4$ , boil and let stand ten minutes; a brown or violet ppt. indicates Au. The result may be confirmed by the other reactions given for this metal.

If Au was found, filter, wash the ppt. with 0.5 c.c. of **HCl** and add  $\text{SnCl}_2$  to this filtrate; a red color shows Pt. If no Au was found add  $\text{SnCl}_2$  directly to a small portion of solution **33**.

**37 (a)** Transfer the ppt. brought from **34** or **35** to an evaporator, add 5 c.c. of fully concentrated hydrochloric acid and warm; if the ppt. does not dissolve remove the lamp, add a small crystal of  $\text{KClO}_3$  and digest till the sulfids are dissolved, or the residue is at least decolorized. Filter if a residue (sulfur) remains, add to the filtrate 5 c.c. of  $\text{FeSO}_4$  and 5 c.c. of  $\text{H}_2\text{SO}_4$ , and proceed as follows.

**(b)** Into the hydrogen generator, described under the reactions of arsenic and prepared for use as there directed, pour this solution very slowly, only a few drops at a time, till all has been added; if before this the zinc is wholly dissolved, lift the cork of the flask for a moment and drop in another piece; be sure that the platinum is in contact with the zinc during the whole operation, which need be continued only for a few minutes after the last portion of the solution has been added.

## CONTENTS OF THE GENERATOR.

## CONTENTS OF THE TEST-TUBE.

## The loose ppt.

**38.** Pour the contents of the generator into a filter, pick out the pieces of zinc, and rinse whatever adheres loosely to them and to the platinum foil into the filter with the jet of the wash bottle, and then with the same jet collect the contents of the filter down into the apex of the cone; when the water has fully drained out, carefully remove the filter from the funnel, tear off that part containing the solid matter, and warm this very gently with about two c.c. of **HCl**, till all action ceases, add about its volume of water to the liquid, filter into a small test tube, and to the filtrate add  $\text{HgCl}_2$ . A white or grayish ppt. shows Sn.

## The fixed ppt.

**39.** If the platinum foil is blackened, and remains black after treatment with **HCl**, antimony is probably present; to confirm the indication wash the residue insoluble in **HCl** in **38**, together with the foil, with water, add a few drops of  $\text{HNO}_3$  and 2 c.c. of tartaric acid, heat nearly to boiling, dilute with an equal volume of water and add to the solution  $\text{H}_2\text{S}$ . An orange ppt. shows Sb. If this ppt. is black, owing to the possible presence of Cu, heat it with two c.c. of tartaric acid for a few minutes, filter, and apply the  $\text{H}_2\text{S}$  test to the filtrate.

**40.** If no black ppt. is formed As and Sb are both absent. If a black ppt. appears, filter, rejecting the ppt., to the filtrate add **HCl** as long as a ppt. is formed, heat just to boiling and filter, pouring the filtrate through the filter a second time to insure complete removal of  $\text{AgCl}$ , and to the filtrate add  $\text{H}_2\text{S}$ . A yellow ppt. shows As. In the presence of a large proportion of Sb, and little As, this ppt. may be so colored by  $\text{Sb}_2\text{S}_3$  that the indication for As is uncertain. In such case collect the ppt. on a filter, wash it down into the apex of the cone, dry it thoroughly in the drying closet, remove it from the filter, and test it for As by heating in the bulb tube with  $\text{Na}_2\text{CO}_3$  and **KCy**.

## THE COPPER GROUP.

90. *Forms of occurrence and reactions.*

COPPER ; Cu :—To be met with as metal, alone or in alloys, as oxids, insoluble, and as copper salts.

*Reactions* :— $H_2S$  ppts. immediately from all solutions containing copper, cupric sulfid,  $CuS$ , flocculent, black, insoluble in cold dilute acids, slightly soluble in  $(NH_4)_2S_x$ , soluble in hot  $HNO_3$  and in  $KCy$  (potassium cyanid) solution.

$NH_4OH$  ppts. immediately cupric hydroxid,  $Cu(OH)_2$  flocculent, greenish-blue, soluble in excess of the precipitant forming a dark blue liquid; the formulas of the double compound of  $NH_3$  and copper salts, causing this blue color, vary with the nature of the acid of the copper salt used, and other conditions.

CADMIUM ; Cd :—To be met with as metal, alone or in alloys, and as cadmium salts.

*Reactions* :— $H_2S$  ppts. immediately from solutions containing cadmium, cadmium sulfid,  $CdS$ , flocculent, yellow, insoluble in cold dilute acids and in  $(NH_4)_2S_x$ , soluble in hot  $HNO_3$ , insoluble in  $KCy$ .

$NH_4OH$  ppts. cadmium hydroxid, flocculent, white, soluble in excess of precipitant.

BISMUTH ; Bi :—To be met with as metal, alone or in alloys, or as bismuth salts.

*Reactions* :— $H_2S$  ppts. immediately from all solutions containing bismuth, bismuth sulfid,  $Bi_2S_3$ , flocculent, black, insoluble in cold dilute acids and in  $(NH_4)_2S_x$ , soluble in hot  $HNO_3$ .

$NH_4OH$  ppts. bismuth hydroxid,  $Bi(OH)_3$ , flocculent, white, insoluble in excess of precipitant, soluble in dilute acids.

$H_2O$  added in large quantity to concentrated solutions containing bismuth and a moderate quantity of  $HCl$  causes the formation of bismuth oxychlorid,  $BiOCl$ , lustrous white, soluble in strong acid.

MERCURY ; Hg :—To be met with as metal, alone or in alloys (amalgams), and as mercurous or mercuric salts.

*Reactions* :— $H_2S$  ppts. immediately from all solutions containing mercuric salts, mercuric sulfid,  $HgS$ , flocculent, black finally when precipitation is complete; color at first may be white, and pass through yellow, orange, and brown to black; if the mercury was originally present as nitrate, long continued action of the  $H_2S$  may be necessary to convert it completely into the black sulfid. The black ppt. is insoluble in  $(NH_4)_2S_x$ , and

is soluble only in aqua regia, forming  $\text{HgCl}_2$ . The lighter colored ppt. consists of compounds of  $\text{HgS}$  with the original salt, the  $\text{HgS}$  predominating more and more as the action of the  $\text{H}_2\text{S}$  is continued.

*$\text{SnCl}_2$  in presence of  $\text{HCl}$  gives mercurous chlorid,  $\text{HgCl}$ , pulverulent, white or gray.* The darker color is due to reduction of some  $\text{HgCl}$  to metal, by the excess of  $\text{SnCl}_2$ .

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**91.** *The preparation and analysis of the copper group precipitate.*

**a.** *The chemistry of the work on this group.*

In the ordinary course of a complete analysis of a substance possibly containing members of all the groups, the members of this group are already separated from those of the other groups, in the residue insoluble in  $(\text{NH}_4)_2\text{S}_x$ , brought from the preparation of the precipitate for the tin group. If, as when working on this group by itself, as in the usual preliminary practice, the original substance is at once examined for this group, or if the substance is known to contain only members of this and following groups, the solution of it is prepared and treated with  $\text{H}_2\text{S}$ , as directed in § 89 **b**, and the members of this group are then obtained in the same form as in the insoluble residue from **34** in that section.

From this precipitate the mercury is separated by the insolubility of its sulfid even in concentrated  $\text{HNO}_3$ . In the solution containing the other members of the group, copper and cadmium are separated from bismuth by the solubility of their hydroxids in  $\text{NH}_4\text{OH}$ , and the copper is finally separated from the cadmium by the insolubility of its sulfid in  $\text{KC}_y$ .

In the ordinary course of a complete analysis of a substance, we have at the opening of this group analysis, sulfids precipitated in **33** and insoluble in  $(\text{NH}_4)_2\text{S}_x$ ; also, possibly, lead from **26 b**, for reasons explained at the close of § 28. By the reagent applied here in the very beginning, the first step in the sub-grouping of the members of this group is effected. The continuance of the red fumes indicates continuance of oxidation of sulfids, and their cessation is evidently, in the simultaneous presence of  $\text{HgS}$  and other black sulfids of this group, the only easily observed indication of the complete solution of

all that can be dissolved by the acid from this mixture of sulfids; incomplete solution might result in missing one or more of the substances to be tested for under 42 to 45, Table V.

For the removal of lead, if still present, in 42, Table V, advantage is taken of a more insoluble precipitate than the chlorid; and if any still escapes precipitation it may be arrested by the  $\text{NH}_4\text{OH}$  added later, so that its troublesome presence in filtrate 43 should never occur with proper care in the previous manipulation.

Because lead may thus be present in the precipitate by  $\text{NH}_4\text{OH}$ , the formation of that precipitate is not of itself sufficient proof of the presence of bismuth.

For copper we have one of those characteristic color tests which might as well be applied in all ordinary cases to the original solution, if, indeed, the presence of this substance is not sufficiently betrayed by the blue or greenish-blue color of that solution, or of the nitric acid solution made in 41.

By the addition of  $\text{KC}_y$  the cuprammonium compound in the deep blue solution, yielded by  $\text{NH}_4\text{OH}$  with the copper, is broken up by the formation of new compounds into which cyanogen enters, the color is destroyed, and we have a solution in which the excess of  $\text{KC}_y$  prevents the formation of  $\text{CuS}$ , and, its color being much lightened, the cadmium precipitate can be more easily distinguished in it.

For bismuth we have a reaction in 45 that is peculiar, in that the precipitate is apparently made by so general a solvent as water; it is due to the tendency of normal salts of bismuth to decompose when added to a large quantity of water, forming basic salts (§ 17). Some of these salts, and especially the oxychlorid, are quite insoluble in water; but as they are readily soluble in acids, the reason for the use of but little acid may be understood, and also, although for another purpose, for the precaution noted in 42 of adding sufficient  $\text{H}_2\text{SO}_4$  in the precipitation of lead; the reason for evaporation to a very small bulk is also indicated, since in the evaporation of an acid solution the free acid is more or less completely expelled.

Since the conditions requisite for the production of this oxychlorid are the presence together of a bismuth salt and  $\text{HCl}$  in certain proportions, and a sufficient degree of concentration of the solution, the precipitate may appear, as well as the similar one,  $\text{Sb}_4\text{O}_5\text{Cl}_2$ , in the group precipitation of the  $\text{Ag}$  group; but only in case of much more caution in adding  $\text{HCl}$  than the

student usually shows ; and, as it is altogether likely that only a part of these metals would be thus precipitated in any case, the occurrence of such a precipitate would do no other harm than to lead to the inference that, having a group precipitate, then certainly one or more of the members of the group ought to be found in it.

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*b. The preparation of the copper group precipitate.*

In the course of a complete analysis of a substance, this precipitate is already prepared. In the case of practice on this group precipitate alone, the precipitate is prepared as described in 32 and 33 under the tin group.



c. *The Analysis of the Copper Group Precipitate.*

TABLE V.

<p><b>41.</b> Heat the precipitate in an evaporator with about 3 c.c. of <math>\text{HNO}_3</math>, with constant stirring and boiling, till red fumes are no longer evolved, add its volume of water to the mixture, and filter.</p>	
<p><b>42.</b> Filtrate.</p>	<p><b>46.</b> Insoluble residue.</p>
<p>Test a small portion for Pb with alcohol and <math>\text{H}_2\text{SO}_4</math> (see reactions of Pb, § 86); if Pb is found treat the whole of the solution with alcohol and <math>\text{H}_2\text{SO}_4</math>, with care to add the acid in excess, that is, more than enough to ppt. the Pb, so as to prevent possible precipitation of Bi, and filter, to remove the Pb. To this filtrate or to the remainder of filtrate <b>41</b>, if Pb is absent, add <math>\text{NH}_4\text{OH}</math> till strongly alkaline. A white ppt. indicates bismuth, but its presence should be confirmed as below. If this ppt. is formed filter.</p>	
<p><b>43.</b> Filtrate.</p>	<p><b>45.</b> Precipitate.</p>
<p>Dissolve in aqua regia, with aid of heat, and add to the solution <math>\text{SnCl}_2</math>. A white or gray ppt. shows Hg present as mercuric salt. Pass on to the iron group, §§ 92 and 93.</p>	
<p>If this filtrate is blue, the presence of Cu is indicated.</p>	
<p><b>44 (a).</b> Copper is absent. To a portion of the solution add <math>(\text{NH}_4)_2\text{S}</math>. A yellow ppt. indicates Cd.</p>	<p><b>44 (b).</b> Copper is present. To a portion of the solution add <math>\text{KCy}</math> till the blue color disappears. Then add <math>(\text{NH}_4)_2\text{S}</math>. A yellow ppt. indicates Cd.</p>
<p>A black ppt. obtained here for Cd may be due to the presence of Pb or Hg; in the latter case because the element was not completely converted into black sulfid in <b>33</b>; filter, wash the ppt., put it with the filter into an evaporator and boil with <math>\text{H}_2\text{SO}_4</math>, filter again and add to the filtrate <math>\text{H}_2\text{S}</math>. A yellow ppt. shows Cd; but if the ppt. is still black, owing to presence of <math>\text{HgS}</math>, it must be boiled with <math>\text{HCl}</math>, which will dissolve the <math>\text{CdS}</math> if present; the solution is then to be diluted, and tested with <math>\text{H}_2\text{S}</math>.</p>	
<p>Dissolve in a little <math>\text{HCl}</math>; evaporate the solution till only a few drops remain; add a little of this solution to a test-tubeful of water. A white ppt. or turbidity indicates Bi. If no insoluble residue in <b>41</b>, pass on to the iron group, §§ 92 and 93.</p>	

## THE IRON GROUP.

92. *Forms of occurrence and reactions.*

NICKEL ; Ni :—To be met with as metal, alone and in alloys, and as nickel salts.

*Reactions* :— $(\text{NH}_4)_2\text{S}$  ppts. from neutral or alkaline solutions nickel sulfid,  $\text{NiS}$ , flocculent, black, insoluble in cold  $\text{HCl}$ , soluble in hot  $\text{HNO}_3$ ; somewhat soluble in excess of the precipitant, giving a brown solution.

$\text{NH}_4\text{OH}$  and  $\text{NaOH}$  ppt. nickelous hydroxid,  $\text{Ni}(\text{OH})_2$ , flocculent, green, soluble in  $\text{NH}_4\text{OH}$ ; it is oxidized by  $\text{Br}$  in presence of  $\text{NaOH}$  to  $\text{Ni}(\text{OH})_3$ ; when this compound, nickelic hydroxid, is boiled with  $\text{NH}_4\text{OH}$  it is reduced, with evolution of nitrogen, to  $\text{Ni}(\text{OH})_2$ , and dissolved.

To the borax bead nickel compounds give a brown color. To make this test, heat the clean loop of the platinum wire in the lamp flame, and then quickly dip it into powdered borax; fuse this mass in the flame, heating gently at first till the effervescence becomes moderate, and finally to redness; if the bead is thin, dip it into the borax again while hot, and fuse again, and repeat till a full oval bead is obtained; then heat it again with a small quantity of the substance to be tested adhering to it, till the bead is clear. If too much substance is taken the bead may be opaque; in such a case break it, and fuse a part of it in a new bead.

COBALT ; Co :—May be met with as metal, and as cobalt salts.

*Reactions* :— $(\text{NH}_4)_2\text{S}$  ppts. from alkaline or neutral solutions cobalt sulfid,  $\text{CoS}$ , flocculent, black, insoluble in cold  $\text{HCl}$ , soluble in hot  $\text{HNO}_3$ ; it is not soluble in excess of  $(\text{NH}_4)_2\text{S}$ .

$\text{NH}_4\text{OH}$  and  $\text{NaOH}$  ppt. cobaltous hydroxid,  $\text{Co}(\text{OH})_2$ , with properties similar to those of nickelous hydroxid; but the corresponding cobaltic hydroxid,  $\text{Co}(\text{OH})_3$ , is not reduced by boiling with  $\text{NH}_4\text{OH}$ .

To the borax bead cobalt compounds give a deep blue color; the test is very delicate.

IRON ; Fe :—To be met with as metal, ferrous and ferric oxids, insoluble, and as ferrous and ferric salts.

*Reactions* :—FERROUS SALTS.  $\text{HNO}_3$  oxidizes ferrous to ferric salts.

$(\text{NH}_4)_2\text{S}$  ppts. immediately from alkaline or neutral solutions ferrous sulfid,  $\text{FeS}$ , flocculent, black, turning grayish on expos-

ure to the air, by oxidation and separation of sulfur, soluble in dilute mineral acids. This oxidation of the sulfid leads to the formation of  $\text{FeSO}_4$ , and finally a basic ferric salt,  $\text{Fe}_2\text{O}(\text{SO}_4)_2$ .

$\text{NH}_4\text{OH}$  and  $\text{NaOH}$  ppt. ferrous hydroxid,  $\text{Fe}(\text{OH})_2$ , dirty green, changing to reddish-brown,  $\text{Fe}(\text{OH})_3$ , on exposure to the air.  $\text{BaCO}_3$  does not ppt. this hydroxid, except from solutions of the sulphate.

$K_4\text{FeCy}_6$  and  $K_3\text{FeCy}_6$  give blue ppts. (see reactions of hydroferrocyanic and hydroferricyanic acids).

$\text{KCyS}$  gives no reaction.

FERRIC SALTS.— $\text{H}_2\text{S}$  reduces ferric to ferrous salts, with separation of sulfur, but in alkaline solutions ppts.  $\text{FeS}$ .

$(\text{NH}_4)_2\text{S}$  ppts. from neutral or alkaline solutions ferrous sulfid,  $\text{FeS}$  (see ferrous reactions), with separation of sulfur.

$\text{NH}_4\text{OH}$  or  $\text{BaCO}_3$  ppts. ferric hydroxid,  $\text{Fe}(\text{OH})_3$ , flocculent, reddish-brown, soluble in acids.

$K_4\text{FeCy}_6$  ppts. from neutral or acid solutions  $\text{Fe}_4(\text{FeCy}_6)_3$  (see hydroferrocyanic acid reactions).  $K_3\text{FeCy}_6$  gives no ppt.

$\text{KCyS}$  gives ferric sulfocyanate,  $\text{Fe}(\text{Cys})_3$ , soluble, deep red; this test is very delicate.

MANGANESE; Mn:—To be met with in alloys, as oxids and as salts of manganese.

Reactions:— $(\text{NH}_4)_2\text{S}$  ppts. from neutral or alkaline solutions manganous sulfid,  $\text{MnS}$ , flocculent, flesh colored, changing to brown on exposure to the air by oxidation, soluble in dilute acids, including  $\text{HC}_2\text{H}_3\text{O}_2$ .

$\text{NH}_4\text{OH}$  ppts. a part of the manganese in a solution as manganous hydroxid, white, turning brown on exposure to the air by oxidation to  $\text{MnOOH}$ . The rest of the manganese, remaining at first in solution as an ammonium salt, is gradually pptd. on standing exposed to the air, as this second hydroxid.

$\text{BaCO}_3$  does not ppt. this hydroxid in the cold except from solutions of  $\text{MnSO}_4$ .

Fused with  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$  compounds of manganese give a dark green color to the fused mass, by formation of sodium manganate,  $\text{Na}_2\text{MnO}_4$ .

ZINC; Zn:—To be met with as metal, as oxid, and as zinc salts.

Reactions:— $(\text{NH}_4)_2\text{S}$  ppts. from neutral or alkaline solutions, zinc sulfid,  $\text{ZnS}$ , white, soluble in cold  $\text{HCl}$ , slightly soluble in  $\text{HC}_2\text{H}_3\text{O}_2$ .

$\text{NH}_4\text{OH}$  ppts. zinc hydroxid,  $\text{Zn}(\text{OH})_2$ , flocculent, white, soluble in excess of precipitant, as  $(\text{NH}_4)_2\text{ZnO}_2$ , reprecipitated on boiling as  $\text{Zn}(\text{OH})_2$ .

$\text{BaCO}_3$  does not ppt. this hydroxid, except from solutions of the sulfate.

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### 93. *Preparation and analysis of the group precipitate.*

#### *a. Chemistry of the work on this group.*

This group precipitate contains also the members of the aluminum group that may be present, precipitated as hydroxids.

The nickel and cobalt are separated from all the other members of both groups by the insolubility of their sulfids, in  $\text{HCl}$  of such dilution as will readily dissolve the other sulfids and the hydroxids. These two sulfids being then dissolved by stronger acid, the metals are separated, if separation is necessary, by the different behavior of their tri-hydroxids with ammonia, after they have been converted into nickelic and cobaltic salts by treatment with bromin.

After the conversion of the iron into a sesquioxid salt by treatment of the group precipitate with  $\text{HNO}_3$ , it is then separated, together with the aluminum and chromium, from the manganese and zinc by precipitation of the three as hydroxids by barium carbonate. This precipitate is used later for the tests for aluminum and chromium.

We bring to this course a rather strongly acid solution charged with  $\text{H}_2\text{S}$ . It contains all the bases of the potassium, calcium, aluminum, and iron groups, and the acids that were combined with these bases originally, except such as would be expelled on the treatment with strong acids, or converted by the reducing  $\text{H}_2\text{S}$  into other forms.

The first operation of the group precipitation, in 47, in the course of analysis following, consists in adding  $\text{NH}_4\text{OH}$  in slight excess for the purpose of saving the  $(\text{NH}_4)_2\text{S}$ , to be added later, from decomposition by the acid present; but even if this were not done, and the  $(\text{NH}_4)_2\text{S}$  were added at once, the final condition of the solution would be the same, namely, decidedly alkaline. The oxalates, phosphates, borates, silicates, and fluorids of the calcium group metals are insoluble in an

alkaline liquid. The possibility is therefore evident of entirely missing metals of that group in their proper place, in the filtrate from the group precipitation for this table, if the solution is made alkaline while these acids are present.

Considering in this course only two of these acids, that are perhaps most likely to be in the way in an ordinary qualitative analysis, one of them is removed at once by gaseous products of its oxidation. The other, not being so easily removed, has to be provided for as in **53 a**. For the course of operations to be followed in case  $H_3BO_3$ , HF, or  $H_2SiO_3$  is also present, the student is referred to larger works, such as Fresenius, or Prescott and Johnson.

Having evaporated the solution and ignited the residue, for the removal of the oxalic acid, ammonium salts are no longer present; but  $NH_4Cl$  is necessary to prevent the precipitation of magnesium as hydroxid, and the consequent danger of missing it in its proper place.

The addition of ammonia here will precipitate a small portion of the members of this group as hydroxids; but a study of the work that follows, and comparison of the solubility of hydroxids and sulfids of the members of this group, will make it clear that these hydroxids cannot be left as such after the treatment with  $(NH_4)_2S$  without leaving the way open to serious errors; that, nevertheless, the precipitate formed by  $NH_4OH$  can be left undissolved indicates another case of metathesis where only one of the reacting substances is in solution.

All of the sulfids precipitated are quite insoluble in  $(NH_4)_2S$  except the  $NiS$ , which is slightly soluble; on this account any unnecessary excess of the reagent should be avoided.

Two of the sulfids,  $FeS$  and  $CoS$ , are liable to be oxidized to sulfate on exposure to the air, or even perhaps by the oxygen dissolved in water (§ 66): washing, as directed in **48** following, serves to avoid the error that one might fall into, if such oxidation were permitted, these sulfates being soluble in water.

In the solution of such portion of the precipitate as is dissolved by  $HCl$ , the iron, in whatever form it was originally, is present now as a ferrous salt: but both for its final test and its precipitation by  $BaCO_3$  in **53 b**, it must be in the ferric form: only those hydroxids corresponding to the so-called sesquioxids, having the general form  $M_2O_3$  in which  $M_2$  represents two atoms of a triad metal, are precipitated by  $BaCO_3$  under the conditions of the

treatment by that reagent: hence the treatment with  $\text{HNO}_3$  in 52, Table VI.

The separation of the  $\text{P}_2\text{O}_5$  from the metals of the calcium group is effected (53 *a*) on the following principle. In the presence of enough of the ferric salt to combine with all the  $\text{P}_2\text{O}_5$  present, forming  $\text{FePO}_4$ , on making the solution exactly neutral, all of this acid will be precipitated, while metals of the second group remain in solution. The exact neutrality is most easily secured by the presence of  $\text{BaCO}_3$ , a portion of which is decomposed by any free acid present, with the formation of a neutral barium salt.

Provision of sufficient ferric salt is secured by its addition till the red precipitate is obtained by ammonia: ferric phosphate is white: as long as there is not enough iron present to satisfy all the  $\text{P}_2\text{O}_5$ , only white  $\text{FePO}_4$  will be precipitated by the  $\text{NH}_4\text{OH}$ ; as soon as there is more than enough, the excess not going down as white phosphate is precipitated as reddish-brown hydroxid.

This condition of the solution having been secured, the neutralization is nearly effected with  $(\text{NH}_4)_2\text{CO}_3$ , to save  $\text{BaCO}_3$ ; but it must be left slightly acid, for any precipitate by excess of  $(\text{NH}_4)_2\text{CO}_3$  might contain metals to be tested for under 54 and following sections; then the  $\text{BaCO}_3$  completes the neutralization for the precipitation of the phosphates, besides doing its other work of throwing down the aluminum, iron, and chromium as trihydroxids.

Here again is an illustration of a metathesis in which one of the substances taking part in the reaction is a solid: and it is not, as in other cases previously noted, necessarily freshly precipitated.

When a liquid is added to a liquid, the two may be at once intimately mixed by agitation, and the conditions are right for the reaction to proceed without further external assistance, the two substances being in intimate contact throughout; but in this treatment with  $\text{BaCO}_3$  the heavy solid soon settles to the bottom after agitation, and the desired reaction can go on directly only at the surface of contact between the particles of the reagent and that part of the solution at the bottom of the flask, and indirectly in the rest of the liquid by the slow process of diffusion. Hence the importance of frequent agitation and considerable time for the full completion of the reaction.

Since, if  $\text{P}_2\text{O}_5$  is present, the metals of the calcium group are

to be tested for in the filtrate from the precipitate by  $\text{BaCO}_3$ , and since for all the work of precipitation of iron, aluminum, and chromium actually done by this reagent a corresponding quantity of  $\text{BaCl}_2$  passes into solution, as will appear on writing out the equation for the reaction, barium cannot of course be tested for in this filtrate. Therefore a small portion of the solution is so prepared in **53 a**, by taking advantage of the solubility of  $\text{Ba}_3(\text{PO}_4)_2$  in acetic acid and the insolubility of the chromate, to get a solution in which barium can be tested for at once. Any part of the precipitate formed in the first part of this operation, and insoluble in acetic acid, would consist of phosphates of iron, aluminum, and chromium.

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*b. Preparation of the iron (and aluminum) group precipitate.*

**46. (a)** Oxalic acid is absent: pass to **47**. **(b)** Oxalic acid is present; add to the solution a little  $\text{HNO}_3$  and evaporate to complete dryness, in the hood, *moisten* the residue with  $\text{HNO}_3$ , dry by gentle heat, and ignite gently; dissolve this residue with a little hot  $\text{HCl}$ , filter if not clear, and add 2 c.c. of  $\text{NH}_4\text{Cl}$  and 25 to 30 c.c. of water.

**47.** Add  $\text{NH}_4\text{OH}$  till slightly alkaline, then whether a ppt. is formed or not add  $(\text{NH}_4)_2\text{S}$  and heat the mixture nearly to boiling. If no ppt. appears pass on to the Ca group, § 97, **b**. If a ppt. does appear, filter and reserve the filtrate for the Ca group, § 97, **b**.

**48. PRECIPITATE.** Wash immediately and very thoroughly with hot water to which a little  $(\text{NH}_4)_2\text{S}$  has been added.

*c. The Analysis of the Iron Group Precipitate.*TABLE VI *a.*

Treat the ppt. either on the filter or after removal from it (see § 58) with 5 to 15 c.c (according to quantity of ppt.) of *dilute* HCl (1 conc. acid to 10 of water), with special care to bring all parts of the ppt. in contact with the acid, by stirring. Filter if necessary, and reserve filtrate for Table VI *b.*

## 49. Residue.

Any residue remaining here should be black; if it is not, it must be treated with more HCl as directed in 48. If black it may consist of NiS and CoS. If the filtrate 47 has a *deep* brown color Ni may safely be put down as present in the substance analyzed.

If the borax bead is colored blue by fusion with a portion of this residue Co is also present; if only a light brown or a nearly colorless bead is obtained Co is absent. If Ni and Co are found by these tests, pass on to Table VI *b.*

If the filtrate 47 is not brown, or if in testing for cobalt with the borax bead the color was so dark a brown owing to the presence of much nickel that the cobalt color might have been masked, proceed as follows.

To the residue 49 in an evaporator, add HCl and a few drops of HNO<sub>3</sub>, boil, in the hood, till the liquid is nearly evaporated, add NaOH till strongly alkaline and then a quantity of bromin solution equal to the volume of the liquid in the dish, boil for a few minutes and filter, rejecting the filtrate; wash the ppt., return it to the evaporator, add NH<sub>4</sub>OH, boil again, and filter if a residue remains.

## 50. Filtrate.

Add H<sub>2</sub>S. A black ppt. indicates Ni.

A mere slight brown coloration may be due to Co, if its presence in considerable quantity is indicated by the bead test.

## 51. Residue.

Test for Co with borax bead.

Pass on to Table VI *b.*



## c. Analysis of the Iron Group Precipitate, concluded.

TABLE VI b.

## 52. Filtrate from Residue 49.

Boil to expel  $H_2S$ , add a few drops of  $HNO_3$  and boil again. To a small portion of this solution add  $NH_4CNS$ . A red color shows Fe. A slight tinge of red is given by very small traces of iron, the test being very delicate.

## 53 a. Phosphate is present.

To a small portion of the solution add  $NH_4OH$  till alkaline, then acetic acid till acid, filter if a ppt. appears, and test the filtrate for Ba with  $K_2Cr_2O_7$  and  $H_2SO_4$ , as in Table VIII. To the remainder of the solution (52) add  $FeCl_3$  till a drop gives a brownish red ppt. with  $NH_4OH$  and proceed as in 53 b, the  $P_2O_5$  being now removed.

## 53 b. Phosphate is not present.

Concentrate the solution to a small bulk, *nearly* neutralize it with  $(NH_4)_2CO_3$ , (if a permanent ppt. forms on addition of  $(NH_4)_2CO_3$ , it must be redissolved with a drop of  $HCl$ ), transfer to a small flask, add about 10 c.c. of  $BaCO_3$ , shake the mixture occasionally, after several hours filter, and *reserve the contents of the filter for the Al group*, Table VIII, after washing two or three times with hot water.

54. FILTRATE. To a portion add acetic acid and then  $H_2S$ . A white ppt., soluble in  $HCl$  shows Zn.

55. Evaporate another small portion carefully to dryness in the platinum cup, and fuse the residue with a mixture of equal parts of  $Na_2CO_3$  and  $KNO_3$ . A bluish-green color in the fused mass shows Mn.

Phosphate was present,

56 a, and Mn and Zn also present.

56 b, and Mn and Zn *not* present.

To the remainder of the filtrate from the ppt. by  $BaCO_3$  in 53 b add  $NH_4OH$  and  $(NH_4)_2S$ , warm and filter; with filtrate pass to 56 c.

There being no Mn or Zn to remove, by  $(NH_4)_2S$  as in 56 a, take remainder of filtrate from ppt. by  $BaCO_3$  in 53 b to 56 c.

## 56 c. Filtrate 56 a (or 53 b).

Add to the filtrate from the ppt. by  $(NH_4)_2S$  in 47, and reserve for § 96 b, remembering in the analysis of the Ca group ppt. that Ba has already been tested for.

## THE ALUMINUM GROUP.

94. *Forms of occurrence and reactions.*

ALUMINUM ; Al:—To be met with as metal and in salts.

*Reactions*:— $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{S}$  or  $\text{BaCO}_3$  *ppts.* aluminum hydroxid,  $\text{Al}(\text{OH})_3$ , flocculent or gelatinous, white, slightly soluble in  $\text{NH}_4\text{OH}$ , soluble in  $\text{NaOH}$  as  $\text{Al}(\text{ONa})_3$ , solution not reprecipitated on boiling, soluble in dilute acids.

CHROMIUM ; Cr:—To be met with as oxid and as salts of chromic oxid, or of chromic acid. The acid is always reduced to the oxid by  $\text{H}_2\text{S}$ .

*Reactions*:— $\text{NH}_4\text{OH}$ ,  $(\text{NH}_4)_2\text{S}$  or  $\text{BaCO}_3$  in solutions of salts of the oxid *ppts.* chromic hydroxid,  $\text{Cr}(\text{OH})_3$  flocculent, green ; the *ppt.* is slightly soluble in excess of  $\text{NH}_4\text{OH}$ , and is soluble in  $\text{NaOH}$  as  $\text{NaOOCr}$ :  $\text{Cr}(\text{OH})_3$  is reprecipitated from this solution on long boiling, more easily in the presence of ammonium salts.

95. *The analysis of the aluminum group precipitate.*a. *The chemistry of the work on this group.*

For the separation of the two metals of this group, advantage is taken of the easy oxidation of chromic oxid compounds to chromic acid compounds, and also of the precipitation of chromic hydroxid on boiling its solution in sodium hydroxid, while aluminum hydroxid is not precipitated under similar conditions. The reactions of chromic acid are very delicate, so that the above oxidation makes it easier to detect the chromium.

The  $\text{Al}(\text{OH})_3$  in the precipitate by  $\text{BaCO}_3$  is dissolved out by  $\text{NaOH}$ , made as it is wanted and in the tube in which it is to do its work, by the action of  $\text{Ba}(\text{OH})_2$  on  $\text{Na}_2\text{CO}_3$ . This solution takes place in accordance with the reactions of aluminum ; the succeeding treatment with  $\text{HCl}$  breaks up the compound,  $\text{Al}(\text{ONa})_3$ , that is in solution, and in this solution now containing no free  $\text{NaOH}$  the precipitation of  $\text{Al}(\text{OH})_3$  takes place by  $\text{NH}_4\text{OH}$  in the usual manner.

Sodium hydroxid, so entirely free from impurities that it will not of itself give a reaction similar to this for aluminum on treatment with  $\text{HCl}$  and  $\text{NH}_4\text{OH}$ , is difficult to make and to keep in good condition ; hence its preparation for this test as wanted,

from materials that are much more easily obtained free from those impurities, such as aluminum compounds or silicate, which would impair the reliability of the test.

*c. The Analysis of the Aluminum Group Precipitate.*

TABLE VII.

<p><b>57 a.</b> Iron was not found in Table VI in more than traces, and phosphate is not present.</p>		<p><b>58.</b> Iron was found in Table VI in more than traces, or phosphate is present.</p>	
<p>Make a preliminary test for Al and Cr as follows: Dissolve a small portion of the precipitate obtained with <math>\text{BaCO}_3</math> in <b>53</b>, in a little HCl, add <math>\text{H}_2\text{SO}_4</math> as long as a ppt. is formed, heat just to boiling, and filter; a slight turbidity in the filtrate will do no harm. To about 3 c.c. of this filtrate, in a 10 cm. test tube, add <math>\text{NH}_4\text{OH}</math> very slowly from a dropping tube, holding the point of the tube close to the surface of the liquid, so that the specifically lighter reagent will fall gently, and float on the solution tested. At the zone of contact between the two liquids there appears:—</p>		<p><b>59 a.</b> Fuse a portion of the ppt. by <math>\text{BaCO}_3</math> in <b>53</b> with about three times its bulk of a mixture of equal parts of <math>\text{Na}_2\text{CO}_3</math> and <math>\text{NaNO}_3</math>, in the platinum cup. The fused mass will usually be yellow if much Cr is present. Extract it with hot water, filter, acidify the filtrate with <math>\text{HC}_2\text{H}_3\text{O}_2</math>, and test for chromic acid with the lead and ammonium acetate mixture, <b>7</b>, § 85, b. A yellow ppt. indicates, as present in the original substance, either in the form of a chromate or of a salt of chromic oxide, Cr.</p> <p><b>59 b.</b> To another portion of the ppt. in an evaporator, add about half a gram of <math>\text{Na}_2\text{CO}_3</math>, a quarter of a gram of <math>\text{Ba}(\text{OH})_2</math>, and 10 c.c. of water, boil and filter, rejecting the ppt.; acidify the filtrate with HCl. To about 2 or 3 c.c. of this solution, in a 10 cm. test tube, add <math>\text{NH}_4\text{OH}</math> slowly from the dropping tube, holding the point of the tube close to the surface of the liquid, so that the specifically lighter reagent will fall gently, and float on the solution to be tested. A flocculent, white ppt. at the zone where the two solutions meet shows Al.</p>	
<p><b>57 b.</b> No precipitate.</p>	<p><b>57 c.</b> A precipitate.</p>		
<p>Even after a few minutes. Al and Cr are absent. Pass to the Ca group.</p>	<p>Treat the rest of the group precipitate as directed under <b>58</b>.</p>		

## THE CALCIUM GROUP.

96. *Forms of occurrence and reactions.*

BARIUM ; Ba :—To be met with as barium salts.

*Reactions* :— $(\text{NH}_4)_2\text{CO}_3$  ppts. from neutral or alkaline solutions barium carbonate,  $\text{BaCO}_3$ , flocculent, afterward pulverulent, or crystalline, white, easily soluble in acids.

$\text{K}_2\text{CrO}_4$  ppts. from acetic acid solutions, if not too dilute and only weakly acidified, barium chromate,  $\text{BaCrO}_4$  yellow, soluble in  $\text{HCl}$ . In order that this precipitation shall be certain, if but little barium is present, it is important that the quantity of free acetic acid be small in comparison with that of the potassium chromate.

$\text{H}_2\text{SO}_4$  ppts. from all solutions, except possibly such as contain but little of the element, and are strongly acid (see reactions of sulphuric acid, § 80), barium sulfate,  $\text{BaSO}_4$ , pulverulent, white, very insoluble.

Soluble phosphates or oxalates ppt. from alkaline solutions the corresponding barium salts.

STRONTIUM ; Sr :—To be met with only as strontium salts.

*Reactions* :— $(\text{NH}_4)_2\text{CO}_3$  ppts. from neutral or alkaline solutions strontium carbonate,  $\text{SrCO}_3$ , resembling  $\text{BaCO}_3$ .

$\text{CaSO}_4$  ppts. slowly from neutral solutions strontium sulfate,  $\text{SrSO}_4$ , pulverulent, white.

$\text{K}_2\text{Cr}_2\text{O}_7$  gives no ppt. in acetic acid solutions.

Soluble phosphates or oxalates ppt. from alkaline solutions the corresponding strontium salts.

CALCIUM ; Ca :—To be met with as oxid or in salts.

*Reactions* :— $(\text{NH}_4)_2\text{CO}_3$  ppts. in neutral or alkaline solutions calcium carbonate,  $\text{CaCO}_3$ , flocculent first, afterward crystalline, white, readily soluble in acids.

$(\text{NH}_4)_2\text{C}_2\text{O}_4$  ppts. from neutral or alkaline solutions calcium oxalate,  $\text{CaC}_2\text{O}_4$ , pulverulent, white, soluble in dilute mineral acids, insoluble in acetic acid.

$\text{K}_2\text{Cr}_2\text{O}_7$  gives no ppt. in acetic acid solutions. Soluble phosphates ppt. from alkaline solutions calcium phosphate  $\text{Ca}_3(\text{PO}_4)_2$ , white.

MAGNESIUM ; Mg :—May be met with as metal, as oxid, or as salts of magnesium.

*Reactions* :— $(\text{NH}_4)_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  do not ppt. magnesium from solutions containing enough  $\text{NH}_4\text{Cl}$ .

$\text{Na}_2\text{HPO}_4$  ppts., often slowly, from solutions made alkaline by

*NH<sub>4</sub>OH*, ammonio-magnesium phosphate, *MgNH<sub>4</sub>PO<sub>4</sub>*, crystalline, white, soluble in acids; it often adheres to the walls of the tube, especially along the lines where the end of a glass rod has been drawn with some pressure; this may not become visible, if the ppt. is abundant, till the contents of the tube are poured out.

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97. *The preparation and analysis of the calcium group precipitate.*

*α. The chemistry of the work.*

The barium is separated from the calcium and the strontium by the greater insolubility of its chromate in acetic acid, the strontium from the calcium by the much greater insolubility of its sulfate in water, and the magnesium from all the others by the formation of a double carbonate of magnesium and ammonium, soluble in solution of ammonium chlorid.

The solution brought to this point, 60 below, contains in addition to the members of the calcium and potassium groups that may have been present in the original substance, a considerable quantity of *NH<sub>4</sub>Cl*, and perhaps other ammonium salts. The presence of this salt is useful, since it lessens the danger of precipitation of *MgCO<sub>3</sub>* by the grouping reagent. On the other hand, all the carbonates which it is desired to precipitate here are slightly soluble in solutions containing *NH<sub>4</sub>Cl*, so that the action of the grouping reagent is thereby rendered more or less imperfect; and it is well in the work of preceding groups to avoid the use of any unnecessary quantity of *HCl*, which must afterward be neutralized with *NH<sub>4</sub>OH* in 47, thus charging the solution excessively with this salt.

The precipitate by *(NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>* being dissolved by acetic acid in 61, Table VIII, it is at once ready for the next step in the separation. The *BaCrO<sub>4</sub>* being slightly soluble in the acid, the separation from strontium and calcium is not perfect if an unnecessary excess of the acid is used in making the solution.

In the separation of strontium from calcium in 63 to 65, Table VIII, we have to deal again with an imperfect action of the reagents used: the *SrSO<sub>4</sub>* is slightly soluble in water and in *HCl*: this is implied by the statement, under the reactions for this element, that it is precipitated *slowly* by *CaSO<sub>4</sub>*. If much water is present, or, in other words, the solution is very dilute, and much more if it is more than weakly acid, and at the same time the conditions are such that only a little *SrSO<sub>4</sub>* can be formed, the salt may remain entirely in solution: the condition

last mentioned would be fulfilled, if but little of either strontium or of  $\text{H}_2\text{SO}_4$  were present:  $\text{CaSO}_4$  is but sparingly soluble in water, and we can have at the most but a very dilute solution of the reagent: therefore the second of these last two conditions is fulfilled. Hence the double reason is plain for the evaporation of the solution as prescribed in **63**, and also for the addition of but little water to the residue. The reason is also plain, from the foregoing, for the direction that the test in **64** be allowed to stand several minutes.

As 1,000 parts of water are required to dissolve one part of  $\text{SrSO}_4$ , and only 400 parts of water for one of  $\text{CaSO}_4$ , while the oxalates are about equally insoluble, and are undistinguishable from each other in appearance, the reason for the treatment with  $\text{K}_2\text{SO}_4$ , much more soluble than  $\text{CaSO}_4$  and therefore yielding a stronger solution of the reagent, is apparent: even if, owing to the concentration of the solution, some  $\text{CaSO}_4$  should also be precipitated, enough would always remain in solution for the final test.

For reasons explained in the foregoing paragraphs, traces of any one of these three metals might be missed in following this scheme of separation: for a method of treatment in such a case the student is referred to Fresenius or Prescott and Johnson.

Either the trace of barium, strontium, or calcium that may remain unprecipitated by the group reagent, as explained above, yielding a *flocculent* precipitate with  $\text{Na}_2\text{HPO}_4$ , in **66**, or the formation of  $\text{Mg}(\text{OH})_2$  by the  $\text{NH}_4\text{OH}$ , owing to an insufficient quantity of  $\text{NH}_4\text{Cl}$  in the solution, may, in case the precipitate for magnesium is slight, make it flocculent instead of crystalline as it should be. By taking advantage of the fact that  $\text{BaSO}_4$  and  $\text{CaC}_2\text{O}_4$  are much more insoluble than the carbonates, a solution can be prepared, if the above-mentioned difficulty is encountered, that is practically free from those metals, although it may still contain traces of strontium. (Fresenius 1880, p. 296.)

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*b. The preparation of the calcium group precipitate.*

**60.** If the filtrate brought from the Fe group (**47**) is brown with Ni in solution, boil and filter again; to this filtrate add  $(\text{NH}_4)_2\text{CO}_3$  as long as a ppt. is formed, and then somewhat more to be sure of an excess of the reagent, and warm. If no ppt. appears, pass to **66**. If a ppt. is formed, filter, and reserve both precipitate and filtrate for Table VIII.

c. *The Analysis of the Calcium Group Precipitate and Filtrate.*

TABLE VIII.

61. Precipitate.		66. Filtrate.	
<p>Dissolve the precipitate, on the filter, by pouring a <i>small</i> quantity of acetic acid over it, two or three times, using the same portion of acid; all of it should be dissolved. To a small portion of the solution add <math>K_2CrO_4</math>; if no precipitate is formed Ba is absent, and the remainder of the solution is used for the Sr and Ca tests.</p> <p>A precipitate is formed: add the reagent to the remainder of the solution, and filter.</p>		<p>Divide in two portions, and reserve the larger one for Table IX. To the other portion add <math>Na_2HPO_4</math> and <math>NH_4OH</math>, draw the end of a glass rod with some pressure over the inner walls of the tube along three or four lines, and set aside for several hours. A white ppt., crystalline if only small in quantity, and in any case adhering along the lines traced by the rod, after the contents of the tube are poured out, indicates Mg.</p>	
62. Precipitate.	63. Filtrate.		
<p>Dissolve this yellow precipitate in HCl, and add to the solution a few drops of <math>H_2SO_4</math>. A white ppt. shows Ba. The white color may not come out plainly till, after allowing the ppt. to settle, the liquid is decanted off, and the ppt. washed with a little water.</p>	<p>Make alkaline with <math>NH_4OH</math> and add <math>(NH_4)_2CO_3</math>. <i>If no ppt. appears</i> Sr and Ca are absent, and this solution need be tested no further. <i>If a ppt. is formed</i> add more <math>(NH_4)_2CO_3</math> till the precipitation is complete, filter, rejecting the filtrate, wash the ppt. with water, dissolve it on the filter with HCl, evaporate the solution almost or quite to dryness, and dissolve the residue in a little water. Divide this solution into two portions.</p>		
	64. Portion 1.	65. Portion 2.	
	<p>Add <math>CaSO_4</math>, heat to boiling, and let stand ten minutes. A fine white ppt. shows Sr.</p>	<p>If Sr was found in portion 1 add <math>K_2SO_4</math>, warm and filter, rejecting the ppt.; to the filtrate, <i>or directly to this portion if Sr is absent</i>, add <math>NH_4OH</math> till alkaline and then <math>(NH_4)_2C_2O_4</math>. A white ppt. shows Ca.</p>	

## THE POTASSIUM GROUP.

98. *Forms of occurrence and reactions.*

POTASSIUM; K:—To be met with commonly only as hydroxid, or as potassium salts.

*Reactions*:—Sodio-cobaltic nitrite,  $(\text{NaNO}_2)_3 \cdot \text{Co}(\text{NO}_2)_3$ , ppts. from neutral solutions containing potassium, potassio-cobaltic nitrite,  $(\text{KNO}_2)_3 \cdot \text{Co}(\text{NO}_2)_3$ , pulverulent, yellow.

SODIUM; Na:—To be met with commonly only as hydroxid and as sodium salts.

*Reactions*:—Compounds of sodium give no ppt. containing that element, which furnishes a satisfactory test for the metal, and is practicable for use by the student.

*Held in the platinum wire loop, in the flame of a Bunsen burner, sodium compounds color the flame yellow.*

This test is so delicate, and sodium is so widely diffused, and common in occurrence, at least in traces, as an impurity in the reagents and other materials of the laboratory, that there is little difficulty in getting this reaction in nearly every substance analyzed. Just before using the wire for the test it should be dipped in HCl and heated in the flame till it gives no color thereto.

AMMONIUM;  $\text{NH}_4$ :—To be met with only as ammonium hydroxid or salts, or as ammonia gas,  $\text{NH}_3$ .

*Reactions*:—*NaOH decomposes ammonium salts, setting free ammonia gas,  $\text{NH}_3$  which colors red litmus paper blue, or yellow turmeric paper brown.*

99. *Chemistry of the analysis of this group.*

**a.** No separation is made of the members of this group from each other, sodium and potassium being tested for in portions of the same residue, and ammonium in a portion of the original substance.

Bringing from the analysis for the calcium group a solution containing much ammonium salts, the first operation performed, preparatory to the analysis for this group, gives us a residue not encumbered with the considerable quantity of ammonium salts in the filtrate from 60, and we can thus get a surer test for sodium. Furthermore, as might be inferred from the great similarity between potassium and ammonium, in all the reactions with which the easy volatility of the salts of the latter does not



interfere, it is necessary to have ammonium salts entirely removed before a reaction with  $(\text{NaNO}_2)_3 \cdot \text{Co}(\text{NO}_2)_3$  can be safely taken to indicate potassium.

*b. Preparation of the substance for the analysis.*

**67.** Evaporate the solution brought from **66** Table VIII to dryness, in the hood, and ignite the residue gently as long as white fumes are given off, to remove ammonium salts.

*c. The Analysis for the Potassium Group.*

TABLE IX.

68 a. Portion 1.	68 b. Portion 2.	69. Original Substance.
<p>Introduce on a platinum wire a small portion of the residue into the flame of a Bunsen burner. If the flame is colored a bright yellow, Na is present.</p> <p>In order to gain any approximate idea of the proportion of Na present, account should be taken of what has already been found in the substance, the quantity of the residue left after the ignition just made, and of the probable proportions of K and Mg in this residue, and finally of the intensity and persistence of the Na flame reaction.</p>	<p>Dissolve the larger portion of the residue in a little water, add to this solution three or four drops of sodio-cobaltic nitrite, and let stand for a few minutes. A yellow ppt. shows K.</p>	<p>To a small portion of this add NaOH and warm gently.</p> <p>If the vapors evolved change moistened turmeric paper from yellow to brown, <math>\text{NH}_4</math> is shown.</p>
<p>If it was necessary to fuse the original substance with <math>\text{Na}_2\text{CO}_3</math> in Table E, in order to get it into solution, prepare a solution for the above tests for Na and K as follows: mix 1 part of the finely pulverized substance with 6 parts of precipitated <math>\text{CaCO}_3</math> and <math>\frac{3}{4}</math> part of <math>\text{NH}_4\text{Cl}</math>, and heat to bright redness in a small platinum crucible for 30 minutes. Cover the crucible with water in a beaker and heat to near boiling for 30 minutes, filter, add a little <math>\text{NH}_4\text{OH}</math> to the filtrate, and proceed further as in <b>60</b>, <b>67</b> and <b>68</b>.</p>		

PART III.  
THE OPERATIONS OF QUANTITATIVE  
ANALYSIS.

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CHAPTER XI.

THE BALANCE AND ITS USE.

100. *Introduction.* Quantitative chemical analysis has for its object the determination of one or more of the constituents of a substance whose qualitative composition is wholly or partially known. It is ultimate analysis when the elementary constituents of the substance are determined, as the carbon and hydrogen of sugar; it is proximate analysis when some or all of the compounds supposed or known to exist in the substance are determined, as the sulfur trioxid of a sulfate, or the calcium oxid in marble, or the sugar and fat in milk.

Its results are obtained by careful measurements, as is the case with all accurate determinations of quantity. From a measured portion of the substance the constituent to be determined is converted into some new form, in which it is capable of measurement, and into which it can be completely transposed, or at least very nearly so. In the quantitative analysis of a solid, or the determination of the substances in a solution, there are two general modes of procedure, called gravimetric and volumetric analysis.

*Gravimetric analysis.* The substance to be determined is usually converted into some compound that is (1) insoluble in the liquid medium in which it is made, (2) has a perfectly definite and well known composition, and (3) is of such a character that it can be finally obtained in a form in which it can be weighed without difficulty. The quantity of the substance sought is then calculated by simple stoichiometric methods.

*Volumetric analysis.* To a solution containing the substance to be determined, a solution is added containing another sub-

stance, that gives with the first a definite reaction; and this addition is made under such conditions that it can be sharply decided when all of the first substance has been acted upon, and just what volume of the solution of the second substance was required to complete the reaction. The strength of this reacting solution being known, and also the exact nature of the chemical change that it produces, so that the same can be expressed by a chemical equation, the quantity of the first substance can be calculated from the quantity of the second substance required.

In setting out with the quantitative analysis of a substance, it must first of all be accurately known how much of it is taken for the analysis. In some laboratories for instruction, it is the practice to give to the beginner carefully measured quantities of a solution of a substance to be determined; in others an indefinite quantity of a solid is given to him, from which he weighs out his own portions for analysis. But even in the first case he very soon has to use the balance to weigh the products of his operations; therefore, weighing on the chemical balance naturally comes up first for explanation.

**101. *The balance.*** When the beam of the balance is swinging, its knife-edges rest on polished agate surfaces; the sharpness of the knife-edges and the polish of the agate must not be impaired, if the balance is to maintain its sensitiveness and accuracy. To be more sure of this preservation of the good condition of the instrument, the knife-edges are always lifted off the agate plates, and kept so all the time when the weighing is not actually going on. The arrangement by which the beam is raised or lowered is controlled by a small, milled-edge wheel on the outside of the balance, in front. The working parts of the balance are inclosed in a glass case not only to protect them from injurious fumes, but also to exclude currents of air that might affect the swinging of the beam, and the indications of the needle as its point moves to and fro over the scale in front of the post.

In order to make this exclusion more complete just when it is most essential, namely, when one is making the last adjustment of the weights so as to exactly counterpoise the object weighed, this final adjustment is effected by means of the rider, that can be placed at any desired position on the right hand arm of the beam, by means of a hook on a rod sliding through a socket, near the top of the end of the balance case; the balance can therefore be entirely closed while this rider is used.

*The weights.* When the equilibrium is established between

substance and weights, this rider gives by its position on the beam, the milligrams and fractions thereof, of the total weight, or what appears in the written expression of the weight as the third and fourth decimals. The number on the beam nearest to the left of the rider gives milligrams (third decimal) and the relative distance between the rider and this number and the next following one indicates tenths of a milligram. The beams of some balances are graduated for milligrams and tenths, of others only to milligrams and halves; in this latter case the tenths must be estimated by the eye.

The brass weights in the weight box give the grams, the number of grams indicated by each weight being stamped on it. The larger weights of foil, of which there are always four, stamped 0.5, 0.2, 0.2, 0.1, or 0.5, 0.2, 0.1, 0.1, give decigrams, expressed by the first decimal, and by the same number and relative denominations of smaller foil weights the centigrams are given, occupying the place of the second decimal in the total weight. In some cases the number of milligrams is stamped on these foil weights, as 500, 200; or 50, 20, and so on.

102. *The proper care and use of the balance.* The strict observance of the following rules and precautions is important.

a. All movements of the beam should be slow, and so moderate in extent that the needle does not swing much beyond the fifth division on either side of the zero mark. No sharp impulse should be given to this movement, either by quick raising of the beam rests, or by making any changes in the weights or on the other pan, while the beam is off its supports, or by touching the beam, while swinging, with the rider hook, or by attempting to move the rider over more than a small portion of one of the divisions. At the moment when the beam is to be actually lifted off the agate plates, the needle should be close to the zero point; this is easily brought about by causing the supports of the beam to follow its movement as it swings towards this position, without allowing them to touch it; then, just as the needle points to zero the beam is lifted easily without any jar.

b. The greatest care should be taken that nothing comes in contact with the substance-pan but clean and dry pieces of apparatus. Of course the weighing may be worthless if anything weighable is detached from the object weighed and left on the pan, if another weighing of the same object is to be made that bears any relation to this first weighing. If the substance so left behind is acid, the pan is liable to be corroded and

seriously damaged. Such a plain precaution as this would seem to be superfluous; but every teacher who has had experience with beginners in quantitative work, has now and then met with an exhibition of such a degree of thoughtlessness, it might almost be called stupidity, in the handling of delicate instruments, as would hardly be supposed possible.

c. Paper should never be used to weigh a substance in. It is more or less hygroscopic, and may therefore itself change in weight during the weighing. For a similar reason, substances that are themselves hygroscopic, or liquids that may lose weight by evaporation, must always be weighed in well closed vessels.

d. Never weigh a piece of apparatus while warm, nor directly after wiping it off; if necessary to wipe it with chamois skin, as may be with a piece of glass apparatus, let it stand in the balance for a few minutes before weighing.

e. Never touch the weights with the fingers, but only with the forceps provided for the purpose. Always use the greatest care to return each weight to its proper place in the box.

f. If the balance is properly adjusted, and the weights on its pans are equal, the needle will stand at zero when the supports are slowly lowered till the beam is free. Also, if the beam is made to vibrate, so that the needle will move, to five divisions to the left for instance, on swinging over to the right side, it will fall a little short of five divisions; on moving back again to the left it will not go quite so far as it did on the right side, and so on till it finally settles at zero when the vibration ceases. In actual weighing, this vibration method is always followed, because much quicker than to wait till the beam comes to rest.

103. It is usually desirable to take approximately a certain quantity of a substance that is to be analyzed; this quantity is sometimes specified in the directions for the determination to be made; when not mentioned, from 300 to 500 mgms. may be considered as a suitable quantity, if the constituent to be determined forms a fairly large proportion of the substance; if, on the other hand, it forms but a very small part, as only a few hundredths of a per cent. for example, a larger quantity of substance must be taken, perhaps as much as four or five grams; in such a case, if a small quantity is taken the error resulting from unavoidable imperfections in the method of analysis, or from want of experience, or both, may be so large in proportion to the amount of the constituent weighed or otherwise measured, at the end of the analysis, as to render the determination of little

value; if the quantity of this constituent carried through all the operations of the analysis is much larger, errors of equal magnitude will count for much less in relation to the quantity of substance determined, and will vitiate the result in a much smaller degree.

On the other hand, unnecessarily large quantities of substance are undesirable, for errors of other kinds may be introduced, and the manipulations may require a longer time. Therefore the quantity of substance to be taken should always be carefully considered on beginning an analysis.

104. When the substance to be weighed is not at all hygroscopic, the following method of weighing out accurately an approximate quantity is convenient. Get the weight of a watch glass; make the sum of the weights on the weight-pan that of the quantity of substance to be taken plus that of the watch glass; turn down the beam-supports till the needle takes a position one or two divisions to the left of zero; then, while holding the beam there, slowly pour the substance from the tube into the watch glass, till the needle swings over to the other side; the glass contains a little more than the quantity desired; proceed now to get the exact weight of the substance in the usual manner.

A hygroscopic substance must be weighed in a weighing tube; the quantity to be taken for the analysis is then to be poured into the vessel in which the first treatment is to be made, and the tube is weighed again. If the hygroscopicity is only moderate, first weigh out the quantity desired, on ordinary scales capable of weighing down to decigrams, pour this quantity into the weighing tube, and mark the space it occupies; then fill the tube to the same mark with a fresh portion of the substance, weigh, empty the entire contents of the tube into the vessel in which the first treatment is to be made, and weigh again.

A convenient pair of weighing tubes is made from two test tubes, one of which will just fit into the other; cut the rim off the smaller tube and draw out the larger one about midway of its length, and seal up and round out the bottom so as to make a tube of about half the length of the other; this serves as a cap that will sufficiently exclude the moisture of the air from the substance within.

Never, unless specially directed to do so, weigh out any particular quantity of a substance, such as exactly one gram or two grams; the last part of such a weighing, consisting, as it must, of abstracting minute quantities of the substance from the con-

tents of the glass on the substance-pan, or adding some of the substance thereto, till the desired weight is obtained, consumes much more time than the usual method, and no important advantage is gained.

For assistance in measuring by the eye approximately the quantity of the substance to be taken, it may be observed that so much of a dry powder of average specific gravity as can be piled on a five-cent piece will weigh from 0.8 to 1.2 grams.

In pouring a substance from the weighing tube into a beaker, hold the latter in an inclined position and pour the substance down the side, so that if the substance is specifically light, and in a fine powder, none of it will be lost; and, finally, tap the tube gently on the rim of the beaker, to dislodge into the beaker any particles adhering loosely to the lip.

**105.** *The operation of weighing.* On seating himself at the balance, the student first ascertains whether its arms are in equilibrium, by setting the beam in oscillation, and observing the swing of the needle; this movement of the beam need not be made to extend beyond five divisions from zero, and can be started easily by dropping the rider on the beam for an instant near the fulcrum; if it does not swing as it should with the arms in equilibrium, that is at a uniformly decreasing rate on each side, raise the beam-supports, and brush off the pans with the camel's hair brush in the balance case; if the equilibrium is not then restored, the attention of the instructor in charge of the balances should be called to the matter; the beginning student must not attempt to correct the fault himself.

When the balance is in order put the object to be weighed on the left-hand pan. If the weight is quite unknown, it is to be settled, first of all, what the largest collection of gram weights is, that is too small. For example, suppose the whole weight is 20.56 grams, and that, being quite sure that it is less than 20 grams, one begins with a 10-gram weight; he will then go on, adding one weight after another, till 19.99 grams is put on the pan before the error in judgment is suspected; ten weights have been taken from the box, only to have to put them back and begin over again. But if one had begun with a 20-gram weight, and then added in succession the 10, 5, 2, and 1 gram weights, finding each one too heavy, it is thus settled that the highest number of whole grams that is too small is 20; having started right with the brass weights, one proceeds in the same way with the decigram foil weights, and then with the centigram weights;

the same number of weights will be handled as in the first case supposed, but this time one has proceeded steadily towards the desired end.

The beam supports must be raised between each change of weights on the pan, but they need be lowered, each time, only far enough to allow the needle to swing out one or two divisions, showing plainly whether the last weight added was too small or too large.

Too great care cannot be exercised in *recording the weights*. In the first place, this record should always be made in the laboratory record book, and *never* on loose slips of paper. Secondly, the reading should be made twice; to this end the student should learn the arrangement of the weights in the box, so that one reading can be made by the vacant places there; the second reading is made on the weights as they are returned from the balance to the box. These two readings, by such different methods effectually check one another. In order that the first method shall be reliable, it is evident that each student using the balance should carefully return every weight to its proper place in the box; there is little danger of any mistake in this respect, except as to the foil weights. Where many are using the same balance, the only safe reading is the second one, that of the figures stamped on each weight.

**106.** When a substance is to be weighed after ignition, which in this case is usually the product of an analysis, this weight is nearly always taken in a crucible or dish of porcelain or platinum. This crucible or dish must always be weighed before it receives the substance; and before being weighed it must be ignited, so that it shall be subjected to the same treatment that is given to it while the substance is ignited in it.

After every such ignition, the vessel, while still warm, is transferred from the platinum-wrapped triangle, which is always used for supporting it on the ring of the lamp-stand, to the desiccator. This transfer, as well as that from the desiccator to the balance-pan, is always to be made with the crucible tongs, never with the fingers.

The desiccator, a shallow, glass jar, with a ground glass cover, contains some powerful absorbent of moisture, as calcium chloride, or sulfuric acid soaked up by pumice stone; in the dry air of this closed jar, the substance can absorb no moisture while cooling. If sulfuric acid is used as the absorbent, there should be no more of it than can be taken up by the pumice stone; if



otherwise, and it stands as a liquid in the bottom of the vessel, a sudden jar, as when the desiccator is set down heavily on the table, or is quickly moved in any way, may cause some of the liquid to spatter up on to the bottom of the crucible; this may then come in contact with the balance-pan, and cause serious damage.

The desiccator should be uncovered only while putting something into it or taking something out.

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## CHAPTER XII.

### MEASUREMENT IN VOLUMETRIC ANALYSIS.

**107.** *The standard of measurement.* In this mode of analysis (§ 100) the quantitative measurements are made partly by weight, and partly by liquid volume. The weighing is confined mostly to the substance taken for the analysis.

In gravimetric analysis, the unit of measurement is the gram; in volumetric work it is partly the gram and partly the cubic centimeter; in the gravimetric method we take such and such a weight of substance, and get such and such a weight of precipitate, the product of the analysis. In the volumetric method we also take a certain weight of substance, for the analysis, but our measurement of the result is made in cubic centimeters, although this is afterwards calculated in weight. In the gravimetric work the gram weight, with its sub-multiples and multiples, answers for all the measurements; but in volumetric work there are many solutions by which we measure, and therefore many analytical values of the cubic centimeter.

It is evident that anything used for a measure must itself have a known value. Some of the solutions used for measuring do their work by oxidizing the substance in solution whose quantity it is desired to measure; others act by neutralizing its acidity or its alkalinity, others by precipitating it out of the solution; the more of the substance to be measured there is in the solution, the larger the volume of the oxidizing, neutralizing, or precipitating solution will be required for the work. We must, then, be able to determine two things with accuracy; how much oxidizing, neutralizing, or precipitating power there is in one

cubic centimeter of the measuring solution ; and, secondly, the exact point at which we have added just enough of the measuring solution to complete the reaction ; this is usually accomplished with the aid of some reagent called the indicator, that gives some sharp color reaction. For the determination of the strength of the measuring solution we must generally use a gravimetric process of some kind.

**108. Standard and normal solutions.** A solution whose strength has been determined for the purpose of volumetric analysis is called a *standard* solution ; when the standard of the solution bears a certain definite relation to the molecular weight of the active agent that it contains, it is called a *normal* solution, which is thus defined: a normal solution is one of which one liter contains a quantity of the substance, expressed in grams, chemically equivalent to one gram of hydrogen.

Volumetric analysis may be divided into three kinds.

a. Analysis by neutralization, or saturation, in which the quantity is measured of a solution of known strength of an acid or a base, that is required to neutralize the unknown quantity of a free base or acid.

b. Analysis by precipitation, in which the quantity is measured of a solution of known precipitating power, that is required to precipitate the unknown quantity of a substance from a solution.

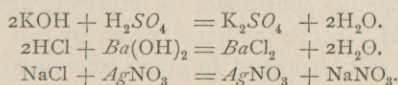
c. Analysis by oxidation or reduction, in which the quantity is measured of the reagent of known oxidizing or reducing power, required to oxidize or reduce the unknown quantity of the substance to be determined in this way.

Standard solutions for use in volumetric analysis are usually solutions of acids, bases or salts ; one important solution contains the elementary substance, iodine, for its active ingredient, and another contains hydrogen peroxide, which do not belong to any of these classes. A standard solution of an acid or a base is used mostly for the determination of free bases or acids in solution ; or an acid may be used for the determination of the basic part of a salt, whereof the acid is one that can be completely and easily expelled, by the acid used, as in the case of carbonates. A standard solution of a salt may be used as a precipitant, either by its basic or its acidic part, or as an oxidizing or reducing agent.

That part of the reagent, of any one of these kinds, which reacts with the substance to be determined is the *active constituent* of the solution. If the reagent is an acid, the acidic part of the

formula of the acid represents the active constituent; if a base, the basic part of the formula represents the active constituent. If the reagent is a salt, and the reaction is the precipitation of some constituent of the solution acted upon, the active constituent of the standard solution is that part of the salt that enters into the precipitate formed. In the same manner, if the action of the standard solution is oxidizing, then that part of the substance in the solution which actually produces the oxidation, whether directly or indirectly, is the active constituent of the solution. If the action is one of reduction, that constituent of the solution which is carried to a higher degree of oxidation or chlorination is the active constituent.

In the following equations, representing reactions of neutralization and precipitation, the active constituent in the reagent, or that part of the reagent containing it, is italicised.



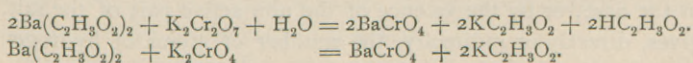
Equations illustrating the action of oxidizing agents will be found further on.

In the formulas of these acids, bases, or *normal* salts, acting as neutralizing or precipitating reagents, the valence of the active constituent, shown by the number of atoms of hydrogen in the acid, replaceable by a metal to form a salt, or of hydroxyl in the base, or by the valence of the non-active part of the salt, gives, directly or indirectly, the number of atoms of hydrogen to which that quantity of the active part of the reagent represented by its molecular weight is equivalent. In  $\text{H}_2\text{SO}_4$ , the acidic and really active constituent is sulfur trioxid,  $\text{SO}_3$ : this can be contained but once in the formula of the acid, hence  $\text{SO}_3$  is equivalent to H taken twice; or, expressed in molecular weight, 80.06 of  $\text{SO}_3$  is equivalent to 2 of H, or 80.06 grams of  $\text{SO}_3$  is equivalent to 2 grams of H. Hence, according to the definition of a normal solution, a liter of a normal solution of  $\text{H}_2\text{SO}_4$  should contain 40.03 grams of  $\text{SO}_3$ ; and the number of grams of  $\text{H}_2\text{SO}_4$  containing this weight of  $\text{SO}_3$  is given by half the molecular weight of  $\text{H}_2\text{SO}_4$ , or 49.03. It is evident, however, that we need not thus resolve the sulfuric acid into its component parts to learn what its ultimate active constituent is, the  $\text{SO}_3$ . The acidigenic part of its formula is the  $\text{SO}_4$ ; it is equivalent to  $\text{H}_2$  in that formula; therefore, we learn directly

that the molecular weight represented by the ordinary formula must be halved to get the figure for the weight of  $H_2SO_4$ , expressed in grams, for a liter of a normal solution. So a liter of a normal solution of  $Ca(OH)_2$  must contain the number of grams expressed by the figure for half its molecular weight: we need not stop to consider that the really active constituent is the  $CaO$ ; that this is equivalent to  $H_2$ ; that its molecular weight must be halved, and, consequently the molecular weight of  $Ca(OH)_2$ ; to consider that  $(OH)_2$  is equivalent to  $H_2$  shows us at once the more direct course that can be taken.

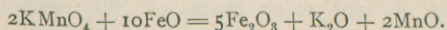
If a normal solution of a salt is to be made for a *precipitant*, consider first whether it is the basic or acid part of the salt that comes into action in the use of the solution. For example, a normal solution of potassium chromate,  $K_2CrO_4$ , is wanted as a precipitant by its chromic acid. The formula of the salt shows that the acidigenic constituent is bivalent, and is therefore equivalent to  $H_2$ ; hence the figure given by half the molecular weight of the salt, expressed in grams, represents the weight of the salt to be taken for a liter of a normal solution.

But the dichromate,  $K_2Cr_2O_7$ , may also be used as a precipitating reagent; this is not a normal salt, and the rule given above applies only to normal salts. The equation for the reaction of this substance, with a barium salt for example, shows that a molecule of it has twice the precipitating power of a molecule of the normal chromate.



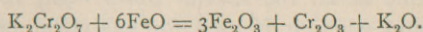
The acidigenic part of this salt in one molecule is therefore equivalent to  $H_4$ .

Passing now to oxidizing agents the same general rule can be applied to them. The following equation represents the oxidizing action of  $KMnO_4$  on ferrous oxid: in order to show more plainly the course of the oxidation, the acid necessary to form salts with the oxids, and to hold them in solution is omitted.



This equation shows that two molecules of the permanganate give up  $O_5$  for oxidizing work:  $O_5$  is equivalent to  $H_{10}$ : or 315.34 grams of  $KMnO_4$  is equivalent to 10 grams of hydrogen; and, calculated in this way, on the basis of the actual working effect of two molecules of the salt, a liter of a normal solution of

it contains 31.5 grams. Likewise, one molecule of potassium dichromate gives up in oxidation three atoms of oxygen, as shown by the following equation, in which also, for greater plainness, the hydrochloric acid, or some other acid necessary to hold the products in solution, is omitted.



$\text{O}_3$  is equivalent to  $\text{H}_6$ : hence the figure expressing grams of  $\text{K}_2\text{Cr}_2\text{O}_7$  in a liter of a normal solution of this salt, when used as an oxidizing agent, is given by one-sixth the weight of a molecule of the salt.

In these cases, therefore, as in those of the neutralizing or the precipitating reagents, the equivalency to hydrogen of the actually working part of the reagent in a molecule of it, is taken as the basis for the calculation in making up normal solutions.

Other standard solutions are used in technical practice, which Mohr calls *empirical* solutions, and of which he gives this example. A standard acid may be so made that it contains in 100 c.c. the quantity of the active constituent required to saturate one gram of pure  $\text{Na}_2\text{CO}_3$ ; then, in assaying a sample of soda ash, exactly one gram is taken, and the number of cubic centimeters required to neutralize the sodium oxid gives, at once, the per cent. of  $\text{Na}_2\text{CO}_3$  in the sample. But this relation of acid required to pure salt in the sample would hold good for sodium carbonate only; another standard acid must be made for potassium carbonate, and another for calcium carbonate, and so on. Such a solution is useful, therefore, only where one substance is to be assayed with it, and by one and the same kind of a reaction.

These definitions and explanations should enable the student to formulate the rule for the calculation of the required weight of substance for any normal solution.

A normal solution of full strength is usually too strong for actual use; it will not measure with sufficient closeness. In order to measure length or weight as closely as we desire, in accurate work with small quantities, we have to use a smaller measure than the meter or the kilogram. In gravimetric work we weigh in grams, and sub-multiples and multiples of the gram. In like manner we reduce our normal solutions to half normal, or one-tenth normal, containing in a liter one-half or one-tenth of the quantity of substance required for a normal solution; such solutions are designated as  $\frac{n}{2}$ ,  $\frac{n}{10}$  and so on.

In the use of these solutions it is better to take such a quantity of the substance for analysis, that not less than about 40 c.c. of the chief standard solution will be required for each determination made with it.

The temperature of any standard solution should be approximately the same at all the several times when its strength is determined, and when it is used for analytical purposes; the temperature of a comfortable room is a convenient one to maintain; therefore, if a solution has been standing so long in a cold room as to have fallen much below this point, it should not be used till it has become warmed to about the right degree.

109. *The special instruments used in volumetric analysis.* These are pipettes, burettes, measuring flasks, and graduated cylinders.

*The pipette* may be simply a graduated tube, showing cubic centimeters and fractions thereof; or it may consist of a short piece of wide tube, connecting two longer pieces of narrow tube, when it is intended to measure only one fixed quantity, as 5, 10, 25 or 50 cubic centimeters: this capacity is indicated by a mark on the stem of the instrument. To use the pipette immerse the point in the liquid to be measured, and with the mouth draw the liquid up till it rises a little above the mark; then quickly close the mouth of the tube with the ball of the index finger, and with the mark on the stem at the level of the eye, looking towards a window or a bright wall, raise the end of the finger just enough to let the liquid flow out slowly, and finally drop by drop, till the lowermost part of the meniscus and the mark on the neck coincide; take off the drop that may adhere to the point by touching it on the side of the glass, and then let the liquid flow out by its own gravity into the vessel destined to receive it, the point of the pipette being held against the side of the glass: then allow the pipette to drain in this position for about a minute.

*The burette*, a long graduated tube, is closed below by a rubber tube about three centimeters long, carrying a short glass jet at its lower end, and a small glass ball within; on grasping the tube around this ball between the ends of the thumb and index finger, and pinching it in such a manner as to draw it out to one side and away from the ball, a passage is opened for the liquid in the burette, and the rate of flow can be easily regulated. The rubber tube should be pushed up on the burette-point till the ball in it is close to the opening of the burette, and the end of the delivery tube in the rubber tube should also be close to

the ball. The size of the ball should be so adapted to the size and elasticity of the rubber tube that, while making a tight closure, still no such effort is required to open it that it cannot be held open as long and as much as may be necessary, without painfully straining the fingers.

The burette is filled at the top through a funnel, till the liquid rises above the zero mark, then the valve below is quickly opened as wide as possible, so that the air in the rubber tube and jet will be completely displaced by the liquid, quite to the point of the jet; the liquid is then allowed to flow out, slowly, till the lower part of the dark zone of the meniscus, or the line on the burette-float if one is used, coincides with the zero line on the burette; the reading of the amount of liquid delivered for any purpose is taken in a similar manner. In delivering a large quantity of liquid at once and rapidly, a minute should be allowed for the walls of the burette to drain before the reading is taken.

*The measuring flask* has a mark on its neck indicating its capacity. It is often used when it is desired to make a certain volume of a solution of a substance, in hand for analysis; aliquot parts of this solution are then taken out with a pipette, for the further treatment. The volume of the whole solution being known, as well as that of each part taken out, the results obtained with each portion can be calculated to the whole amount of substance taken in the beginning for analysis.

*The graduated cylinder.* This is a cylinder of uniform diameter, on a foot, not graduated to less than one cubic centimeter; measurements made with it are not so accurate as with the measuring flask or pipette, because the diameter of the column of liquid where the reading is taken is so much greater.

When the liquid flows from a pipette or burette, *it should leave no streaks on the walls*, showing more adhesion in one place than in another; in such case the readings cannot be accurate. Such irregularity in the flow is caused by dirt of some kind on the glass, usually oily matter; this can be removed most easily by means of a strong oxidizing agent, as chromic acid. Directions will be found in Part V, under the head of reagents, for the preparation of this solution and for its use.

110. *The calibration of graduated instruments.* Successful work in volumetric analysis requires that the instruments used be correctly graduated. The testing of their graduation is called calibration. Not only should the correctness of the several parts

of the burette and the graduated pipette be tested, but also that of the total capacity of each instrument, as the full pipette and the measuring flask, and their relations to one another. To the beginner in quantitative analysis, taking only the course in Part IV of this work, the calibration of his burette, 25 c.c. pipette, and 250 c.c. measuring flask is of most importance.

*Calibration of the burette.* After it has been properly cleaned, fill it to the zero mark with distilled water at a temperature of about  $20^{\circ}$ , run out exactly 10 c.c. into a light weighing flask, previously weighed with a small watch glass over its mouth, and weigh on a balance sensitive to centigrams; nothing is gained by weighing more accurately than this. Run in another 10 c.c. and weigh again, and so on till the lowest 10 c.c. has been weighed. Repeat, and take the average for each 10 c.c.

For the correct scale of reading for this calibration, for 1 c.c. on the burette scale put down in your note book one-tenth of the weight of the first 10 c.c.; for 2 on the burette scale, two-tenths of that weight, for 3, three-tenths, and so on; then when 10 on the burette scale is reached the corrected number will be the same as the weight of the first 10 c.c., if the calculations have been rightly made. Proceeding in the same manner, for 11 on the burette scale, add to the corrected number for 10 c.c. on the burette scale, one-tenth of the weight of the second 10 c.c., and so on. If the deviation for any 10 c.c. is less than 0.05 gram, the graduation of that part of the burette is sufficiently accurate, and no correction need be made.

To calibrate the pipette, weigh its contents, delivered exactly as has been directed (§ 109) into the same weighing flask that was used in the calibration of the burette. Then calibrate the measuring flask by means of this pipette, delivering it ten times filled into the flask, and repeating the operation till results agree closely. If the mark on the neck of the flask does not coincide very nearly with the lowest part of the dark zone of the meniscus at the level of the liquid, when the flask is thus filled, a new mark should be made for this calibration by putting on a short, narrow strip of a gummed label, at the proper place. Now, with the aid of this measuring flask and pipette, one can get exactly one-tenth of the weight of a substance taken for analysis and brought into solution, this solution being made up to 250 c.c. in the flask, or one-tenth of the soluble part of it if not entirely soluble.



III. *Special directions for the use of these graduated instruments.* When it is desired to get a certain volume of a solution of a substance, as 250 c.c. for example, in the measuring flask, and heat can be used with advantage, always treat the substance first in another flask, or in a beaker, with not more than half this volume of the solvent. When the solution is completed, or when carried as far as it can be if the substance is not wholly soluble, with a funnel in the mouth of the measuring flask pour this solution into it, and carefully rinse the flask or beaker into it with distilled water; then pour in more water cautiously almost to the mark on the neck, and finally, holding the flask in a vertical position, with the mark on a level with the eye, let water drop in from a pipette, or a dropping tube, till the mark is reached; close the flask tightly with its glass stopper, or with a soft cork, and mix its contents by repeated inversion. After this, while the solution is being used for the analysis, the flask should be uncorked only while some of its contents is being withdrawn.

If the solution has stood for some time undisturbed, it is well to mix the contents, except when there is some special reason for not doing so, by inverting the flask two or three times, before taking out a portion for analysis. If two or three portions are to be used take all of them out at the same time; if but one is taken, and the pipette is laid on the table while the analysis of that portion is carried through, some of the solution on the point of the pipette will evaporate, leaving a solid deposit there; this cannot be washed off without danger of getting a little water into the pipette; of course the pipette must not be dipped into the liquid in the flask with this deposit still on it, or with water in it.

Always after using a pipette rinse it out, finally with distilled water, and dry it; do the same with a burette when through with the use of it for a particular solution, or when the work must be left for some time. Only when clean and dry are these instruments ready for use.

Never attempt to fill a burette at its mouth otherwise than through a funnel; without this precaution, some of the liquid may flow down on the outside; if it is a solution of any salt the water will evaporate, leaving a deposit on the glass that will obscure the readings; or if a beaker containing a solution to be analyzed should happen to be under the burette, some of the

overflowing solution might drop into it, and the analysis would be ruined.

Always close the mouth of a burette carefully, on leaving a standard solution in it that you expect to use again in a short time; if the work will not be continued within a very few days, it is better to empty the solution out and clean and dry the burette.

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## CHAPTER XIII.

### SEVEN IMPORTANT OPERATIONS OF QUANTITATIVE WORK.

112. Every gravimetric analysis brings into use seven important operations namely, weighing of the substance and the product of the analysis, the preparation of the solution, precipitation of the new compound, filtration, washing of the precipitate, preparation of the same for weighing, usually by ignition, and the calculation of the result.

The first, sixth and seventh operations are peculiar to quantitative analysis; the others are common to both qualitative and quantitative work, and they differ in manipulation in the two cases only in this one respect, but a very important one, that they must be carried through in such a manner as to involve neither loss of any of the substance that is under manipulation, nor the addition of any foreign matter to it that will make it other than the chemically pure product, of definite chemical composition, which the process requires to be weighed, when these manipulations are completed.

The first operation has been fully described (Chap. XI). To what has already been given in Part I concerning the other operations, the following considerations are added as bearing specially on the two conditions emphasized above.

113. *The solution of the substance.* The liquid in which the solution is being made must not be boiled, unless special directions are given to that effect; if boiled, it must be in a beaker covered with a beaker cover, or if in a flask, with the flask turned over on its side and securely supported in that position. If any gas is given off during the solution, as in the treatment of a carbonate with an acid, the beaker must also be covered, and the

reagent causing the effervescence should be added slowly and with constant stirring. The conical Erlenmeyer flask, which can be covered with a small watch glass, is most suitable for such solution. When the solution is completed in such cases as these requiring the covering of the vessel, the cover and the sides of the beaker should be thoroughly rinsed down with distilled water, after the solution is completed. Unless otherwise directed, the volume of the solution when ready for the analysis may well be about 150 c. c., unless otherwise directed, and it should never be strongly acid unless so directed.

114. *The precipitation.* In this operation, two important points are to be looked after: the precipitate must be obtained in the best possible condition for easy filtration and washing, and the precipitation must be beyond all doubt complete. If a Table of the strength of the reagents used is given (see Part V) it is easy to calculate how much of the precipitant will be required in any given case, if the composition of the substance given out for analysis is approximately known, and it is assumed to be a chemically pure substance; the calculated quantity having been added, and then one or two cubic centimeters more, it may be safely considered as sufficient; and yet it is better even in such a case to make the test for complete precipitation, either in the supernatant liquid, partly clarified by the settling of the precipitate, or in a small filtered portion.

The special directions given in many cases for the preparation of the solution, and the management of the precipitation, often have reference to the first condition, and should be closely followed. In general, it may be said that precipitates made in hot solutions, and with the gradual addition of the precipitant, stirring it in as fast as added, and the avoidance of a large excess of the precipitant, will lead to better results than the reverse methods.

115. *The filtration.* If, as is usually the case, the filter on which the precipitate is collected is to be ignited, the filter is burned with it; the filters used in quantitative work leave a small but uniform weight of ash, which is deducted from the total weight of the product. Full directions for fitting the filter have already been given (§ 55); it is much more essential for the attainment of the best results that those directions should be followed in quantitative work. The filter should never be filled to within less than about three millimeters or one-eighth of an inch, of the rim. It is usually best, for rapid and clear filtration,

to have the liquid hot, and to decant off into the filter the supernatant clear or partially clear liquid, before transferring the precipitate.

Occasionally a filtrate from a fine precipitate is at first clear, while the later portions are turbid; therefore in the case of such precipitates it is well to throw out the filtrate from time to time, as long as it is clear; then, if turbidity appears only a small portion instead of the whole has to be re-filtered. The vessel for receiving the filtrate should be perfectly clean at the beginning, so as to be prepared for a second filtration if it becomes necessary.

On proceeding to the filtration, hold a glass rod (with the straight end downwards), against the lip of the beaker, with its end well into the filter, and slowly pour the liquid down this rod, thus preventing it from running under the lip of the beaker; when the filter is full, draw the rod upwards for a little distance, while still in contact with the lip, and the drop of the liquid, with perhaps some of the precipitate suspended in it, that is liable to form under the rod and lip, will be taken off on the rod. If a beaker is nearly full, pouring from it without having some of the liquid run down the side will be very difficult, even with the rod against the lip; this matter of the proper size of the beaker must therefore be thought of before making the precipitation.

The loosening of every particle of the precipitate from the sides of the beaker, and the transfer of these last portions to the filter, are sometimes difficult. A short piece of rubber tube slipping tightly on the end of a glass rod, and projecting just a very little beyond it, is commonly used to loosen a strongly adhering precipitate; or, an eighth of a filter may be folded into a wad, and with a few drops of water in the beaker, rubbed over the surface of the glass, under the end of the rod pressed down on it firmly, and finally dropped into the filter; another eighth of a filter may be used in the same manner, if necessary; this method has the advantage, which is of importance in some cases, that if any of the precipitate adheres strongly to the swab, it is not lost, as it would be if the rubber tube were used.

Sometimes a very fine precipitate, such as barium sulfate, crawls up the sides of the beaker, apparently as fast as it is washed down; in such a case, get as much of it as possible down into the bottom of the beaker with a continuous current from the jet of the wash-bottle; then, holding the beaker between the

thumb on one side, and the second and third fingers on the other, lay the rod across the top, and hold it there with the index finger; all the pouring from the beaker can now be done with this hand; and while the beaker is still inclined over the funnel, a jet of water from the wash-bottle can be directed into it, and all over the sides and bottom, which will immediately flow out into the funnel, carrying with it in this continuous stream all of this fine precipitate; the jet-tube of the wash-bottle being connected with the main tube by rubber, making a flexible joint, by means of the index finger of the hand holding the wash-bottle, pushing the jet-tube upwards, the stream can be directed even against the upper sides of the beaker while still flowing down the rod into the filter.

This transfer of the precipitate is completed only when the inside of the beaker is perfectly clean, the outside being clean also in order that one may plainly see anything adhering to the inner walls.

**116.** *Filtration by suction.* The assistance of suction to hasten filtration is much used in quantitative work. It is applied in two ways, with paper filters, and with asbestos filters.

The paper filter is usually supported by a perforated platinum cone in the throat of the funnel; when the filter is crowded down snugly against this cone, its rim should touch the sides of the funnel at all points of its circumference; if it does not, the opening of the funnel is too wide, and another one should be taken, or the filter should be folded with a wider opening, which is easily done. When the filter is put into the funnel and wetted as described in § 55, special pains must be taken to fit it down against the cone and against the glass above the cone, everywhere from the apex of the cone to the rim of the filter; creases made in the paper in doing this will do no harm; but wherever the paper is not directly backed up by the platinum or the glass, it will probably be torn when the suction is turned on, and some of the substance will pass through. Only slight suction should be used at the beginning of the filtration, and more, later, when the filter is well covered with the precipitate; without care in this regulation of the suction much time may be lost on account of spoiled work. By the use of filters whose points have been dipped in nitric acid of sp. gr. 1.42, and afterwards washed with water till the acid is all removed, the use of the platinum cone can be dispensed with.

When the suction is in use, it should never be turned off

entirely, till first disconnected from the filtering bottle; otherwise the water at the suction-pump, which is commonly attached to the water supply at each student's table, may rush back into the bottle, and the work may be spoiled. Strong bottles or flasks specially made for the purpose must always be used to receive the filtrate: never use an ordinary flask. Flasks of the conical, Erlenmeyer form, with a lateral tube for connection with the suction are now provided, and are very serviceable.

It is advisable to start every paper filtration in filters carefully fitted into the cones, or treated with  $\text{HNO}_3$ , so that suction may be applied later if desirable.

117. *Washing precipitates.* Upon the thoroughness with which the precipitates are washed depends in largest measure the fulfillment of the second requirement for successful work stated in § 112. When the filtration is completed, the precipitate and the filter are saturated with a solution containing all the products of the reaction by which the precipitate was made, as well as, sometimes, other substances that one needed to add to make the precipitation as perfect as possible: and so far as these are not volatile at the temperature of the burning of the filter, they will remain and add to the weight of the product. It must not be forgotten, therefore, that it is the filter as much as the precipitate in it that needs washing.

Hot water, unless proscribed, should always be used for this washing, to save time; the jet should be made to play all over the filter, from as near the rim as possible down, till the contents are covered with water, or till the filter is about two-thirds filled; when all this has drained out, repeat the addition of water; the washing will be sooner completed with several small quantities of water, than with as many larger quantities.

The first spurt of water from the wash-bottle is apt to be so strong as to cause spattering of the precipitate up on the sides of the funnel above the filter; this may be avoided by first filling the whole delivery tube and jet with water, while the jet is pointed in another direction; then, while the tube is full, pinch the rubber tube between the jet and the main tube, direct the jet into the filter, and release the pressure on the rubber tube while the blowing in at the mouth tube is continued. Also, while the delivery tube is thus held full of water, if the wash-bottle is held in a much inclined position with the jet pointing downwards, the delivery tube becomes a siphon by which the water can be run into the filter fast or slow at pleasure, by inclin-

ing the flask more or less; by letting the flow run dropwise on the rim of the filter for a few rounds, that more difficult part of the washing may be facilitated; but this must be done with care in the case of very fine precipitates, lest they begin to crawl up on the glass.

If channels are formed in the precipitate by shrinkage, while it is being washed on the filter, these are to be broken up, most easily by stirring the precipitate with a glass rod. This shrinkage will happen only in the case of somewhat gelatinous or very flocculent precipitates, such as ferric hydroxid, and it is best to wash these largely by decantation before putting them on the filter—pouring considerable water over the precipitate in the beaker, after as much as possible of the liquid in which the precipitation was made has been poured off through the filter, without removing much of the precipitate, stirring it vigorously, pouring this liquid off after partial settling of the precipitate, and repeating the operation several times.

There should be no guess-work as to the question of the completion of the washing of the precipitate; in every case a test should be made from time to time in a cubic centimeter of the washings, for that substance in the solution for which there is the most delicate as well as simple qualitative reaction. If, for instance, we know that the solution contains a chlorid and a nitrate, as the delicate test for the former by silver nitrate is more simple than the very delicate test for the latter, given under nitric acid in § 81, we would use the former test; and when we can no longer get any reaction with silver nitrate in the washings acidified with nitric acid, we can usually assume that, together with the chlorids thus proved to be washed out, nitrates and all other salts are removed. The test may be made in another way, by the evaporation of a drop of the washings to dryness on a clean watch glass; if no residue remains, the washing is complete.

**118.** *The asbestos filter.* For this, instead of a funnel, a large platinum crucible is used (the Gooch crucible) with perforated bottom, or a porcelain crucible without bottom, except a narrow ledge to support a perforated platinum disk (the Caldwell-Gooch crucible). The crucible is put in a funnel with short, perpendicular sides, the upper edge of which is covered with a ring of sheet rubber, in such a manner that as soon as the suction is turned on, and the crucible is pressed down gently, this rubber makes a tight joint between it and the rim of the funnel.

To prepare the filter, while the crucible is pressed down in this

manner and the full force of the suction is turned on, pour on a very little of the asbestos pulp, shaken up with very much water; then pour in a little more, down a glass rod, the end of which is held close to the bottom of the crucible, so as to leave the first coating over the perforated bottom undisturbed; a third or fourth portion may be added; but the layer of asbestos should be no thicker than moderately heavy filter paper, and uniformly distributed over the whole surface; the finer the precipitate to be collected, such as barium sulphate or calcium oxalate, the greater the care that must be bestowed on the preparation of the filter. After it has been properly made, wash it with water poured in on a glass rod the end of which is close to the asbestos, till the washings are clear; the washings must be frequently poured out of the filtering bottle, in order that one may be able to determine when the last washing is free from fibers of asbestos. The crucible and filter is then to be dried and ignited over a low, direct flame, the lamp being held in the hand so that the flame can be made to play evenly and lightly over the whole crucible, and not merely impinge forcibly against the bottom; the drying flame should be applied very gently at first, by moving it in and out, under and around the crucible; the ignition, later, is complete as soon as the bottom of the crucible has reached a dull redness, unless higher heating is specially directed.

When this filter is to be used, first turn on the suction and then put the crucible in its place in the funnel, moisten the filter with a few drops of water, and proceed with the filtration, always having the end of the glass rod well down in the crucible. When the washing is completed the crucible and contents can be dried and ignited in the same manner as directed for the treatment of the filter before the filtration.

This method of filtration is so useful and so widely applicable, especially with the cheaper porcelain crucible, that the student should learn to use it very early in his course. If a thin platinum jacket is made for the crucible, fitting it just a little loosely, the ignition can be made as satisfactorily as in a platinum crucible; and as the platinum can be spun much thinner than would be practicable for a crucible, with this arrangement one can have all the advantages of a platinum Gooch crucible at much less cost. Any worker in platinum can make the jacket. In using it lay two or three long, slender fibers of asbestos in the jacket before putting the crucible into it, to avoid danger



of adhesion between the two if the ignition must be made at a high temperature.

**119.** *Preparation of the precipitate for weighing.* In case the asbestos filter is used it is a very simple matter to prepare the precipitate for weighing, as has already been explained. If the precipitate is collected on paper the operation is less easy.

The precipitate must first be dried for a few hours in the drying chamber provided for this purpose; to this end cover the funnel with a common filter, on which your name and the number of the analysis have been written; this filter must be about a centimeter larger than the funnel, and be folded down tightly over the edge, so that it will stay in place; the moisture will easily escape through the porous paper. To put this cover on so that it will remain in place, set the funnel in the funnel-holder, lay the filter on the edge of the funnel, and hold it in position by pressing it down on this edge with the finger-ends and thumb of one hand; then with the index finger of the other hand fold the edge of the filter down over the edge of the funnel at one point on the circumference, and while holding this fold in place with this finger, with the thumb make the next fold tightly over the first one; move the index finger to this second fold and hold it in place, and at the same time tucking it under a third fold laid over it by the thumb; while doing this, this side of the funnel is gradually moved round and away from the operator; at no time is the pressure of the fingers of the other hand to be released. Each fold is to be drawn down as tightly as possible without tearing the paper.

Meanwhile the crucible is to be ignited and weighed, if this has not already been done (§ 126). In this ignition adjust the height of the crucible above the lamp so that about two-thirds of a flame ten centimeters long will be below the crucible; there should of course be no deposit of carbon from the lamp flame on the crucible: if there is it must be burned off before putting the crucible in the desiccator.

To guard against any possible loss of the precipitate in transferring it to the crucible, the operation is to be performed over glazed paper; this paper should be in four pieces; one (a) about 37 by 50 centimeters, one (b) about 22 by 25 centimeters, and two small pieces, (c, d,) each about 14 by 22 centimeters: these pieces can be cut out of a sheet of the ordinary size. All these pieces should be trimmed smooth at the edges; this

paper should never be on the table except when in actual use for the transfer of the precipitate to the crucible.

Lay the largest piece of paper *a* on the clean, dry table, on that the piece *b*, and on that the piece *c*, and finally on that the crucible. In a place where there are no strong currents of air, touching the filter only on the outside, press and rub it together gently, where the precipitate is, all the time holding it over the glazed paper, and empty as much as possible thereof into the crucible; then carefully open the filter completely; it will be seen that the precipitate is entirely confined to one half of it; with the other half towards you take hold of the rim of it with the thumbs and second fingers of both hands, bring the two quarters of the other half together by means of the index fingers pressing upwards on the outside, and then by a backward and forward motion of the right and left halves of the filter rub the inside surfaces together, and thus loosen as far as possible those portions of the precipitate that still adhere to the paper; change the positions of the index fingers about, so as to rub different parts of the filter together, and then empty it into the crucible; now that as much as possible of the precipitate has been transferred to the crucible, fold in that edge of the filter over which the precipitate was emptied, so that no particles loosely adhering to it shall drop off and be lost in subsequent operations, fold the filter up again as it was originally, roll it up and wind the long piece of platinum wire (in a glass tube handle) about it, as much as may be necessary to keep it together; hold the roll with the closed end downwards directly over the crucible, touch the lower end with the lamp flame, and lower it at once into the crucible; when the burning and glowing have ceased, raise it a little above the crucible and let the flame play on any unconsumed parts, thus burning the filter as completely as possible in this free access of air, before the remains drop out of the wire; a gentle tapping of the wire on the edge of the crucible will then detach any particles adhering to it.

If all this work has been carefully and skillfully done, very little of the precipitate will fall outside of the crucible; set the crucible aside on the other small piece of paper *d*, and gather all visible particles of the precipitate from sheet *a* on to sheet *c* on which the crucible stood; then putting *c* on *a* gather whatever is on *b* on to *c*; then, setting the crucible and the piece it is now on, on *b*, transfer what has been collected on *c* to the crucible. By

conducting the operation in this manner the direct transfer of precipitate to the crucible is always done from a small piece of paper, and more easily than from a large one; and each part of the operation is conducted over a sufficiently large piece of paper so that no particles are likely to get out of sight; if any do not move readily on the glazed paper, they can be pushed along to the edge by means of the platinum wire; this is better than a brush or a feather, for adhesion to either of these is quite as easy as to the paper, if not more so.

Now set the crucible in the platinum-wrapped triangle on the lamp ring, and put the glazed paper away in its drawer. Cover the crucible, and ignite it at first gently and afterwards to full redness, or as much as may be directed in any special case; remove the cover, lay the crucible on its side with its mouth towards one of the twisted arms of the triangle, and the cover partly on this arm and partly on the crucible, and so far down as to leave its mouth about two-thirds uncovered; some access of air is thus provided for the combustion of the small remnant of carbon that usually remains; apply the full heat of the lamp to the bottom of the crucible, this being set high enough so that about two-thirds of the length of the flame is below it. When no further change appears to take place in the contents of the crucible put it in the desiccator to cool.

In a few cases there is no danger of any reduction of the substance to be weighed, by contact with the burning organic matter; then the filter and contents may be put at once into the crucible, and at first gently ignited with the cover on; after the filter is thoroughly charred the ignition is continued in the partly covered crucible, as described above. In other cases the precipitate is so easily reduced that it must receive special treatment after the ignition, to restore it to its normal condition; it is better to collect such precipitates on the asbestos filter.

**120.** *Calculation of the results of the analysis.* In the calculation of these results, two important ideas are specially prominent: first, the product of the analysis, that is weighed, rarely consists of that substance alone for the determination of which the analysis was made, or in the same form in which it existed in the compound subjected to analysis. If, for example, we seek to determine phosphorus in cast iron, we finally weigh it as magnesium ammonium phosphate, a form of combination totally different from that in which it existed in the iron. Secondly, the result is nearly always to be given in percentage, or parts

per hundred parts of the substance analyzed; only by comparing results thus calculated can they be checked against one another, since different quantities of substance are in nearly all cases taken for the several determinations that are made.

In order to be able to make the first part of the calculation, it is essential that the chemical composition of the product of the analysis weighed be accurately known, so that its formula can be written; as one way of verifying this formula, the equation for the reaction by which the precipitation is made should always be written out by the student. Knowing the formula of the substance weighed, the amount of the substance sought is calculated by stoichiometric rules. Make the molecular weight of the product of the analysis, or substance found, the first term of a proportion; the atomic or the molecular weight of the substance sought, according as this substance is elementary or compound, taken as many times as it occurs in the formula of the compound weighed, the second term; the weight of substance found, the third term; the fourth term will be the amount of substance sought, for the determination of which the analysis was made. With this result, and the weight of substance taken for analysis, the percentage of the substance determined in the substance analyzed is calculated.

In the larger works on analytical chemistry, Tables are given for facilitating this calculation, to which the advanced student will usually refer; but the beginner should make it without such aid till he is thoroughly familiar with the methods, and can understand the principles upon which these Tables are constructed.

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## CHAPTER XIV.

### MISCELLANEOUS MATTERS.

121. *The determination of the specific gravity of solutions.* When a solution contains only one substance, the relation between the specific gravity of the solution and the quantity of the substance in it can be determined and put in the form of a Table; this Table can then be used for ascertaining the per cent. of this substance in any solution of it, whose specific gravity is known. A number of such Tables are given in the

larger text-books on analytical chemistry, as well as in many smaller books devoted exclusively to Tables of various kinds. In these Tables, the figure in the column under the formula of the substance in the solution, against any specific gravity figure, gives the number of grams of the chemical substance having that formula, in 100 parts of the solution having that specific gravity. If the substance column is headed  $\text{SO}_3$ , it is the number of grams of sulfur trioxid in 100 parts of the solution of the acid of the specific gravity found; if the substance column is headed  $\text{H}_2\text{SO}_4$ , it is the number of grams of this chemical compound in 100 parts of the acid of the specific gravity found, and so on.

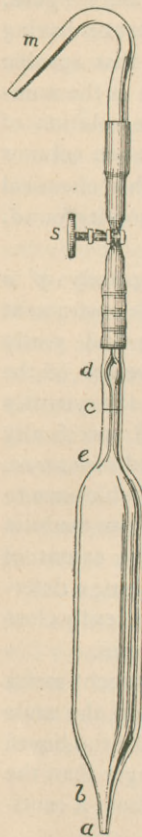
*The approximate determination of the specific gravity of a liquid, by means of the areometer.* The use of this instrument depends upon the principle that a body floating and partly immersed in a liquid displaces exactly its own weight of the liquid. If the liquid is a solution, and increase of the quantity of the substance in the solution makes the liquid specifically heavier, the floating body will not sink so deep, and *vice versa*. The graduated scale on the stem of the instrument enables one to measure the extent of the immersion; this scale being so made as to indicate the specific gravity corresponding to the extent of immersion, we have thus a very quick method of making a determination of the specific gravity of a liquid with sufficiently close approximation to the truth to answer for many purposes.

The reading is taken where the stem of the instrument meets the surface of the liquid. It is well to learn to read the scale before putting the areometer into the liquid. Take the liquid at the temperature of about  $15^\circ \text{C.}$ , in a cylinder longer than the areometer, and with an inner diameter of at least about a centimeter greater than the bulb of the instrument.

**122.** *The accurate determination of the specific gravity of a liquid.* This determination is made by comparing the actual weights of equal volumes of the liquid and of water, at the same temperature. Many forms of apparatus are used for this purpose. The special points to be looked after are, (1) exact equality of volumes of the two liquids weighed, (2) exact equality of their temperatures at the time the volumes were measured, and (3) absolute security against any loss of these measured volumes by evaporation till the weighings are made.

The specific gravity pipette is a convenient instrument for making this determination. In this instrument the volume of

liquid to be weighed is that which will fill the space from the point *a*, to the mark *c* on the stem. The weight of this volume of distilled water is to be determined first: although  $15^{\circ}$  C. is the temperature usually adopted,  $20^{\circ}$  is nearer the ordinary temperature of the room, and is therefore more easily maintained during the manipulation.



*Drying and weighing the pipette.* Remove the rubber tube, lay the pipette in the drying closet, and when it is hot connect it with the air blast. Then weigh it with rubber tube and screw-clamp on, the tube being pushed quite down to the bulb *d* and the clamp being close above the end of the stem of the pipette. This tube should slip easily on the glass tube; if it does not, wet the latter a very little over its whole surface. By the platinum wire loop, which goes with the pipette, hang it on the left arm of the balance, and put a small watch glass on the pan underneath, to protect the pan if any of the liquid should drop from the pipette during the weighing.

*Filling the pipette.* With water: fill a large beaker with tap water, bring its temperature to  $20^{\circ}$ , and suspend in this, by means of a copper wire triangle over the mouth, your smallest beaker, filled with distilled water: as soon as this water has taken the temperature of  $20^{\circ}$  immerse the point of the pipette in it, and with the clamp *s* open just enough, and no more, to admit of suction through the rubber tube, by means of another rubber tube from the tube *m* to the mouth, slowly draw the water up, while seated at the table so that the eye is nearly at the same level with the upper part of the instrument; as the liquid approaches *e* fill very slowly, and at the instant when this space is full close the clamp, the screw of which is all the time held between the thumb and finger of the right hand, while the stem of the pipette above the bulb *d* is held by thumb and finger of the other hand. Screw up the clamp as long as it yields to the pressure, but not any longer; it is easy to break it by screwing unnecessarily tight. Now detach the tube *m*, and with the point of the pipette still in the water, grasp the rubber tube by the part that is on the stem

between the clamp and the bulb, and carefully raise this tube by a somewhat spiral movement, till the liquid is drawn up exactly to the mark  $c$ ; if it is drawn higher the pipette must be emptied, dried, weighed and filled again.

Remove the pipette from the liquid, by a quick movement of the finger around the point take off the adhering drop, and then by further raising of the rubber tube draw the liquid up a little and thus away from the point; now, any slight expansion of the liquid while being weighed will not cause any to drop out, and also the point can be wiped dry without danger of removing any of the liquid. If the clamp was properly closed the contents of the pipette will remain perfectly stationary. If any of the liquid does drop out, before the weighing is completed, or even if a drop collects about the point, the pipette must be emptied, dried and refilled. Duplicate and closely agreeing results must be obtained, both when the pipette is filled with water, and when filled with the liquid whose specific gravity is to be determined.

When the pipette is to be laid aside, slip the rubber tube off, and open the clamp.

This instrument may also be used very conveniently for accurate weighing of small quantities of a liquid. When thus used it must be filled at least up to the stem at  $c$ ; if only partly filled, the liquid is apt to drop out on account of changes in the volume of the air in the upper part of the bulb. The size of the bulb must therefore correspond to the quantity of liquid to be weighed. In emptying the pipette, force out the last drops of the liquid by closing the upper end of the rubber tube on the stem with the thumb and finger, and then quickly compressing the tube just above the stem.

**123.** *The use of platinum ware.* Ignitions are so much more easily, quickly, and satisfactorily made in platinum than in porcelain crucibles, that every student intending to make chemistry his special work should own his own crucibles, and will be expected to procure either these or platinum jackets for the porcelain Gooch crucible.

Platinum is attacked by free chlorine. Therefore it should never be allowed to come in contact with any mixture containing free  $\text{HCl}$  and  $\text{HNO}_3$ , or with any salts of these metals under such conditions that their acids can be set free, as, for instance, in the presence of free  $\text{H}_2\text{SO}_4$ ; nor should any other mixture that can evolve chlorine be allowed to come in contact with the crucible under conditions that make such evolution possible.

At ignition temperatures platinum should not come in contact with any easily fusible metal, or with any mixture of a salt of such a metal and a reducing agent.

After a platinum dish or crucible has been used for an ignition, the outside should be polished down by rubbing with sea sand on the moistened fingers till the surface is bright. If by this treatment the surface of the platinum is scratched, the sand is not suitable for this use, its grains not being sufficiently rounded by attrition.

**124.** *The quantitative note book.* This book is to be provided by the student for recording all the notes of the work done in the quantitative laboratory. In it are to be made the original entries of the results of the qualitative analysis of the substance, if such analysis is required; a brief statement of the method of determination followed; answers to the questions on the method, if such are given out; all the figures of the weighings, or the volumetric readings; and the calculations and results. In short, it is required, in the author's laboratory, that a full and orderly record of every analysis shall be given in this book, ready for inspection at any time. The manner in which it is desired that these records shall be entered is illustrated below.

Before beginning the actual work of the analysis, the written questions are to be answered, if any are issued. The student is not prepared to make a successful quantitative determination till he understands the reason for every step in the work and every precaution mentioned; hence this requirement. When, as in more advanced work, questions are not given, he should still study the directions no less carefully, and work out the equation for every unfamiliar reaction.

The beginner in this work will find the needed information for the answers to the questions under the description of each determination, or in Part II on qualitative analysis. The more advanced students will need to consult the larger works in the chemical library, such as those of Fresenius. In his quantitative analysis, that author describes the properties of the products of the determinations under the running title "Forms;" the manner of making the determinations under the title "Determination;" and under the title "Separation," the special methods of separating the substances from one another, when present together in a mixture or compound, preparatory to their determination. Answers to questions or inquiries, not indicated under any of these heads, must be sought for in other works of reference in the library.



This note book is the property of the student. If neatly and honestly kept, and for the time given to the practice showing a large amount of work, with good results and few errors, and full, intelligent and carefully written notes and references on the work, it may be more useful than any letter of recommendation, by the evidence it gives of the actual quantity, kind, and quality of the work accomplished as a student.

125. *Sample pages of records of a gravimetric determination.*

SUBSTANCE NO. 10 (magnesium carbonate).

Received March 15th, 1890.

Qualitative Analysis (if called for).

Found:                      Mg.                      Co<sub>2</sub>.

Quantitative Analysis.

Determination of Mg:

Method:

(Give here all references consulted.)

Answers to questions (if called for, or suggested by the work).

1.

2. Etc.

	Mg; Det. 1.	Det. 2.
Vial + s,	5.6643	
Less s,	4.8231	
	.8412	
Subst.		
Cr + ppt.	16.8794	
Cr.	16.2486	
	.6308	
Ppt.		
Less ash,	.0006	
	.6302	

Calculation of results:

	Det. 1.	Det. 2.
$Mg_2P_2O_7 : 2Mg = .6302 : x$		
$222.6 : 48.6 = .6302 : x$		
$x \times 100$		
$\frac{\quad}{.8412} = \text{Per cent. Mg.}$		

(Work the above calculations out by logarithms, putting all the figures down here.)

*A volumetric determination; iron by dichromate.*

The record should be about as follows, with such modifications as may be necessary in individual cases.

Give first all the preliminary matter as indicated at the head of the preceding page.

Det. 1.	Det. 2.
Vial + s,	6.7304
“ less s,	5.8613
	.8691
Subst.,	.8691
St. sol. required,	15.6 c.c.
1 c.c. =	0.01713 gm. Fe.
	$15.6 \times 0.01713 \times 100$
	= per cent. Fe.
	.8691

(Work this out by logarithms, giving all the figures here.)

If two or more constituents of a substance are determined, making a complete analysis, sum up the work as follows:—

Summary of results on feldspar.

	I.	II.	III.
Al <sub>2</sub> O <sub>3</sub> . . . . .	64.13	64.25	
K <sub>2</sub> O . . . . .	18.40	18.21	18.56
SiO <sub>2</sub> . . . . .	16.91	16.80	
	99.44	99.26	

**126. *Miscellaneous maxims.*** The best economy of time is secured by doing the work as carefully as possible, from first to last. All analytical processes are affected more or less by conditions beyond control, none of them being absolutely perfect. The strict observance of all known rules and precautions is therefore the more essential for the best success in the work. The student who values his time cannot afford to disregard a single one of the general directions and precautions for the management of his work, given in the preceding pages, or of the special directions and precautions given in the description of each determination. Repetition of work made necessary by poor results hastily obtained consumes more time than is required to do the work carefully in the first instance, and, moreover, makes the record poor.

Be always on the watch to exclude from the work in hand, in all its stages, the accidental addition to it of any substance, solid or in solution, that does not belong there, or the loss of any of the substance to be weighed or measured.

Make duplicates of every determination, and further repetitions if results do not agree on the first two. A single determination is of little value till confirmed by another giving practically the same result. In the case of every analysis undertaken, the student should consider that he is to learn for himself, as correctly as he can, what the actual proportion is in the substance of the constituent that he is called upon to determine, or the actual composition of the substance as a whole if that is required, before making any report. This knowledge he has not gained if the results that he has obtained are discordant.

Many students make the mistake in this matter of supposing that if the first two determinations do not agree sufficiently well, another two must be made, and then perhaps even another two. An analytical method is worth little if only by carrying through two analyses simultaneously, concordant results can be obtained. The right course is this: the first two determinations do not agree; if the work has been done with reasonable care one of them is probably correct; make one more determination to ascertain which one of the first two is correct. But if the first two results and this third are all widely apart and otherwise incorrect, it is fair to presume that the student is working carelessly, and that he must reform his ways of working in general, paying more scrupulous attention to the general directions for quantitative work in Part III of the text-book, or to the special directions given for each determination. After reading this matter over again, carefully, he may as well begin anew on the analysis that has made him so much trouble.

Be orderly, and scrupulously clean. There is no excuse whatever for slovenliness and disorder in respect to apparatus or work-table. Better work can surely be done under a neat and orderly system than otherwise.

Avoid use of unnecessarily large quantities of reagents. Avoid the use of unnecessarily large beakers or flasks; when precipitates are to be filtered from them, the larger the vessel the larger the surface to be washed in transferring the precipitates to the filter.

Be sure that your solution is of about the right degree of concentration before beginning any operation with it; it may be too late after reagents are added.

Without careful planning of the work, very much time is easily spent in accomplishing but little. In estimating the capacity of a student in the laboratory, account must be taken

of the amount of work done, as well as of its quality. Celerity is important, as well as accuracy, in all kinds of laboratory practice. Always keep as many determinations in progress as you can without confusion, so that you will be busily occupied with some manipulation or study in connection with your work, either that in hand or that to come, during all your laboratory time. A slow filtration will not go on any more rapidly for your watching it. Ignite and weigh your crucibles in any moments of leisure; then, kept in the desiccators, they will be ready for use just when wanted, and you will not be obliged to wait for your turn at the balance before you can go on with the work at your own table.

## PART IV.

### EXAMPLES FOR PRACTICE IN QUANTITATIVE ANALYSIS.

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#### CHAPTER XV.

##### THE DETERMINATION OF IRON AND OF SULFUR TRIOXID.

###### 127. *The determination of iron.*

*The gravimetric method.* In the gravimetric determination of iron, it is nearly always weighed as ferric oxid, after precipitation as ferric hydroxid.

Iron may be precipitated from its solutions as ferrous or as ferric hydroxid, according to its state of oxidation in the solution precipitated. Ferrous compounds in solution, or in the solid form and freshly precipitated, tend to pass rapidly into ferric compounds on exposure to the air; solutions of the chlorid oxidize more rapidly than those of the sulfate. The ferric compounds are much more stable than the ferrous compounds, and they are therefore better adapted for quantitative precipitation.

Ferric hydroxid,  $\text{Fe}(\text{OH})_3$ , is insoluble in water and in dilute solutions of alkaline hydroxids or of ammonium salts, easily soluble in acids. If precipitated with the alkaline hydroxid, not in excess, a basic salt (§ 17) is obtained; if, on the other hand, the alkali is in excess, some of it adheres to the precipitate with great tenacity, and is difficult to remove unless volatile.

On ignition the hydroxid is converted to oxid; if only superficially dried before the ignition, there may be loss of particles of the substance thrown out of the crucible by the sudden formation of steam from the inclosed moisture.

Ferric chlorid, volatile at the temperature of the ignition, can

be formed by reaction between ferric hydroxid and ammonium chlorid.

Ignited ferric oxid is not easily soluble in acids.

*The operation.* To the solution, not less than about 200 c. c. in volume, better in a porcelain dish than in a beaker, add  $\text{NH}_4\text{OH}$  in small excess, heat almost to boiling, let settle, decant into the filter, add boiling water, and stir well; let settle and decant again; wash in this way two or three times, then transfer the whole of the precipitate to the filter, and wash with hot water. Dry it thoroughly before ignition.

Give the results as Fe.

128. *The volumetric method.* The ready passage of iron from one state of oxidation or chlorination to the other, and the delicate qualitative tests that can be used to show when this conversion is complete, combine to provide several very satisfactory volumetric methods for the determination of this element. The permanganate method and the dichromate method are more commonly used; in both of these the iron is first completely transformed by reducing agents into the ferrous condition, and it is then ascertained how much of a standard solution of the oxidizing agent is required to convert it to the ferric condition. If permanganate is used, the highly colored oxidizing agent itself is its own indicator, a single drop of it perceptibly coloring a large quantity of solution, while the products of its decomposition when reduced and held in solution are nearly colorless. The only objection to this method is its unreliability in solutions containing  $\text{HCl}$ ; a reaction takes place between the  $\text{HCl}$  and the  $\text{KMnO}_4$ , by which chlorin is set free, the manganese compound being changed to manganous chlorid; although chlorin should ordinarily chlorinate ferrous salt to the ferric condition, it will not readily in so dilute a solution of the iron salt as must be used in this process.

Since  $\text{HCl}$  is a much more convenient solvent of iron ores than  $\text{H}_2\text{SO}_4$ , the dichromate method, in which the presence of even a large excess of this acid does no harm, is the better one for general purposes.

In this method the reducing agent used to convert all the iron to the ferrous condition, before the treatment with oxidizing solution, is stannous chlorid; the excess of it is removed by mercuric chlorid, the presence of a moderate quantity of which in the solution does not affect the result. The chromic acid is converted in this operation to chromic chlorid.

The indicator used is potassium ferricyanid. This may sometimes contain ferrocyanid, which can be changed to the ferricyanid by treatment of the solution with chlorin, the excess of which must be removed by boiling.

*The preparation of the standard solution.* To 5 grams of pure  $K_2Cr_2O_7$ , approximately weighed on the reagent-shelf scales, add about 500 c.c. of water in a beaker, and heat the mixture on the hot plate till solution is complete; cool the solution, transfer it to a one-liter glass-stoppered bottle, fill the bottle up to the shoulder, and mix the contents thoroughly.

Weigh out two portions of about 150 mgms. of clean piano wire, whose contents of pure iron should be determined if not known (ordinarily very nearly 99.6 per cent.), dissolve the wire in small, covered beakers, in about 40 c.c. of  $HCl$  with the aid of a gentle heat; to the hot solution add a little  $SnCl_2$  dropwise and with constant stirring, till the yellow color that may have been present at first is entirely removed, and with care to add only a small excess; dilute to about 150 c.c., cool quickly, add at once  $HgCl_2$ , of which about 20 c.c. will usually suffice; the precipitate should be white; next proceed without delay with the addition of the  $K_2Cr_2O_7$  from a burette, till no reaction appears with the  $K_3FeCy_6$  after the test drops have been in contact for half a minute.

Time will be saved, and some useful practice gained in stoichiometrical calculation, by figuring out in advance the probable quantity of the standard solution that will be required, and then running the solution in at once up to within 5 c.c. of this amount, with constant and rapid stirring, before making any tests. When first beginning to make the tests, from 0.5 to 1 c.c. of the standard solution can be added between them; but as the end is approached the quantity should be diminished till, close to the end, it should be only a tenth of a cubic centimeter at once.

At this part of the operation, also, when the proportion of ferrous iron in the solution has become very small, somewhat larger drops of it should be taken out for the tests.

To make these tests conveniently, put some of the solution of  $K_3FeCy_6$  in a test tube, and set this tube in a small beaker of water; put a drop of the solution under analysis on a porcelain plate, by means of the stirring rod, and with a dropping tube bring a small drop of the indicator in contact with it; put the dropping tube in the water in the beaker, thereby rinsing it for the next test. In order that the progress of the reaction can be

followed, toward the end of the operation, in the gradual weakening of the color in the tests, drops as nearly alike in size as practicable should be taken for all tests, except at the close as above noted, from both solutions; and, in order that the strength of the solution of the indicator in all the drops shall be about the same, the water should be blown out of the dropping tube each time before taking up a fresh portion of this reagent.

When the operation is completed with both solutions of the iron, calculate the value of 100 c. c. of the solution in Fe as a factor for permanent use. Two determinations of this factor should agree within 2 mgms., if the work has been carefully done.

For every determination of iron in a substance make the solution acid with 40 c. c. of **HCl**, and dilute it afterward as in this operation of standardizing the solution. If it is a ferric compound that is analyzed, more  $\text{SnCl}_2$  will of course be required than in the treatment of the above solution of the iron wire.

**129. Assay of limonite.** Supposing the ore to have been previously ignited to remove organic matter, which must not be in the solution, proceed as follows:—

To a weighed portion of about 3 grams add 100 c. c. of **HCl**, and boil gently in a covered beaker, in the fume closet, till the residue is entirely changed to a gray sand. Rinse the cover into the beaker, and make the volume of the solution up to 250 c. c. in a measuring flask (§ 111). Measure out three portions of 25 c. c. each into beakers, add to each about 10 c. c. of **HCl**, and proceed in the same manner as in the standardization of the dichromate, beginning with the addition of the  $\text{SnCl}_2$ ; use the first determination only as an approximate one, adding a cubic centimeter of the dichromate between each test. Proceed in the same manner with another weighed portion of the limonite. Report the result in Fe, giving the average of the last two determinations on each weighed portion.

**130. The determination of sulfur trioxid.** Sulfur trioxid in salts is always determined by precipitation as barium sulfate. One part of this salt requires 400,000 parts of water to dissolve it; it is appreciably more soluble in acids, even if dilute, and its solubility increases with the strength of the acid. Alkaline nitrates in the solution hinder its complete precipitation.

The precipitate is very fine, and often causes trouble by pass-



ing through the filter, especially if made in a cold solution and filtered at once; a clear filtrate is more easily obtained if HCl or  $\text{NH}_4\text{Cl}$  is present in the solution. The precipitate readily carries down with it other substances present in the solution, especially nitrates, and it is almost impossible to remove some of these foreign matters, even with hot water or dilute acids; if nitrates are present they must first be converted into chlorids by repeated evaporation of the solution to dryness with HCl.

Barium sulfate can be ignited to redness without change, but if the heat is carried up to whiteness, it loses  $\text{SO}_3$ . At a red heat in the presence of reducing substances it passes readily into the sulfid.

*The operation.* To the well diluted solution, acidified with HCl and heated nearly to boiling, add a hot solution of  $\text{BaCl}_2$  slowly and with constant stirring, as long as a precipitate is formed, and with some care to avoid any large excess of the reagent; let the liquid stand, still kept hot but not boiling, till the precipitate has nearly settled, decant the supernatant liquid into the filter, pour about 100 c. c. of boiling water over the precipitate, let settle and decant again, and repeat till the washings give no notable reaction for chlorids; then transfer the whole of the precipitate to the filter, complete the washing, and dry and ignite in the usual manner, after careful separation of the precipitate from the filter. When the ignition is completed and the crucible cooled, moisten the contents very slightly with  $\text{H}_2\text{SO}_4$ , dry over a *very* low flame, and then ignite gently. Give the result as  $\text{SO}_3$ .

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## CHAPTER XVI.

### ACIDIMETRY AND ALKALIMETRY.

131. This kind of analysis, as the names imply, is the determination of an acid or an alkaline substance, and as commonly understood it refers to their determination by volumetric methods. It can be directly applied to acids only when in the free state and soluble in water, and only indirectly to their determination in salts. Bases can be determined by the alkalimetric methods, when free, and also when in the form of carbonates.

The method consists simply in the addition of a standard solu-

tion of a base to the solution containing the acid to be determined, or in the addition of a standard solution of an acid to the solution of the base to be determined, till the point of neutrality is reached; or the addition of a standard acid in excess to the carbonate, and, when the salt is completely decomposed, determining by means of the standard solution of the base how much acid was used in excess; this subtracted from the total quantity of acid used gives the quantity required to form a neutral salt of the basigenic constituent of the carbonate.

Any base or acid soluble in water can be used for standard solution. The most convenient solutions for general use are an  $\frac{n}{10}$  solution of ammonia, and an  $\frac{n}{5}$  solution of hydrochloric acid. The presence of carbonic acid, dissolved in the liquid in which an alkalimetric or acidimetric determination is made, is usually objectionable, because it may interfere with the distinctness of the color reaction of the indicator used to show when the neutral point is reached. Potassium and sodium hydroxids absorb carbon dioxid from the air much more readily than ammonium hydroxid does; furthermore, they act more rapidly on the glass of the bottles or the burettes. A fifth normal solution of HCl can be heated up to boiling without loss of strength; even a tenth normal solution of  $\text{NH}_3$  cannot be heated without escape of ammonia; but as there is never any occasion in this work to heat a solution containing an excess of standard ammonia, this is no objection to its use.

The indicators most employed are litmus, cochineal, and methyl orange; as the preparation of a really serviceable solution of litmus is difficult, it is used mostly in cases where the others do not give a sharp reaction, as in the titration of organic acids.

Although the calculation of an acidimetric or alkalimetric determination is somewhat easier if the solutions are exactly one-tenth and one-fifth normal, when but small quantities are required, as for this practice, it is not advisable to take the time for their preparation; it is more convenient to make solutions approximating closely to the desired strength, by the aid of areometric specific gravity determinations, and Tables, and then to determine their exact strength by other means.

If, however, it is desired to make a solution whose strength is exactly equal to that of a normal solution, or to some aliquot part of such strength, proceed as follows. Prepare the first, approximately correct solution in such a way that it shall surely be somewhat too strong. Determine its exact strength in

accordance with the special directions given; calculate the quantity of the active constituent of the reagent in 1000 c. c. of this solution; calculate the number of cubic centimeters of this solution, which really contains that quantity of the active constituent of the reagent, required to make 1000 c. c. of solution of the correct strength; then 1000 minus this volume gives the quantity of water that must be added to this quantity of the solution to make 1000 c. c. of a solution of the correct strength.

For example: it is desired to make an exactly  $\frac{n}{5}$  solution of silver nitrate, silver being the active constituent. The first solution is prepared as directed above, and when its strength is determined it is found to contain 22.5 grams of silver per 1000 c. c., 21.58 grams being the correct quantity; the solution is too strong. Then

$$\begin{aligned} 22.5 : 1000 &:: 21.58 : 951.1. \\ 1000 - 951.1 &= 48.9. \end{aligned}$$

Therefore, on adding to 951.1 c. c. of the solution, which quantity contains the right quantity of silver for 1000 c. c. of an  $\frac{n}{5}$  solution of the nitrate, 48.9 c. c. of water, we shall have 1000 c. c. of an  $\frac{n}{5}$  solution of the reagent.

Since of these two solutions above mentioned, for alkalimetry and acidimetry, the hydrochloric acid is the more stable one, more care is usually given to the determination of its absolute strength than of the ammonia: the strength of the latter can be verified from time to time by comparison with the acid.

**132. Preparation of the standard solutions.** With the aid of the areometer (§ 121), and the specific gravity Tables in Part V, determine the strength of the shelf  $\text{NH}_4\text{OH}$ , and the **HCl** of the laboratory. Then prepare a liter of an approximately one-tenth normal solution of ammonia by measuring out the proper quantity of the reagent with the graduated cylinder into a one-liter measuring flask, filling the flask up to the mark with water, and mixing thoroughly by repeated inversion of the flask. Transfer this solution to a liter glass stoppered bottle; the bottle should be rinsed out with distilled water but not necessarily dried before using it. In like manner prepare a liter of an approximately one-fifth normal solution of hydrochloric acid.

*The determination of the relative strength of the acid and the alkaline solutions.* Fill one burette with one solution and another burette with the other; run 10 c. c. of the acid into a

small beaker, add enough of the indicator (about 0.5 to 1 c. c. of cochineal or litmus, or three or four drops of the methyl orange) to give a decided color to the solution, put the beaker on a large sheet of white paper in a good light, and run in ammonia with constant stirring, till the proper change of color appears, produced by, at the most, two or three drops of the solution; if it is feared that too much may have been added, 0.1 to 0.2 c. c. of acid may be run in to restore the original color; then add ammonia again. By repeating this operation, several times back and forth, the point of neutralization can be very accurately determined. If sharp results are not obtained with one indicator, try another. Note the total quantities of acid and ammonia used, and repeat the operation with 25 c. c. portions of acid till closely agreeing results are obtained. Finally, calculate the quantity of acid required to neutralize one cubic centimeter of ammonia solution and the quantity of ammonia solution required to neutralize one cubic centimeter of the acid solution. If all the preliminary measurements and the rest of the work have been carefully performed, the acid should prove to be very nearly twice as strong as the ammonia.

**133.** *The determination of the absolute strength of the solution of acid.* This determination is made by precipitation with silver nitrate, and weighing the chlorid obtained.

The precipitate of  $\text{AgCl}$  is white, and mainly flaky, while a part of it remains quite persistently in a finely divided form that passes easily through the filter; but on vigorously shaking or stirring the liquid containing the precipitate, the fine portion becomes attached to the flocculent part, and the liquid clears more readily on standing, especially if it is hot and contains  $\text{AgNO}_3$ , in excess, instead of  $\text{HCl}$ . It is very insoluble in water and in  $\text{HNO}_3$ , soluble in traces in  $\text{HNO}_3$ , more soluble in  $\text{HCl}$ ; it is appreciably soluble in solutions of other chlorids, and of nitrates, including silver nitrate; much excess of this last mentioned reagent should therefore be avoided in the precipitation.

On exposure to sunlight, and especially the direct rays, it turns violet, losing chlorin, and forming  $\text{Ag}_2\text{Cl}$ ; the change is superficial, but it may affect the weight of the product if allowed to go too far. When gently ignited it fuses to a yellowish liquid, without decomposition.

*The operation.* Procure a 130-150 c. c. Erlenmeyer flask, a good cork that when properly softened fits tightly in its mouth,

and a small piece of black cloth to protect the precipitate from the light. To 25 c. c. of the standard solution in this flask, add about 1 c. c. of  $\text{HNO}_3$ , 75 c. c. of water, and then  $\text{AgNO}_3$ , slowly and with constant agitation of the solution by moving the flask gently in a small circle, while resting on the table, till the reagent is in slight excess.

Since it is very necessary that this excess of the reagent should be present, and the reaction be completed before the precipitate is collected together in the manner described below, time will be saved by making a preliminary calculation of the quantity of silver nitrate required; see § 114. This is easily done, since the strength of the standard solution is very nearly known, and that of the reagent is given in § 147. The precipitate settles so slowly that it is very difficult to determine in the usual manner when enough of the precipitant has been added.

Cork the flask, wrap it in the black cloth and shake the contents vigorously for about five minutes; by this operation the precipitate is flocculated, and it will settle very quickly, leaving a supernatant liquid that must be entirely free from turbidity; if it is not, the shaking must be repeated. The filtration should not be attempted till a perfectly clear supernatant liquid is obtained.

When all is ready for the filtration, by a quick movement of the flask while held in the hand, throw some of the clear liquid up against the cork, and repeat this till the particles of the precipitate adhering to the cork and the neck of the flask are completely rinsed down: transfer the precipitate at once to the carefully prepared and rather thick Gooch filter; the mass on the filter becomes very compact and somewhat fissured; stir and break it up fine, with the rod, with care not to penetrate so far as to disturb the asbestos, and wash with cold water containing about one hundredth of its volume of  $\text{HNO}_3$ , till fifteen or twenty cubic centimeters of the washings give no turbidity with two or three drops of  $\text{HCl}$ . If during the washing the wash-water becomes turbid, it must of course be passed through the filter again; it is well to empty the filtering flask frequently, as mentioned in § 115, so that at no time will it be necessary to filter again more than a small quantity of liquid. If any fissures appear in the mass on the filter during the washing, close them in the same manner as at first.

Dry the precipitate for two or three hours at  $110^\circ$ – $120^\circ$ ; then ignite it, at first very gently for a few minutes, with crucible

covered, and then more strongly till it just begins to fuse. This last part of the operation should be performed with the crucible uncovered, so that its progress can be closely watched; the crucible should be laid as far over on its side as possible, and the lamp, with a high flame turned on, should be moved in and out under the side of the crucible till fusion begins, not only in detached portions of the chlorid in that part of the crucible directly exposed to the flame, but also on the edges of the main mass of the substance on the asbestos.

A better way is to hold the crucible by the tongs, in a still more nearly horizontal position, and by a motion of the hand and arm turn it over and back, so that it will be heated on different sides while holding it in the flame; thus danger of overheating any portion of the chlorid is more easily avoided. When the crucible is thus heated on its sides and only when in a horizontal position, or nearly so, and the flame is not at any time allowed to impinge directly against the bottom, the fused chlorid will not run through or around the asbestos to the platinum disk.

Repeat the operation with other portions of the acid till concordant results are obtained. The fused silver chlorid can be loosened from the asbestos and the disk of platinum by digestion with HCl while in contact with pieces of zinc.

Now calculate the mgms. of HCl in one cubic centimeter of the standard acid: and, knowing the exact relation between this acid and the standard ammonia, calculate the absolute strength of this alkaline solution, or the number of milligrams in one cubic centimeter. Next, for practice, calculate the value of one cubic centimeter of the acid in sodium carbonate, potassium carbonate and calcium carbonate, and the value of one cubic centimeter of the ammonia solution in sulfur trioxid and nitrogen pentoxid. It now remains to test the accuracy of this work in the preparation of these standard solutions, by the analysis of test substances.

If the substance is a carbonate, add water, which will dissolve it if an alkaline carbonate; add the indicator, and then standard acid very slowly and with constant stirring, till plainly in excess, with the substance itself entirely dissolved. If it is a carbonate insoluble in water, this solution in the acid will take place rather slowly, especially towards the end, unless a large excess of acid is used, which is inadvisable.

Before titration back with ammonia in the case of a carbon-

ate, the solution should be heated just to boiling, in a covered beaker, and kept boiling *gently* for about five minutes. The cover and sides of the beaker are then rinsed down with water, and the liquid cooled.

In all this work be careful not to dilute the solution of the substance to be determined, too much; the volume should not exceed 100 c. c. when the liquid is ready for the titration, and should be within 75 c.c. if practicable.

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## CHAPTER XVII.

### THE DETERMINATION OF LEAD, PHOSPHORUS PENTOXID AND CALCIUM. IODOMETRY. DETERMINATION OF ANTIMONY.

134. *The determination of lead.* Lead is most conveniently determined as lead sulfate. This salt is nearly insoluble in water, more insoluble in water containing sulfuric acid, much more soluble in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , and in water containing ammonium salts in solution, especially the nitrate, acetate or tartrate; it is insoluble in alcohol. Ignited, at a red heat it is unchanged, but at a white heat gives off  $\text{SO}_3$ ; it is easily reduced at ignition temperatures in contact with incompletely burned combustion products, the metal separating out; the filter upon which it has been collected cannot, therefore, be wrapped in platinum wire for the ignition (§ 123).

*The operation.* To the solution, which should not be concentrated, add  $\text{H}_2\text{SO}_4$  in slight excess; if nitric acid or a nitrate is possibly present, evaporate the solution down nearly to dryness on the water-bath, leaving the beaker uncovered; when taken from the bath, the liquid should not give any odor of nitric acid. If hydrochloric acid or a chlorid is possibly present, the solution must receive the same treatment. These obstacles to complete precipitation of the lead as sulfate being removed, add about 50 c.c. of water to the residue in the beaker, and after stirring well add about 100 c.c. of alcohol; let the mixture stand for a few hours, filter, wash with alcohol, and dry. Transfer as much of the precipitate as possible from the filter to a crucible, in the usual manner and ignite gently. Fold the filter up and burn it directly in another crucible, heating at first very gently with the

cover partly on, and complete the ignition in the usual manner; when the crucible is cool moisten its contents with  $\text{HNO}_3$ , evaporate to dryness at a gentle heat, moisten the residue with  $\text{H}_2\text{SO}_4$ , dry and ignite gently. Add the two weights of substance obtained and calculate the result as Pb.

For a somewhat shorter method, requiring but one weighing of substance, and much more careful manipulation, but permissible only where there are no currents of air, see Fresenius, § 52.

**135.** *The determination of phosphorus pentoxid.* Phosphorus pentoxid is nearly always weighed as magnesium pyrophosphate,  $\text{Mg}_2\text{P}_2\text{O}_7$ , after precipitation as magnesium-ammonium phosphate,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . This salt forms a white, crystalline powder, slightly soluble in water, easily soluble in acids, less soluble in water containing ammonia, less insoluble if ammonium chlorid is also present, easily soluble in acids. Excess of magnesium sulfate increases the insolubility in ammoniated water, but unless much ammonium chlorid is present, magnesium hydroxid, or a basic magnesium sulfate is liable to be precipitated also; excess of sodium phosphate diminishes the solubility of the precipitate.

Heated to  $100^\circ$  the water of crystallization escapes, and on ignition, the ammonia also; too rapid heating, producing a sudden evolution of the ammonia, may cause a loss of substance mechanically. The pyrophosphate is white or grayish, often quite dark in color, unchanged at a white heat, easily soluble in acids.

*The operation.* To the solution containing in 75 c. c. about 500 mgms. of phosphorus pentoxid, as nearly as can be estimated from previous knowledge of the composition of the substance to be analyzed, add about 5 c. c. of ammonia, or till in excess, and then with constant stirring and care not to touch the side of the beaker with the rod, add the magnesia mixture drop by drop, most conveniently from a burette, at the rate of about a drop per second; 20 c. c. of the reagent will usually be sufficient, if the quantity of the substance present has not been underestimated. Let the mixture stand three or four hours before filtering. Filter and use water containing one-fourth its volume of ammonia for cleaning the beaker and washing the precipitate; wash till the chlorin reaction disappears, or is at least no stronger than is given by a few drops of the washing solution added to half a cubic centimeter of silver nitrate acidified with  $\text{HNO}_3$ .

It is often necessary to complete the ignition over the blast-lamp, if a nearly white residue cannot be obtained by the



ordinary treatment; after one ignition over a Bunsen lamp, if the product is not white or nearly so, moisten it with a drop of  $\text{HNO}_3$ , and dry very carefully over a low flame, then ignite strongly over the blast-lamp and weigh; if the residue is still not nearly white, repeat the treatment with  $\text{HNO}_3$  and the ignition, and weigh again; if the loss in weight is null, or insignificant, do not carry the operation any further, but report the result obtained, with a statement of the condition of the precipitate. Give results as  $\text{P}_2\text{O}_5$ .

136. *The determination of calcium.* For the determination of calcium it is usually precipitated as the oxalate; with this precipitate four courses may be taken. It may be dried at  $100^\circ$  till the weight is constant, the product then having the composition given below; it may be ignited very carefully and weighed as carbonate, or ignited very strongly and weighed as oxid; its complete conversion into carbonate without carrying a little of it on to the oxid is somewhat difficult; and it is even more difficult to convert a large quantity of the oxalate completely into oxid.

Therefore another course, which is open to none of these objections is described here, namely, the volumetric method, with potassium permanganate; this reagent causes the conversion of all the oxalic anhydrid into carbon dioxid, as the result of a process of oxidation in the mixture in which the reaction is made to take place.

Calcium oxalate,  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , forms a white, very fine, crystalline precipitate, insoluble in water, and in solutions of alkaline chlorids, easily soluble in mineral acids; ignited, it passes into the carbonate at a moderate heat, and into the oxid at a high heat.

*The precipitation.* To the hot solution, of about the average degree of dilution, and containing, as near as may be estimated from previous knowledge of the composition of the substance to be analyzed, about 100 mgms. of calcium, add ammonia till in moderate excess, and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  with constant stirring, till no further precipitation takes place, and let the mixture stand for several hours in a warm place.

Decant the clear liquid into a weighed Gooch filter, with as little disturbance of the precipitate as possible, wash several times with hot water by decantation, and finally transfer the precipitate itself to the filter; wash the precipitate till no further reaction is obtained for oxalic acid in a test with 5 c. c. of the washings.

Unless a very carefully prepared filter is used, and all these directions are followed, there may be difficulty in getting a clear filtrate.

Dry the crucible and contents to constant weight, at  $100^{\circ}$  C., and calculate the result as Ca.

**137.** *Volumetric determination of the calcium in this precipitate.* Make an approximately  $\frac{n}{10}$  solution of  $\text{KMnO}_4$  (see § 108), and standardize it by means of ferrous oxide in the form of ammonium ferrous sulfate,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 + 6\text{H}_2\text{O}$ , taking carefully weighed portions of about 1 gram each. Dissolve the salt in about 200 c. c. of water, add at once about 10 c. c. of  $\text{H}_2\text{SO}_4$ , and, with the beaker on a white tile or plate, add the permanganate from a glass-stoppered burette, dropwise, and with constant stirring. At first the color of each drop disappears immediately, and then more and more slowly; towards the end of the operation, add the drops very slowly, with stirring between each, till the color disappears; the end point is reached as soon as the last drop added gives to the whole of the solution an unmistakable faint reddish tinge. This color may be permanent only for a very few moments, but nevertheless the ferrous iron is completely oxidized, and the reaction is completed. Repeat till closely agreeing results are obtained.

The equation is given in the section above referred to, for the reaction between the ferrous oxid and permanganate. In the actual operation, the ferrous oxid is present in the form of sulfate, and in the presence of the  $\text{H}_2\text{SO}_4$  added we have sulfates in the right-hand member of the equation instead of oxids; but this does not affect the process of oxidation in any other way than to facilitate it. The equation shows that ten atoms of Fe in the form of ferrous salt are converted into ferric salt by the oxygen yielded by two molecules of  $\text{KMnO}_4$ .

From the formula of the ferrous salt used, calculate the quantity of Fe in the weight of salt taken, and then from the results of the titration calculate the exact strength of the  $\text{KMnO}_4$  solution. Then calculate the value of one cubic centimeter of this solution in  $\text{CaC}_2\text{O}_4$ ; for the equation for this reaction between the  $\text{KMnO}_4$  and  $\text{CaC}_2\text{O}_4$ , take five molecules of the oxalate and two of the permanganate, with the necessary quantity of  $\text{H}_2\text{SO}_4$ ; the products of the reaction are calcium sulfate, manganese sulfate, potassium sulfate, carbon dioxide and water; then calculate the quantity of calcium in this quantity of calcium oxalate, and thus obtain the value of 1 c. c. of the

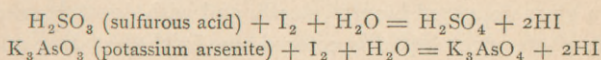
permanganate in calcium. Or the value of the permanganate in Ca can be calculated directly, without first calculating its value in calcium oxalate.

Now determine the quantity of calcium oxalate in the precipitate obtained and weighed above, by the same kind of an operation as that performed in standardizing the permanganate; to this end, transfer the precipitate with the asbestos to a beaker, add about 100 c.c. of water, and 50 c.c. of  $H_2SO_4$ , warm to about  $60^\circ$ , and then titrate with permanganate.

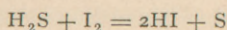
Give the result in Ca.

### 138. Iodometry.

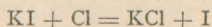
This method of volumetric analysis depends upon the action of iodine as an indirect oxidizing agent. In the presence of water hydriodic acid is formed, while oxygen in its nascent state acts on any oxidizable substances present.



If the substance combined with the hydrogen is not readily oxidized it may be set free.

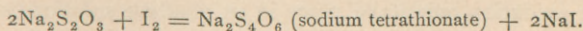


Iodine may be set free in a solution of potassium iodide by a substance capable of displacing it from its combination with the metal.



The extreme delicacy of the reaction of free iodine with starch, and the sharpness of its reaction with thiosulfate, give the means for measuring the quantity of free iodine in a solution with exceptional accuracy.

The reaction with sodium thiosulfate is as follows:—



#### *The preparation of the solutions.*

*Iodine in potassium iodide.* For 500 c.c. of an  $\frac{n}{10}$  solution dissolve about 12 gms. of potassium iodide in about 200 c.c. of water; weigh out about 6 gms. of powdered iodine in a covered watch glass, and at once put it into a glass-stoppered measuring flask, rinsing the glass into the flask with some of the iodide solution; add the remainder of this solution, and shake up the contents of the flask frequently till the iodine is completely dissolved, using no heat; make the solution up to 500 c.c. with water, and mix

as usual. If a larger quantity of the solution is made it should be put into a number of 250 c.c. bottles, nearly filled; in this manner it may be kept unchanged in strength for a long time.

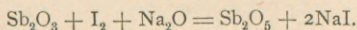
*Sodium thiosulfate.* Dissolve 12.4 gms. of the pure and well crystallized salt in 500 c.c. of water, previously boiled to expel  $\text{CO}_2$  in solution. If this solution is kept in a cool, dark place, its strength will remain unchanged for a considerable time.

*The starch solution.* To about a gram of powdered starch add about 100 c.c. of water with constant stirring, and heat the mixture, with continued stirring, to boiling; let cool, and pour off the nearly clear liquid from the sediment. The solution is not permanent, and should be fresh when used.

*Standardizing the iodine solution against the thiosulfate.* To 20 c.c. of the latter solution, run from a burette into a beaker, add three to four c.c. of the starch solution, and then iodine solution from a glass-stoppered burette, slowly and with constant stirring, till the whole of the liquid is colored blue by the last drop added. Repeat till closely agreeing results are obtained.

*The standard of the iodine solution.* Break up some crystals of pure sodium thiosulfate to a coarse powder, dry this over sulfuric acid for a short time, then pulverize the effloresced residue very fine, and dry it for several days over sulfuric acid, with a watch glass containing pieces of potassium hydroxid to absorb any carbon dioxide that might be present and act on the salt. Take about 200 mgms. of the powder for each test, dissolving it in about 20 c.c. of water. Calculate the iodine in one c.c. of the solution.

139. *Determination of antimony, in the form of antimonous oxid.*



The oxidation must take place in an alkaline solution, and in the presence of a large excess of alkaline carbonates. Fresenius gives the following directions, which are to be found also in Fleischer's *Titrimethoden*.

Dissolve a quantity of the substance containing about 100 mgms. of antimony in about 10 c.c. of a solution of tartaric acid (one to ten), add sodium carbonate till the solution is nearly neutral, and about 20 c.c. of a cold saturated solution of sodium bicarbonate, then the starch, and finally the iodine solution, dropwise and with constant stirring, till the whole of the liquid assumes a briefly permanent blue color; that the color disappears after a

little time is not to be taken as an indication that more iodine solution is required. Fleischer commends the usefulness of this determination, since antimony can be precipitated as tersulfid from any of its compounds; and after dissolving the precipitate in HCl, boiling out the hydrogen sulfid, adding tartaric acid and the alkaline carbonates as above directed, the solution is ready for the titration.

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## CHAPTER XVIII.

### ANALYSIS BY ELECTROLYSIS—SEPARATION AND DETERMINATION OF SILVER AND COPPER.

**140. Method 1** (Classen's). Silver oxalate, precipitated by  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  is insoluble in excess of the precipitant, while copper oxalate is soluble. The two metals are separated by this reaction and subsequent filtration, the silver oxalate is dissolved in potassium cyanid, and each solution is electrolyzed separately.

The re-solution of the copper oxalate in excess of the reagent is easy, but since the silver oxalate settles very slowly, it is difficult to decide when the precipitation is complete, and when the addition of the ammonium oxalate in excess really begins, or when, in the solution colored bluish-green by the dissolved copper salt, the undissolved residue consists only of the white silver salt. It is better, therefore, to estimate by calculation, or ascertain by experiment, how much of a cold saturated solution of the precipitating reagent is required to effect a complete reaction: any excess of the reagent does no harm. For a solution containing about 500 mgms. of copper and silver together, 60 to 70 c. c. of the saturated oxalate solution will be enough, even if copper predominates very largely; the larger the proportion of silver, the less oxalate will be needed.

*Classen's arrangement of electrodes* consist of a platinum dish for the cathode, with vertical sides, holding about 225 c. c., and for the anode a platinum disk 4.5 cm. in diameter, pierced with several holes 5 mm. in diameter, and fastened to a stout platinum wire. These electrodes are supported on a stand, with a glass post carrying a brass ring for the dish and a short rod for the disk, with binding screws for connection with the battery. The wire fastened to the anode passes through a small

hole in the centre of a cover-glass; the platinum dish is filled with the solution to such a level that, when the cover is in place, the lowest part of its convex surface is in contact with the liquid directly over the anode, and for an area a little larger than that of the anode; thus all spattering of the liquid on to the cover from the bubbles of gas evolved at the anode is avoided, and also the consequent necessity for rinsing the cover into the dish towards the close of the operation.

The most convenient source of the current is a storage battery.

*The analysis.* Dissolve about 500 mgms. of the alloy in dilute nitric acid, evaporate almost to dryness on the water bath, add 15 c.c. of water, evaporate again almost to dryness, and add 50 c.c. of water to the residue. A clear solution, containing very little free acid, should result. To this add 60-70 c.c. of a cold, saturated solution of ammonium oxalate, allow the precipitate to settle, filter, and wash first with ammonium oxalate, and then with cold water.

Dissolve this silver oxalate in a solution of pure potassium cyanid, transfer the solution to the weighed platinum dish, make its volume up as directed above, and precipitate the silver with a current corresponding to 0.2 to 0.5 c.c. of oxy-hydrogen gas per minute. Before disconnecting always ascertain whether the precipitation is complete; for this purpose add to the contents of the dish enough water to raise the level of the liquid about 2 mm., and then allow the current to flow half an hour longer; if no silver is deposited on the walls of the dish above the level of the first solution, the precipitation is complete. Confirm by testing with HCl.

Remove the cover-glass and anode, pour out the liquid in the dish quickly, and wash the deposit first with water; holding a wash-bottle mouth lowermost, and with the outer arm of the mouth tube nearly horizontal and very near the inner rim of the dish, direct the stream of water from the mouth-tube on to the inside of the dish *above* the deposit, while revolving the dish in such a manner as to bring this impact of the water in an oblique direction against the whole circumference of the rim; pour this water out, and repeat the operation three times. Then wash three times with strong alcohol in the same manner. Remove the last portions of alcohol by blowing into the dish while held in the hand, dry for an hour in the desiccator, and weigh.

*Determination of the copper.* Evaporate the filtrate and washings from the silver oxalate down to about 150 c.c. if the

volume is much larger than this, transfer at once to the weighed platinum dish, add 20 c.c. of a cold saturated solution of ammonium oxalate, and electrolyze with a current of the same strength as above. Test for complete precipitation as directed for the silver determination, and also by taking out about one c.c. of the liquid with a small pipette and applying the ferrocyanide test. When precipitation is complete wash and dry the dish, as directed above, and weigh.

**141.** *Method 2. Precipitation and determination of the silver as chlorid and the copper by electrolysis.* In this method the less expensive platinum foil electrodes can be used, the cathode being about      cm. and the anode      cm.

Dissolve a quantity of the substance containing 250 to 300 mgms. of the metals in water, or in  $\text{HNO}_3$  if the substance is metallic. In this last case evaporate the solution down till fumes of nitrous acid are no longer evolved, add about 75 c.c. of water and then HCl as long as a precipitate is formed; make this addition and carry out the subsequent operations as directed for the estimation of HCl in § 133. The liquid will not clarify so readily as in that operation, HCl being in excess instead of silver nitrate.

Since the filtrate is to be used for the estimation of the copper, none of it or of the washings are to be lost; as is usual in the separation of substances from one another preliminary to their quantitative estimation, the filtrate and washings must be concentrated by evaporation.

**142.** *The determination of the copper.* The solution must be free from HCl or chlorids, and contain nitric acid as its only free acid, except that a very little free sulfuric acid is permissible. If HCl has been added in any previous operation, or the salt is a chlorid, add to the concentrated solution about 20 c. c. of  $\text{HNO}_3$  and evaporate to dryness on the water bath. Take up the residue with a little water and about 20 c. c. of  $\text{HNO}_3$ , of 1.2 sp. gr., in a beaker of about 250 c. c. capacity, heating a short time if necessary to get complete solution, with the beaker covered, and finally add 180 c. c. of water.

Shape the electrodes into a curved form so that they will fit evenly against the sides of the beaker containing the solution, clean them of any organic matter by heating to redness for a moment in the lamp-flame, and lay them in the desiccators; do not handle the broader parts with the fingers after they have been thus cleaned. Only the larger electrode of each pair is to be

weighed, unless there is reason to suppose that a little lead may be deposited on the other as  $PbO_2$ , as in the analysis of brass. In weighing, suspend the electrode, by the loop in its platinum wire, on the hook over the balance pan.

Put the electrodes in the beaker so that they nearly touch the bottom, bend the platinum wires over the edge of the beaker, thus suspending each one in its place, and make the connections with a current corresponding to three to four c.c. of oxyhydrogen gas per minute. Cover the beaker during the electrolysis.

From twelve to twenty-four hours will be required for the completion of the electrolysis, with 250-300 milligrams of copper in the solution. When the solution appears quite colorless, rinse the cover into the beaker, add a little more water so as to raise the level of the liquid by about half a centimeter, stir gently to mix in the added water, and after one or two hours observe whether any copper is deposited on that part of the electrode freshly immersed; if not, confirm the test by adding ammonia to about five c. c. of the liquid till in slight excess, then acetic acid till acid, and then  $K_4FeCy_6$ ; there should be no red precipitate or coloration.

The deposition of the copper being complete, slowly raise the electrode out of the liquid while it is still in the circuit, rinsing it off on both sides with water as it is raised, finally leaving only one corner immersed; then lift it quite out, and rinse off this corner; finally rinse off with alcohol, and dry as directed in Method 1.

In the place of an ordinary beaker, one with a lateral tubulure near the top is often used; the washing of the electrode is done by conducting a small stream of water to the bottom of the beaker, till the overflow through the tubulure is no longer acid; then the current can be discontinued without danger of redissolving any of the copper.



## PART V.

### LISTS OF APPARATUS AND REAGENTS, SPECIFIC GRAVITY AND OTHER TABLES.

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#### 143. *The qualitative set of apparatus.*

One apparatus, Marsh (flask, funnel-tube, rubber cork, conducting tube, and platinum foil); one bottle, glass-stoppered, 60 c.c., with  $\text{AgNO}_3$ ; one bottle, glass-stoppered, with alcohol; one crucible, porcelain, No. 8; one evaporator, porcelain, 70 mm.; one package of 50 filters, 7 cm.; one package of 100 filters, 9 cm.; one finger cap, rubber; two flasks, conical (Erlenmeyer), 60 c.c.; two flasks, conical (Erlenmeyer), 100 c.c.; one flask, ordinary, flat bottom, 60 c.c.; one forceps; three funnels, 50 mm. opening; one mortar and pestle; one lamp with 60 cm. of 6 mm. rubber tube; one piece plain glass, 10 x 10 cm.; one platinum cup and wire; two 10 cm. rods of glass; one sand bath; one spatula of horn; one sponge; one stand, of iron, with rings; six test-tubes, 10 cm. long; twelve test-tubes, 15 cm. long; one test-tube holder; one test-tube rack; one test-tube brush; three tubes, bulbed for arsenic test; one tube, dropping, drawn out at one end; one tube, with loop, for  $\text{CO}_2$ ,  $\text{H}_2\text{SO}_3$ , and  $\text{HCy}$  tests; one wash-bottle; one watch-glass, 28 mm.; one wire triangle.

144. *Directions concerning the use of this apparatus.* This set of apparatus comprises all that is essential for the work in qualitative analysis. Some of the pieces will, of course, be broken sooner or later, and may perhaps have to be replaced many times during the term. The student is advised to keep his set always full; there is nothing superfluous in it, and it is mistaken economy to attempt to carry on the work with any pieces wanting.

The *Marsh apparatus* is used only in the test for arsenic in the course for the tin group.

Use the *evaporator* only for evaporating liquids ; set it directly over the lamp without the intervention of a sand-bath, not more than a centimeter above the mouth of the lamp tube, and turn the gas down so low that the flame will not rise higher on the outside than the level of the liquid within.

Use the *crucible* for heating the residues from evaporations ; see § 47 on ignition.

The *finger cap* is convenient for protecting the skin from contact with corrosive liquids, when it is necessary to close the mouth of a test-tube, to be inverted for mixing its contents.

Always use smaller *filters* when only small quantities of a substance are to be filtered out.

The *flasks* can be heated over a direct flame, with the same precautions as given above for heating evaporators. Consult §§ 53, 54, on digestion and boiling.

Keep the *forceps* entirely from contact with solutions that you are analyzing, lest you may report copper and zinc incorrectly.

To light the *lamp*, turn on the full flow of the gas, and not till after it is lighted turn it down to the desired point ; a flame from five to seven centimeters high is the most suitable for ordinary work, and should always be used except when special directions are given for a lower or a higher flame. Be particularly careful in turning the flame down very low, that it does not "strike down" and burn at the little jet by the air inlets ; when this has taken place, the gas burns also at the mouth of the tube with a pale, light-colored, slender flame, and not with an almost colorless, somewhat bulging flame, without light, as it should ; when burning in this way the whole lamp may become hot and burn the fingers if touched ; it is to avoid this that the directions are given as above for lighting the lamp. The only way to set the matter right when the lamp is burning in this way, is to shut the gas off entirely and light it again in the manner directed above.

Keep your *platinum cup* bright and clean ; fuse a little potassium bisulfate in it, and soak the fused mass off with hot water when it cannot be cleaned by heating with **HCl**.

Do not bring the horn *spatula* in contact with strong acid or alkaline liquids, or the *sponge* in contact with strong acids.

See § 54 about heating liquids in *test-tubes*. Do not have any acid in the test-tube when cleaning it with the brush.

Put only sand enough in the *sand-bath* to fill it about one-third. Put only distilled water in the *wash-bottle*.

145. *The apparatus for quantitative work.*

The smaller of the two sets of apparatus given below is issued to students taking only the short course of quantitative work laid out in Part IV, and occupying about one hundred and ten hours of actual practice. The other set is issued to those taking a longer course and working more hours.

There is occasional use for some expensive pieces of apparatus, especially by students taking the longer course of work, which are not included in these sets. In the author's laboratory these can be obtained, for such temporary use, of the supply clerk, checks being in all cases deposited for each piece; *any piece of apparatus drawn on check is to be returned, as soon as the special work for which it was required is completed, and the check is to be reclaimed.* Checks missing at the end of the term may be charged for at a rate much above their actual cost, since, under this system, they may represent apparatus of great value; therefore it behooves the student to look after them carefully.

146. *The smaller quantitative set of apparatus.*

Twenty apparatus checks; seven beakers (one 30 c.c., four 200 c.c., two 300 c.c.); six beaker covers (two 62 mm., four 80 mm.); five bottles (one 60 c.c. with  $\text{AgNO}_3$ , one 250 c.c. with alcohol, two 1000 c.c., flat stoppered, one 500 c.c., wide mouth); two burettes, 50 c.c. graduated in  $\frac{1}{10}$  c.c., with rubber tube, glass ball, and jet; two burette floats; two crucibles, porcelain, No. 7; one crucible, Caldwell-Gooch, with perforated platinum disk; one crucible tongs; two desiccators, with glass covers and triangles; two evaporators, 110 mm.; fifty filters (25 for quantitative filtration, 25 common); three flasks (one 60 c.c., two 250 c.c., conical, with lateral tube and rubber stopper, for suction filtration); one forceps; five funnels (four, usual form, 50 mm., one cup-shaped for the Gooch crucible); one lamp, Bunsen, with 60 centimeters of 6 mm. rubber tube; one sheet glazed paper, cut (see § 119); one pipette, 25 c.c., with mark on neck; one white plate; four rods of glass; one spatula, horn; one thermometer; two triangles, platinum-wrapped; one tube, dropping, drawn out at one end; ninety centimeters rubber tube, 3 mm.; three test-tubes, 10 cm.; one tube, graduated; one wash-bottle (flask with rubber cork and tubes); two watch-glasses, 38 mm.; one wire, platinum, in glass handle; one Y-tube.

Also, one iron rod with two lamp rings, one rod with funnel holder, and one with burette holder, all for the fixed iron stand on the table.

147. *The larger set of apparatus.*

Twenty apparatus checks; seven beakers (one 30 c.c., four 200 c.c., two 300 c.c.); ten beaker covers (two 62 mm., six 80 mm., two 95 mm.); ten bottles (one 60 c.c. with  $\text{AgNO}_3$ , one 250 c.c., with alcohol, one 1000 c.c. with distilled water, one 500 c.c., wide mouth, two 250 c.c., two 500 c.c., flat stopper, two 1000 c.c., flat stopper); two burettes, 50 c.c. graduated in  $\frac{1}{10}$ , with jet, rubber tube, and glass ball; two burette floats; two cones, platinum, for suction filtration; four crucibles, porcelain (two No. 7 ordinary, two No. 6 Caldwell-Gooch, with perforated platinum disks); one crucible tongs; one cylinder, 100 c.c., graduated; two desiccators, with glass covers and triangles; six evaporators (two 110 mm., two 145 mm., two 180 mm.); one hundred filters (twenty-five ordinary, twenty-five 7 cm., and fifty 9 cm. for quantitative filtration); seven flasks (one ordinary 60 c.c., two 500 c.c. Erlenmeyer, with lateral tubulure for suction filtration, two Erlenmeyer, 250 c.c., two ditto, 400 c.c.); one forceps; eight funnels (six ordinary, 50 mm. opening, two cup-shape for Gooch crucible); one lamp, Bunsen, with 60 centimeters of 6 mm. rubber tube; one mortar and pestle; one sheet paper, glazed, cut (see § 119); four pipettes (one 10 c.c., one 25 c.c., one 50 c.c., each with mark on neck, one 10 c.c., graduated); one white plate; eight rods, glass, 15-18 cm. long; one spatula, horn; one thermometer; two triangles, platinum-wrapped; one dropping-tube; ninety centimeters of 3 mm. rubber tube; twelve test-tubes (six 10 cm., six 15 cm.); one test-tube brush; one test-tube holder; one test-tube rack; one test-tube, graduated; two wash-bottles (one 250 c.c., one 500 c.c.) with rubber corks and tubes complete; four watch-glasses (two 35 mm., two 50 mm.); one pair of weighing tubes, made from two test-tubes; one Y-tube; one wire, platinum, in handle; one wire gauze, 10 cm. square; also, one iron rod with two lamp rings, one rod with funnel holder, and one with burette holder, all for the fixed iron stand on the table.

148. *List of the reagents used in the work described in this book, arranged in the alphabetical order of their full names and*

giving, when practicable, the number of grams to be taken for 1000 c.c. of solution. In the case of those given in italics, refer to § 150 for special directions for making the solutions.

Acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ .

Alcohol,  $\text{C}_2\text{H}_5\text{OH}$  or  $\text{C}_2\text{H}_6\text{O}$ .

Ammonia alum.

*Ammonium carbonate*,  $(\text{NH}_4)_2\text{CO}_3$ . 250

Ammonium chlorid,  $\text{NH}_4\text{Cl}$ . 100

Ammonium ferrous sulfate  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 + 6\text{H}_2\text{O}$ .

*Ammonium hydroxid*,  $\text{NH}_4\text{OH}$ .

*Ammonium molybdate*,  $(\text{NH}_4)_2\text{MoO}_4$ .

Ammonium oxalate,  $(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$ . 75

*Ammonium sulfid*,  $(\text{NH}_4)_2\text{S}$

(or, with excess of sulfur,  $(\text{NH}_4)_2\text{S}_x$ ).

Aqua regia, 3  $\text{HCl}$ , 1  $\text{HNO}_3$ .

Barium carbonate,  $\text{BaCO}_3$ .

Barium chlorid,  $\text{BaCl}_2 + 2\text{H}_2\text{O}$ . 75

Barium hydroxid,  $\text{Ba}(\text{OH})_2$ . saturated solution.

Borax,  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ .

*Bromin* (solution), Br.

Calcium carbonate,  $\text{CaCO}_3$ .

Calcium hydroxid,  $\text{Ca}(\text{OH})_2$

(or milk of lime). saturated solution.

Calcium sulfate,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ . saturated solution.

Carbon dioxid

(or carbonic acid),  $\text{CO}_2$ .

Carbon disulfid,  $\text{CS}_2$ .

Chlorin (water), Cl.

*Chromic acid cleaning mixture*.

*Cochineal, tincture of*.

*Ferric chlorid*,  $\text{FeCl}_3$ .

*Ferrous sulfate*,  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ .

*Hydrochloric acid, concentrated*,  $\text{HCl}$ .

*Hydrochloric acid, dilute*,  $\text{HCl}$ .

Hydrosulfuric acid, or hydrogen sulfid,  $\text{H}_2\text{S}$ .

*Indigo solution*.

*Iodin solution*.

Iron filings, Fe.

Iron wire, piano.

Lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$ . 100

*Lead acetate and ammonium acetate*.

Lime water. saturated solution.

*Litmus solution.**Magnesia mixture.*

Mercuric chlorid $\text{HgCl}_2$ .	50
Methyl orange, indicator.	0.5
<i>Nitric acid, concentrated, <math>\text{HNO}_3</math>.</i>	
Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$ .	100
<i>Phenyl-sulfuric acid.</i>	
Potassium acetate, $\text{KC}_2\text{H}_3\text{O}_2$ .	saturated solution.
Potassium bisulphate, $\text{KHSO}_4$ .	
Potassium chlorate, $\text{KClO}_3$	
Potassium chromate, $\text{K}_2\text{CrO}_4$ .	100
Potassium cyanid, $\text{KCy}$ , or $\text{KCN}$ .	50
Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ .	50
Potassium ferricyanid, $\text{K}_3\text{FeCy}_6$ , or $\text{K}_3\text{Fe}(\text{CN})_6$ .	10
Potassium ferrocyanid, $\text{K}_4\text{FeCy}_6$ or $\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{H}_2\text{O}$ .	50
Potassium iodid, $\text{KI}$ .	50
Potassium nitrate, $\text{KNO}_3$ .	
Potassium permanganate, $\text{KMnO}_4$ .	
Potassium sulfate, $\text{K}_2\text{SO}_4$ .	100
Potassium sulfocyanate, $\text{KCNS}$ or $\text{KCyS}$ .	50
Silver nitrate, $\text{AgNO}_3$ .	50
<i>Sodio-cobaltic nitrite, <math>(\text{NaNO}_2)_3 \text{Co}(\text{NO}_2)_3</math>.</i>	
Sodium carbonate, $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ .	200
Sodium hydroxid, $\text{NaOH}$ .	150
Sodium phosphate, $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ .	75
Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$ .	
Sodium sulfite $\text{Na}_2\text{SO}_3$ .	100
<i>Stannous chlorid, <math>\text{SnCl}_2</math>.</i>	
Starch.	
<i>Sulfuric acid, concentrated, <math>\text{H}_2\text{SO}_4</math>.</i>	
<i>Sulfuric acid, dilute, <math>\text{H}_2\text{SO}_4</math>.</i>	
Tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .	100
Zinc (metallic), $\text{Zn}$ .	
Zinc, sulfate, $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ .	100

149. List of such reagents as are usually named only by their formulas, in the description of the analytical work, arranged in the alphabetical order of their formulas.

$\text{AgNO}_3$ , silver nitrate.

$\text{BaCl}_2$ , barium chlorid.

$\text{BaCO}_3$ , barium carbonate.

$\text{Ba}(\text{OH})_2$ , barium hydroxid.

- CaCO<sub>3</sub>, calcium carbonate.  
Ca(OH)<sub>2</sub>, calcium hydroxid or lime water.  
CaSO<sub>4</sub>, calcium sulfate.  
C<sub>2</sub>H<sub>5</sub>OH, or C<sub>2</sub>H<sub>6</sub>O, alcohol.  
Cl, chlorin (water).  
CO<sub>2</sub>, carbon dioxid, or carbonic acid.  
CS<sub>2</sub>, carbon disulfid.  
Fe, iron (filings).  
FeCl<sub>3</sub>, ferric chlorid.  
FeSO<sub>4</sub>, ferrous sulfate.  
HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, acetic acid.  
H<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>, tartaric acid.  
**HCl**, hydrochloric acid, concentrated.  
HCl, hydrochloric acid, dilute.  
H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, oxalic acid.  
**HNO<sub>3</sub>**, nitric acid, concentrated.  
HNO<sub>3</sub>, nitric acid, dilute.  
H<sub>2</sub>S, hydrogen sulfid.  
**H<sub>2</sub>SO<sub>4</sub>**, sulfuric acid, concentrated.  
H<sub>2</sub>SO<sub>4</sub>, sulfuric acid, dilute.  
HgCl<sub>2</sub>, mercuric chlorid.  
KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, potassium acetate.  
KCl, potassium chlorid.  
KClO<sub>3</sub>, potassium chlorate.  
K<sub>2</sub>CrO<sub>4</sub>, potassium chromate.  
K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, potassium dichromate.  
KCy, or KCN, potassium cyanid.  
KCyS, or KCNS, potassium sulfocyanate.  
K<sub>3</sub>FeCy<sub>6</sub>, or K<sub>3</sub>Fe(CN)<sub>6</sub>, potassium ferricyanid.  
K<sub>4</sub>FeCy<sub>6</sub>, or K<sub>4</sub>Fe(CN)<sub>6</sub>, potassium ferrocyanid.  
KHSO<sub>4</sub>, potassium bisulfate.  
KI, potassium iodid.  
KMnO<sub>4</sub>, potassium permanganate.  
KNO<sub>3</sub>, potassium nitrate.  
K<sub>2</sub>SO<sub>4</sub>, potassium sulfate.  
NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, sodium acetate.  
Na<sub>2</sub>CO<sub>3</sub>, sodium carbonate.  
Na<sub>2</sub>HPO<sub>4</sub>, sodium phosphate.  
NaNO<sub>3</sub>, sodium nitrate.  
(NaNO<sub>2</sub>)<sub>3</sub>Co(NO<sub>2</sub>)<sub>3</sub>, sodio-cobaltic nitrite.  
NaOH, sodium hydroxid.  
Na<sub>2</sub>SO<sub>3</sub>, sodium sulfite.

- $\text{Na}_2\text{S}_2\text{O}_3$ , sodium thiosulfate.  
 $\text{NH}_4\text{Cl}$ , ammonium chlorid.  
 $\text{NH}_4\text{CNS}$ , ammonium sulfocyanate.  
 $(\text{NH}_4)_2\text{CO}_3$ , ammonium carbonate.  
 $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , ammonium oxalate.  
 $(\text{NH}_4)_2\text{MoO}_4$ , ammonium molybdate.  
 $\text{NH}_4\text{OH}$ , ammonium hydroxid.  
 $(\text{NH}_4)_2\text{S}$ , ammonium sulfid.  
 $(\text{NH}_4)_2\text{S}_x$ , ammonium sulfid, with excess of sulfur.  
 $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , lead acetate.  
 $\text{SnCl}_2$ , stannous chlorid.  
 $\text{Zn}$ , zinc (metallic).  
 $\text{ZnSO}_4$ , zinc sulphate.

**150.** *Special directions for the preparation of reagents or solutions.*

*The strength of the acids.* *Hydrochloric acid*:—Only for the solution of the precipitated sulfids of the metals of the 6th group is acid of full strength (about 1.2 sp. gr.) required. For ordinary use, this acid diluted with its volume of water is sufficiently strong; this moderately diluted acid is indicated by the heavy-faced symbol **HCl**, and is about 1.1 sp. gr.

For dilute hydrochloric acid, indicated by HCl, add to the fully concentrated acid eight parts of water.

*Nitric acid*:—For the concentrated acid for ordinary use, indicated by **HNO<sub>3</sub>**, add to the fully concentrated acid its volume of water, making an acid of about 1.2 sp. gr.

*Sulfuric acid*:—For the dilute acid,  $\text{H}_2\text{SO}_4$ , add one part of ordinary concentrated acid, **H<sub>2</sub>SO<sub>4</sub>**, to four parts of water.

*Ammonium carbonate*:—Dissolve 250 gms. of the salt in a mixture of 200 c.c. of ordinary aqua ammonia and 800 c.c. of water.

*Ammonium hydroxid*:—The solution for laboratory use should have a specific gravity of about 0.96.

*Ammonium molybdate*:—For two litres of solution take 1300 c.c. of water; to 200 c.c. of  $\text{NH}_4\text{OH}$  add 300 c.c. of this water, and dissolve 100 gms. of molybdic acid in this diluted ammonia. To 500 c.c. of fully concentrated nitric acid add the rest of the water, and to this add the ammoniacal molybdic solution, *slowly and with constant stirring*; let the whole stand in a warm place 48 hours, and decant off the clear solution for use.



*Ammonium sulfid*:—Pass  $H_2S$  through ordinary ammonia water till the solution gives no precipitate with  $MgSO_4$ , and to 700 c.c. add 300 c.c. of  $NH_4OH$ . For the sulfid indicated by  $(NH_4)_2S_x$  dissolve sulfur in this solution to saturation.

*Bromin solution*:—To a solution of 50 gms. of potassium bromid in 500 c.c. of water, add bromin till no more is dissolved when the mixture is well shaken.

*Cochineal, tincture of*:—Digest 3 grams of cochineal for a long time in 250 c.c. of a mixture of 3 to 4 parts of water and 1 part of alcohol, and filter, or decant. If the solution to be titrated is heated when this indicator is used, the presence of free carbonic acid does not appreciably mask the change of color.

*The chromic acid cleaning mixture*:—To about 150 c. c. of warm water in a beaker add about 40 grams of ordinary powdered  $K_2Cr_2O_7$ ; when all the salt is dissolved, cool the solution and pour it slowly and with constant stirring into about 230 c.c. of  $H_2SO_4$ . When the mixture is cold transfer it to a 500 c. c., wide-mouth, glass-stoppered bottle; any portion of it once used for cleaning can be poured back into the bottle. Shake it up when about to pour it into a vessel to be cleaned, for the red crystals are the most effective part for cleansing purposes. As it is a strongly corrosive liquid, any of it dropped on the table should be at once washed off with much water. It is to be used only for cleaning glass ware that cannot be cleaned by ordinary treatment with water, or with a little hot  $HCl$ , and then with water; it is never to be used for cleaning beakers, flasks, or evaporators, unless they have had some organic matter in them, such as fat or oil, that water will not remove.

To clean a burette, put it mouth downward into the bottle containing the mixture, and, opening the ball valve in the rubber tube, slowly suck the liquid up, with as much of the red precipitate of chromic acid as possible, to within three or four centimeters of the rubber tube; on letting the valve close the liquid will stand at that height, and can be left undisturbed as may be desired, with the simple precaution to so support the burette that it cannot upset the bottle by its weight. On rinsing the burette out afterward, take off the rubber tube; the cleaning mixture should never come in contact with that.

To clean a pipette, attach a short piece of rubber tube to the mouth, and with the point in the cleaning mixture in the bottle,

cautiously draw the liquid up to the mark on the neck; then pinch the rubber tube tight while closing its open end with a short piece of glass rod.

*Ferric chlorid*.—For this solution use the ammonio-ferric chlorid, which is not so deliquescent as the ferric chlorid itself, dissolving 100 gms. in a litre of water.

*Ferrous sulfate*.—This solution should be freshly prepared; or if kept on the shelves it should be acidified with  $H_2SO_4$  (100 gms.  $FeSO_4$ , 500 c. c. water, 5 c. c.  $H_2SO_4$ ), and should always be kept acid, and have a little undissolved iron in it.

*Indigo solution*.—To 5 parts of fuming sulfuric acid, add *slowly* and with constant stirring one part of finely pulverized indigo, in a beaker immersed in cold water; let the mixture stand 48 hours, the beaker being covered, then pour it into twenty times its volume of water, mix and filter.

*Iodin solution*.—In 500 c. c. of water dissolve 18 gms. of potassium iodid, and then 7 gms. of iodin.

*Lead acetate and ammonium acetate*.—Acidify with acetic acid a mixture of equal parts of solution of lead acetate and a ten per cent. solution of ammonium acetate.

*Litmus solution*.—Boil the litmus three or four times with 85 per cent. alcohol, and finally filter. Wash the insoluble residue once with a little water, by decantation, and then digest it with hot water and filter. Divide this extract in two portions. Just barely acidify one portion with  $H_2SO_4$ , make the other portion very weakly alkaline with NaOH solution, and mix the two portions together. The solution will keep better if in a loosely stoppered bottle. A few drops of a solution of salicylic acid in 20 to 30 parts of alcohol added to 100 c. c. of the litmus solution will preserve it completely from mould.

*Magnesia mixture*.—Dissolve 100 grams of  $MgCl_2$  and 200 grams of  $NH_4Cl$  in 400 or 500 c. c. of water, add 400 c. c. of ammonia, sp. gr. .96, make the solution up to one liter, let stand several days in a closed bottle, and decant off the clear liquid from any precipitate that may have separated out.

*Phenyl-sulfuric acid*.—Dissolve one part of carbolic acid in four parts of  $H_2SO_4$ , and add two parts of water.

*Sodio-cobaltic nitrite*.—Dissolve 100 gms. of sodium nitrite in 300 c. c. of water, add acetic acid to feeble acid reaction, and 10 gms. of cobaltic nitrate; let the solution stand for several hours and filter if not clear. Since the reagent decomposes slowly, it is better not to make a large quantity at once. If it

loses its precipitating power for potassium, the addition of more sodium nitrite will restore its efficiency.

*Stannous chlorid*.—To a saturated solution of tin in hot **HCl** add four parts of water and a few pieces of granulated tin; the solution should always have an excess of tin and a slight quantity of free acid in it.

*As to the important matter of the purity of these reagents*, pure nitric and hydrochloric acids will be found on the reagent shelves, except that there may be slight traces of sulfuric acid in the latter, and of hydrochloric acid in the former; pure ammonia is supplied also. The quality of the other reagents will be as good as practicable, but the student should form the habit of testing them in cases where any impurities that they might contain, such as chlorid or sulfate, would affect his results. Fresenius gives, in his works on qualitative and quantitative analysis, a full account of the tests that should be made. It may sometimes occur that a reagent is not perfectly clear, in which case some of it should be filtered for use, especially in quantitative work.

## 151. TABLE OF ATOMIC WEIGHTS.

These atomic weights are taken from a revised table by F. W. Clarke, and issued December 6th, 1890; the rare elements are omitted. The full table, as stated by the revisor, "represents the latest and most trustworthy results, reduced to a uniform basis of comparison with Oxygen = 16."

NAME.	SYMBOL.	ATOMIC WEIGHT.	NAME.	SYMBOL.	ATOMIC WEIGHT.
Aluminum, . . .	Al	27.	Manganese, . . .	Mn	55.
Antimony, . . .	Sb	120.	Mercury, . . . .	Hg	200.
Arsenic, . . . .	As	75.	Molybdenum, . .	Mo	96.
Barium, . . . .	Ba	137.	Nickel, . . . . .	Ni	58.7
Bismuth, . . . .	Bi	208.9	Nitrogen, . . . .	N	14.03
Boron, . . . . .	B	11.	Oxygen, . . . . .	O	16.
Bromin, . . . . .	Br	79.95	Phosphorus, . . .	P	31.
Cadmium, . . . .	Cd	112.	Platinum, . . . .	Pt	195.
Calcium, . . . .	Ca	40.	Potassium, . . . .	K	39.11
Carbon, . . . . .	C	12.	Selenium, . . . .	Se	79.
Chlorin, . . . .	Cl	35.45	Silicon, . . . . .	Si	28.4
Chromium, . . .	Cr	52.1	Silver, . . . . .	Ag	107.92
Cobalt, . . . . .	Co	59.	Sodium, . . . . .	Na	23.05
Copper, . . . . .	Cu	63.4	Strontium, . . . .	Sr	87.6
Fluorin, . . . .	F	19.	Sulfur, . . . . .	S	32.06
Gold, . . . . .	Au	197.3	Tellurium, . . . .	Te	125.
Hydrogen, . . . .	H	1.007	Tin, . . . . .	Sn	119.
Iodin, . . . . .	I	126.85	Titanium, . . . .	Ti	48.
Iron, . . . . .	Fe	56.	Tungsten, . . . .	W	184.
Lead, . . . . .	Pb	206.95	Uranium, . . . .	U	239.6
Lithium, . . . .	Li	7.02	Zinc, . . . . .	Zn	65.3
Magnesium, . . .	Mg	24.3	Zirconium, . . . .	Zr	90.6

152.—TABLE giving grams of  $\text{NH}_3$  in 100 c.c. of solution of  $\text{NH}_4\text{OH}$ , of different specific gravity, at  $15^\circ \text{C}$ .

(Lunge and Wernik : Zeit. ang. Chemie, 1889.)

SPECIFIC GRAVITY.	GRAMS $\text{NH}_3$ IN 100 C.C.	SPECIFIC GRAVITY.	GRAMS $\text{NH}_3$ IN 100 C.C.	SPECIFIC GRAVITY.	GRAMS $\text{NH}_3$ IN 100 C.C.
.960	9.51	.932	16.81	.904	24.39
.958	10.03	.930	17.34	.902	24.94
.956	10.54	.928	17.86	.900	25.50
.954	11.07	.926	18.42	.898	26.05
.952	11.59	.924	18.93	.896	26.60
.950	12.10	.922	19.47	.894	27.15
.948	12.62	.920	20.01	.892	27.70
.946	13.13	.918	20.56	.890	28.26
.944	13.65	.916	21.09	.888	28.86
.942	14.17	.914	21.63	.886	29.46
.940	14.69	.912	22.19	.884	30.14
.938	15.21	.910	22.74	.882	30.83
.936	15.74	.908	23.29		
.934	16.27	.906	23.83		

153.—TABLE giving grams of  $\text{SO}_3$  in 100 c.c. of solution of different specific gravity, at  $15^\circ \text{C}$ .

(Lunge and Isler : Zeit. ang. Chemie, 1890. p. 129.)

SPECIFIC GRAVITY.	GRAMS $\text{SO}_3$ IN 100 C.C.	SPECIFIC GRAVITY.	GRAMS $\text{SO}_3$ IN 100 C.C.	SPECIFIC GRAVITY.	GRAMS $\text{SO}_3$ IN 100 C.C.
1.08	10.3	1.35	49.4	1.61	91.3
1.10	12.9	1.36	50.9	1.62	93.0
1.11	14.3	1.37	52.5	1.63	94.7
1.12	15.6	1.38	54.1	1.64	96.4
1.13	16.9	1.39	55.7	1.65	98.1
1.14	18.3	1.40	57.3	1.66	99.8
1.15	19.6	1.41	58.9	1.67	101.6
1.16	21.0	1.42	60.4	1.68	103.4
1.17	22.4	1.43	62.0	1.69	105.3
1.18	23.8	1.44	63.6	1.70	107.1
1.19	25.3	1.45	65.1	1.71	108.9
1.20	26.8	1.46	66.7	1.72	110.8
1.21	28.2	1.47	68.3	1.73	112.7
1.22	29.7	1.48	69.9	1.74	114.6
1.23	31.2	1.49	71.5	1.75	116.5
1.24	32.7	1.50	73.1	1.76	118.5
1.25	34.1	1.51	74.8	1.77	120.4
1.26	35.6	1.52	76.4	1.78	122.8
1.27	37.0	1.53	78.1	1.79	125.2
1.28	38.5	1.54	79.7	1.80	127.7
1.29	40.0	1.55	81.3	1.81	130.5
1.30	41.6	1.56	82.9	1.82	133.8
1.31	43.2	1.57	84.5	1.83	137.6
1.32	44.7	1.58	86.1	1.84	143.6
1.33	46.2	1.59	87.7		
1.34	47.9	1.60	89.5		

154.—TABLE giving grams of HCl in 100 parts of hydrochloric acid of different specific gravity, at 15° C. (Ure.)

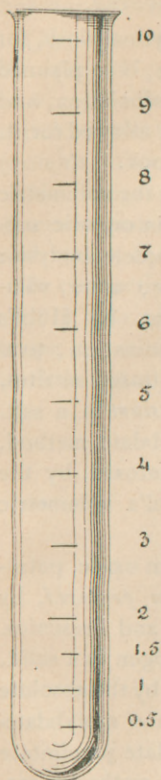
SPECIFIC GRAVITY.	GRAMS HCl IN 100 PTS.	SPECIFIC GRAVITY.	GRAMS HCl IN 100 PTS.	SPECIFIC GRAVITY.	GRAMS HCl IN 100 PTS.
1.0259	5.3	1.0859	17.53	1.1473	29.77
1.0298	6.12	1.0899	18.35	1.1515	30.58
1.0337	6.93	1.0939	19.17	1.1557	31.40
1.0377	7.75	1.0980	19.98	1.1599	32.21
1.0417	8.56	1.1020	20.80	1.1641	33.03
1.0457	9.38	1.1061	21.61	1.1681	33.85
1.0497	10.19	1.1102	22.43	1.1721	34.66
1.0537	11.01	1.1143	23.24	1.1762	35.48
1.0577	11.83	1.1185	24.06	1.1802	36.29
1.0617	12.64	1.1226	24.87	1.1846	37.11
1.0657	13.46	1.1267	25.69	1.1875	37.92
1.0697	14.27	1.1308	26.51	1.1910	38.74
1.0738	15.09	1.1349	27.32	1.1946	39.55
1.0778	15.90	1.1389	28.14	1.1982	40.37
1.0818	16.72	1.1431	28.95	1.200	40.78

155.—TABLE giving grams of  $N_2O_5$  and  $HNO_3$  in 100 c.c. of nitric acid of different specific gravities at 15° C.

(Lunge and Rey : Zeitschrift für angewandte Chemie, 1891, p. 16.)

SPECIFIC GRAVITY.	GRAMS $N_2O_5$ IN 100 C.C.	GRAMS $HNO_3$ IN 100 C.C.	SPECIFIC GRAVITY.	GRAMS $N_2O_5$ IN 100 C.C.	GRAMS $HNO_3$ IN 100 C.C.	SPECIFIC GRAVITY.	GRAMS $N_2O_5$ IN 100 C.C.	GRAMS $HNO_3$ IN 100 C.C.
1.02	3.3	3.8	1.19	31.5	36.7	1.36	67.1	78.3
1.03	4.9	5.7	1.20	33.3	38.8	1.37	69.8	81.4
1.04	6.4	7.5	1.21	35.1	40.9	1.38	72.5	84.6
1.05	8.1	9.4	1.22	36.9	43.0	1.39	75.3	87.9
1.06	9.7	11.3	1.23	38.7	45.2	1.40	78.3	91.4
1.07	11.3	13.2	1.24	40.7	47.5	1.41	81.6	95.2
1.08	12.9	15.1	1.25	42.7	49.8	1.42	84.9	99.1
1.09	14.5	16.9	1.26	44.7	52.1	1.43	88.5	103.2
1.10	16.1	18.8	1.27	46.7	54.4	1.44	92.1	107.5
1.11	17.7	20.7	1.28	48.7	56.8	1.45	96.1	112.1
1.12	19.5	22.7	1.29	50.8	59.3	1.46	100.1	116.8
1.13	21.1	24.6	1.30	52.9	61.7	1.47	104.5	121.9
1.14	22.8	26.6	1.31	55.1	64.3	1.48	109.2	127.4
1.15	24.5	28.6	1.32	57.3	66.9	1.49	114.4	133.5
1.16	26.2	30.6	1.33	59.7	69.7	1.50	121.0	141.1
1.17	27.9	32.6	1.34	62.1	72.5			
1.18	29.7	34.7	1.35	64.5	75.3			

156. *Comparison of measures and weights.*



Directions are often given, especially in the qualitative work, to add a certain volume of a liquid to a substance or solution under treatment. The adjoining figure represents the actual size of the 10 centimeter test-tubes usually issued to the students in the author's laboratory; with the aid of this graduation in cubic centimeters, a close approximation to any desired quantity of liquid is easily made.

APPROXIMATE RELATIONS BETWEEN ENGLISH AND METRIC WEIGHTS AND MEASURES.

1 Kilo. equals	2.2 lbs. av.	1 lb. av. equals	454 grms.
1 Gram "	15.4 grains.	1 grain "	64.8 mgms.
1 Gram "	0.035 oz. av.	1 oz. av. "	28.35 grms.
1 Liter "	2.1 pints.	1 quart "	946 c.c.
1 Liter "	33.8 fluid oz.	1 fluid oz. "	30 c.c.
1 Meter "	39.4 inches.	1 inch "	2.54 cm.

$$\frac{\text{Inches} \times 5}{2} = \text{centimeters.}$$

$$\frac{\text{Centimeters} \times 2}{5} = \text{inches.}$$

## COURSE OF LABORATORY WORK IN CHEMISTRY.

157. The following course of quantitative analytical work, for special students of chemistry at Cornell University, is so planned as to give practice in the greatest variety of manipulation, and also of difficult processes, as is possible in the time allowed for it. It follows the introductory course given in this book.

(1) *Limestone*, complete analysis. (2) Sugar by the volumetric and by the gravimetric method. (3) *Nitrogen* in organic substances, by the Kjeldahl method. (4) *Milk*, complete analysis: total solids, fat, sugar, proteids, ash. (5) *Butter*; water, volatile and insoluble fatty acids, iodine equivalent, by Hübl's method, melting point. (6) *Water*, sanitary examination; total solids, free and albuminoid ammonia, chlorids, nitrates, nitrites, oxygen consumed, oxygen dissolved. (7) *Potassium* in a salt. (8) *Phosphorus pentoxid* in a salt, by the molybdate method. (9) *Urine*; urea by hypobromite, phosphorus pentoxid, by the volumetric uranium method, chlorine by Volhard's volumetric method.

(10) *Feldspar*, complete; silicic oxide, aluminum oxide, potassium oxide, calcium oxide, etc. (11) *Nitrogen pentoxid*, by modified Kjeldahl method, by method of Pelouze and Fresenius. (12) *Organic ultimate* analysis; carbon and hydrogen in a solid, and in a volatile liquid; sulfur, chlorine: nitrogen by the absolute method. (13) *Iron and steel*; phosphorus by the molybdate-magnesia method, and by titration of the molybdate precipitate with permanganate; manganese, by the Williams method; carbon, by the chromic acid method. (14) *Chemical toxicology, inorganic*; detection and determination, in a mixture with organic matter, of arsenic, and one other substance from the following list: antimony, lead, copper, mercury, cyanogen, phosphorus.

(15) *Chemical toxicology, organic*; detection, in mixture with organic substance, of two alkaloids selected from the following list: atropine, aconitine, brucin, coniine, morphine, narcotine, nicotin, strychnin, veratrin. (16) *Tannin* in tanning materials, or *indigo*, analysis for valuation; by two methods. (17) *Alloys*, two from the following list: type metal, solder, bronze, Wood's metal, tin and lead, bismuth and lead, phosphor bronze. (18) *Complete analysis of two minerals* selected from the following list: beryl, chromite, franklinite, cassiterite, sphalerite, chalcopyrite, wavellite, celestine, bornite, stibnite, molyb-



denite, lepidolite, rutile, fahlerz, strontianite, wolframite, petalite, boronatrocalsite.

(19) *Separations*; nickel and cobalt; arsenic, antimony and tin. (20) *Wine, or tobacco, or food substance*, complete analysis; in wine, alcohol, extract, sugar, free acid, tannin, glycerine; in tobacco, nicotin, nitrate, ammonia; in food or fodder, ash, proteids, ether-extract, fiber, nitrogen-free extract, non-albuminoid nitrogen. (21) *Analysis by electrolysis*; separation and determination of copper and manganese, copper and lead, copper and nickel, antimony and tin.

In connection with this work, and partly following it, instruction is also given in gas analysis, and the use of the microscope, spectroscope, colorimeter, polariscope, and refractometer, in chemical analysis.



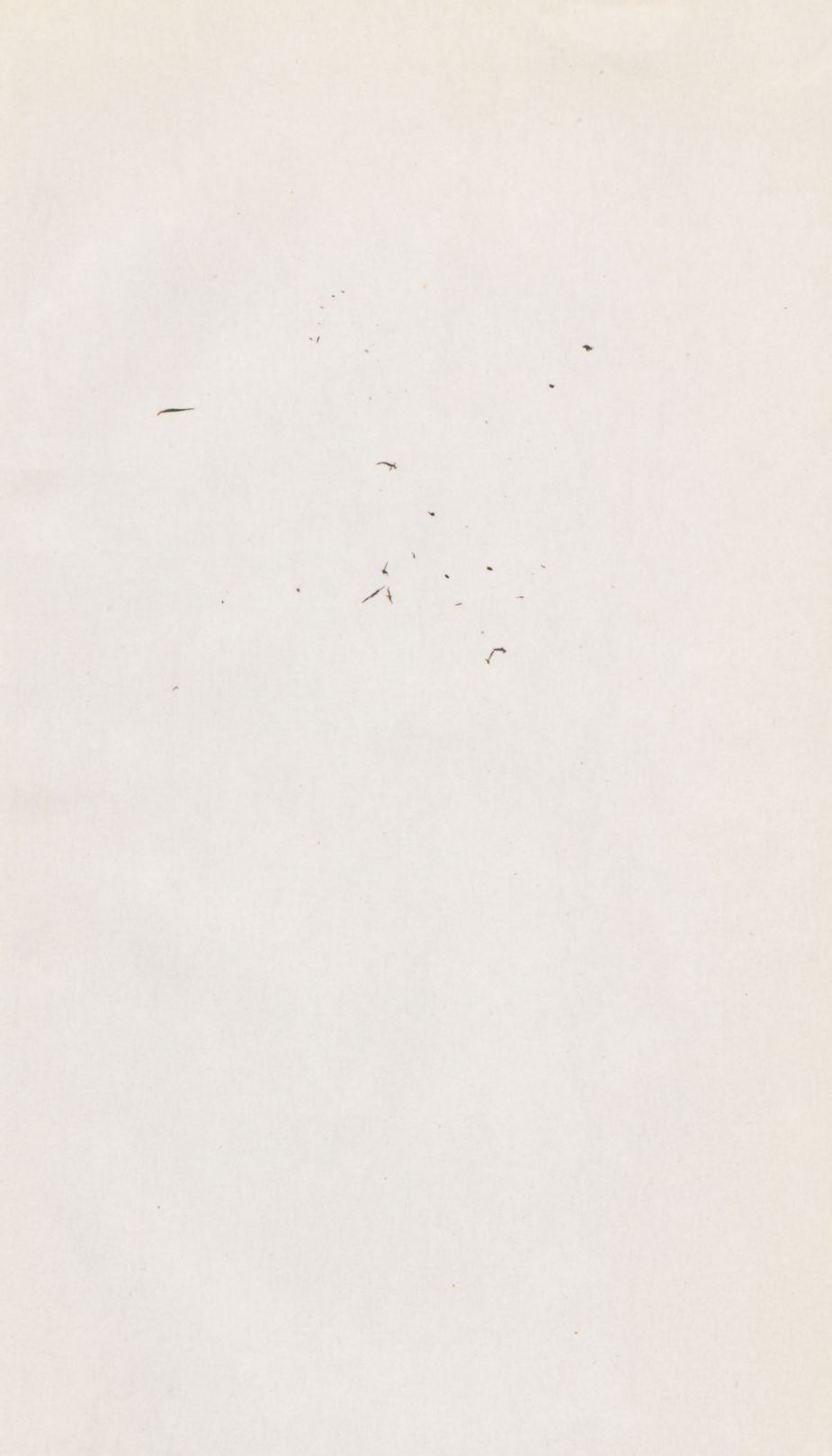
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