ANALYTICAL CHEMISTRY

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PREFACE

In a systematic course of chemical study the analytical branch of the science is given a sharply-defined position. The student learns from general, so-called inorganic, chemistry, the nature of chemical phenomena, the properties of the elements and their compounds, and the regularities and laws by which their interaction is governed. To fit himself for a deeper and independent occupation with the science he must learn how to value the facts acquired in his study of general chemistry; the methods of experiment upon which chemistry, as an experimental science, is based, must be understood; and the ability to think chemically, *i.e.*, to draw logical conclusions from observed phenomena, must be attained. Analytical chemistry, in thoroughly illustrating the important phenomena which enable the qualitative detection and quantitative estimation of the elements in any of their almost innumerable compounds, is a great aid in reaching this point. After its methods have been acquired, the student can turn to organic, and finally to physical chemistry, and terminate his systematic study of the science with that of the latter branch.

It must be remarked that analytical chemistry, instead of being assigned the above position among the various branches of the science, is often commenced at the same time as general chemistry. In view of the end for which it is pursued, however, its study demands that the student be as self-reliant in his work as possible. The practical analytical operations can in no other way attain their proper importance as a means of instruction, or assume their proper value. The student cannot rightly turn to analytical chemistry until he has obtained a thorough preparation in the general science; and his knowledge of the latter is measured, not by the number of single and isolated facts with which he is familiar, but by the clearness with which he understands the fundamental chemical phenomena and theories. For these reasons I strongly advise the beginner not to devote himself too quickly to analytical chemistry, and my advice is justified by the character which its study must assume if it is to be of value.

If the above conclusions are correct, the practice of chemical analysis must be pursued in the same way as purely scientific investigations. The chemist proves the correctness of an induction in the latter by means of suitable experiment, in obtaining the best possible conditions for which he must be governed by analogy. The same method of procedure should be adopted by the analytical student, in continually proposing questions to himself and answering them by means of properly selected experiments. In analytical chemistry the formation of such questions, and the methods by which they are experimentally solved, are presented in clear and definite form. This method of studying is so important in its bearing upon the chemical training, that it will be well to show how to apply it in the daily analytical work of the laboratory.

The elements, in accordance with their chemical properties, are divided in this book into the customary two classes, metals and metalloids—a classification which is most advantageous for our purpose. In studying the methods for detecting the metals the student is at first confronted only by the simplest questions, and the passage to more complicated cases is gradual. For this reason the laboratory work is preceded by the study of the properties of the metals and their compounds. The questions put to the student he must work out independently, by the intelligent employment of such characteristics of the metallic compounds as are suitable for the purpose. In studying the methods for the detection of the metalloids, the opposite course is taken. The student first meets complicated questions, and learns only subsequently how to simplify them and to finally arrive at their solution.

The metals are divided into groups according to the properties and certain methods of formation of their sulphides. The explanation of the methods for detecting each metal is preceded by that of the properties of such of its compounds as are important in analysis. A thorough acquaintance with the latter, as well as their intelligent use in solving the problems of analysis, is of the greatest importance. Consistently with the character of the questions which arise in the detection of the metals, the properties of the important compounds of any metal must be studied not only alone, but also in comparison with those of the corresponding compounds of other metals of the same group. The consideration of the properties of each element is accordingly arranged in a separate chapter, under the title "Special Reactions." In the "General Reactions," on the contrary, the corresponding compounds of all the metals of a group are studied, and the conditions necessary for the separation of one group from another deduced.. The general reactions are placed before the special—an arrangement necessitated by the fact that, in addition to the analogous compounds of the metals of each group, the discussion on the general reactions includes that of practical methods employed for the separation and detection of many of the metals, and also the theoretical demonstration of important reactions. The "Special Reactions" include those which are necessary for the detection of the respective single metals. The rare metals are not included in the general scheme of exposition, but have been given a place in the supplements of the proper groups. Our knowledge concerning these rare metals is so incomplete, that their practical study in the laboratory affords the student but little advantage.

The separation of groups is explained in the same way as that of single elements from one another. The properties of analogous compounds, and the analogous reactions of the metals of the different groups, are discussed, and the best means of separation logically derived by their combination. This is the most difficult problem presented to the student in studying the metals.

On passing to the metalloids, he will find this method reversed. The special reactions of these elements and their compounds are first considered, and the complicated methods for detecting them when occurring together taken up only when the study of their individual reactions has been finished.

These general statements concerning the course to be pursued in the study of qualitative analysis can also be applied to that of quantitative, the methods of separation and determination used in the latter being likewise deduced from the properties of the compounds which have the most analytical importance. It may here be remarked that the qualitative methods of *separation*, which are usually based upon the same reactions as the quantitative, also require from the student the greatest degree of care and precision.

Although the method of exposition which I have adopted in this book has been extended to the discussion of quantitative, as well as of qualitative analysis, the beginner must at first confine himself strictly to the latter. His first object is to make himself familiar with the simplest experimental methods of chemical investigation, and, furthermore, to learn how to answer clearly and rightly the questions which arise in his work; and for this purpose qualitative analysis is much the more important of the two. When its methods have become thoroughly familiar to him he may pass to quantitative analysis, in which he will find the same principles used, and there accustom his hand to accurate work.

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PART FIRST

QUALITATIVE ANALYSIS

INTRODUCTION

§ 1. **Object of Analytical Chemistry.**—Analytical chemistry is the study of the methods of determining the nature and quantitative relations of the constituents in chemical compounds (artificial or natural) and their derivatives. It divides, according to the character of the problems presented, into qualitative and quantitative analyses; the former determining the nature, the latter the amount of the element or elements in a substance. The analytical methods are based upon the properties of the elements and certain of their compounds, and upon the behaviour of the compounds of different elements to each other. This being so, and as analytical chemistry simply teaches which properties are to be employed, it is inseparably connected with general chemistry, and is in fact a subdivision of the latter. The distinction between quantitative and qualitative analyses is also more or less one of convenience, as is obvious when we consider that the study of the properties of chemical compounds yields the methods employed in both. The beginner should first turn his attention to qualitative analysis alone, as the manifold conditions upon which quantitative estimations depend can be much better understood after the other branch has been mastered.

§ 2. **Reactions.**—When elements or their compounds are brought into interaction a *Reaction* is said to take place. Reactions occur between substances in solution (in water or other liquids), or which melt when subjected to a high temperature. The latter class of reactions is called "Analysis in the dry way," in distinction to "Analysis in the wet way," a term which is sometimes used to designate reactions which take place between substances in solution. In the usual course of analysis both kinds are used. Those which are employed in qualitative work must have easily distinguishable characteristics; for example, the formation of insoluble bodies from soluble ones, *i.e.*, the formation of a precipitate; the solution and consequent disappearance of a precipitate; the escape of gases or vapours, which may sometimes be coloured, or possess odour; the colouring of a solution, or the disappearance of its colour, etc. The substances which bring about these changes or reactions are called "Reagents." A reagent which causes an especially marked change, such as the above, is called a *characteristic reagent;* the change involved, a *characteristic reaction.* Starch-paste, for instance, is a characteristic reagent for iodine, being turned in its presence to a dark blue liquid; the reaction between these two substances is a characteristic reaction. If but a very small quantity of the substance need be present to show the reaction, the latter is called *delicate;* and the reagent a *delicate* reagent. Starch-paste is a delicate reagent for iodine, since even a minimal quantity of one or the other will cause the blue coloration. This relation between the two classes of reactions is not universal, however, for the characteristic reagents are often not the most delicate, and the latter may not be characteristic. As the reagents and reactions must satisfy one or both of these conditions, only a few of the great number of chemical compounds known can be used to characterise the various elements.

Conditions of Reaction.—The reciprocal action between chemical compounds is dependent upon many conditions. A reaction proceeding in a certain direction at a given temperature may take a very different course at another; the influence of a third body may often modify, or even entirely suppress it, etc. *Every reaction therefore depends upon definite conditions, and the normal conditions, under which it proceeds in the required direction, must be known. The conditions of reaction are determined by the properties of the compounds which act upon one another and result from this action.* In studying the various reactions, therefore, the properties of both the reacting and the resultant compounds must be closely observed. This is absolutely necessary to ensure the fulfilment of the conditions and, consequently, the proper course of the reaction. An experiment which miscarries always indicates that these properties have not been heeded, and the conditions of reaction only partially, or not at all obtained. Since the analyst is compelled to bring about a reaction under the most varied conditions, he must know how to convert the unfavourable ones into those necessary for the success of the experiment. The connection between the reactions and their conditions may be illustrated by the action of tartaric acid upon potassium salts. In this reaction the precipitate of acid potassium tartrate characteristic of potassium is to be obtained. But since this compound can exist only in neutral solutions, the conditions necessary for its formation are not present if the solution contains any free mineral acid. In such a case the conditions must be modified before the test is performed, *i.e.*, the solution must be neutralised. This is a condition resulting from the properties of acid potassium tartrate. The same method of study should be extended to all the reactions used in analysis, and the student must learn exactly the properties of the compounds which he uses or obtains in his experiments.

Confirmatory tests.—This knowledge of the characteristics of the compounds employed, which is necessary in determining the normal conditions of reaction, is also required in devising tests by which to control the results of an experiment. These *confirmatory tests*, as they are called, are made in order to ascertain whether the reaction has really taken place in the desired direction, and the expected compound been obtained. Such tests are especially useful in the analysis of unknown compounds, where there is no other guarantee that the conditions of reaction have been fulfilled. A confirmatory test is made by examining the compound obtained, to ascertain whether it actually possesses the characteristic physical and chemical properties (crystallographic form, behaviour toward other substances, etc.) of the compound which it is supposed to be. Although the slightest indication of these properties suffices for the experienced analyst, the beginner, to whom they are less familiar, must resort to confirmatory tests for their identification. The methods of employing the latter vary greatly, according to the characteristics of the compounds, so that a general discussion of their nature is impossible; their principle, however, may be seen in the following example:—If a barium salt, the nitrate for instance, be added to a solution of sulphuric acid, it causes a white precipitate of barium sulphate, which is soluble in neither water nor dilute acids. The barium salts, therefore, serve for the detection of sulphuric acid. Assume that an acid solution has been treated with barium nitrate, and a white precipitate obtained. This precipitate may or may not be barium sulphate; for, under certain circumstances, barium nitrate may itself be precipitated from an acid solution which contains *no* sulphuric acid—it gives, for example, a white precipitate with concentrated nitric acid. The formation of a precipitate, therefore, does not establish the presence of sulphuric acid, and a confirmatory test must be resorted to. Barium nitrate, though insoluble in strong nitric acid, differs from the sulphate in dissolving readily in water or the dilute acid. The effect which the addition of water has upon the precipitate should, therefore, be ascertained. If it still remains undissolved it must be the sulphate, and the presence of sulphuric acid in the solution examined is proved by the *two* tests.

Combination of reactions (systematic plan of analysis).—We now understand the nature of individual reactions, and the necessity of exact knowledge of the properties of the compounds, without which it would neither be possible to secure the correct conditions, nor to make confirmatory tests. Qualitative analysis is not limited to the study of these reactions alone. An element can be characterised by its special reactions only when in an isolated state; when several are present at once, the reactions of the one may be hidden or prevented by the influence of another, and the proper conditions for individual reactions can rarely be obtained. The various reactions must, therefore, be combined into a system which permits the detection of any element when others are present. For this purpose the elements are arranged in groups, the course of study being to first consider the members of each group alone, then those of all the groups and subdivisions together. Here the problems of qualitative analysis, solved by the study of reactions and their combination, may be brought to an end.

§ 3. **System of Exposition.**—The student, whose familiarity with general chemistry and the natural system of the elements and their compounds is presupposed, meets in analytical chemistry an artificial classification. This arrangement is based upon the *analytical* characteristics of the elements, *i.e.*, upon those which best aid the solution of analytical problems. A classification of this nature may depend upon any suitable properties and reactions of the different elements and compounds, though the most convenient are the characteristics and certain conditions of formation of the sulphides. Such conditions are found in the action of ammonium sulphide and hydrogen sulphide on the solutions of different elements. The term "Metal" denotes, analytically, a class of elements to which belong all the actual metals, and also those of the other elements which form sulphides with hydrogen sulphide (arsenic, selenium, tellurium), or hydroxides with ammonium sulphide (chromium, etc.) The second class embraces the remaining elements, which are called metalloids. Their sulphides are not precipitated by hydrogen sulphide, or ammonium sulphide, and are usually decomposed by water. These two classes are divided, according to the analytical behaviour of their members, into several groups. The latter are often the same as in the natural system, but sometimes include dissimilar elements which have a similar analytical behaviour.

The classification of the chemical facts with which we shall be occupied must also be considered. The properties of each group of elements are studied according to their application in qualitative or quantitative analysis. Observation of the properties and reactions of any one element enables its detection when alone. When several elements enter into the substance to be examined, however, a combination of reactions is necessitated, as the proper tests can be made only after their separation. Each element must therefore be studied from two sides. For its *special reactions*, it must be studied by itself. To simplify the combination of reactions, a comparative examination of analogous compounds of metals of the same, or of different groups, is required. These are called *general reactions*.

The methods to be used in any problem in qualitative analysis will be clearly pointed out during the course of study pursued in this manner.

§ 4. **Plan of Practical Work.**—The practice of analytical chemistry involves the same principles as have been discussed in the foregoing paragraphs. *The basis of practical work in the laboratory is likewise the study of the properties and reactions of compounds; together with all deductions made in the course of the analysis, whether it be quantitative or qualitative.* Practice is most conveniently commenced with the simplest group—that of the alkali metals. Each metal must be studied both alone and in comparison with other members of the same group. The discussion begins with the general reactions and consideration of analogous compounds of the different elements, and is given the character of a study, in which the student must form and answer the problems himself. The questions arising may be presented in this form. A property of a compound has been studied which is to be used, for example, in the detection of an element. How is it to be employed?—in other words, what conditions of reaction does this characteristic demand? As acid potassium tartrate, for instance, is more soluble in hot than in cold water, what condition must be fulfilled in order to obtain the salt as a precipitate? This property requires that the reaction be performed in the cold. The study of the properties of the compounds entering into and resulting from a reaction points out the necessary conditions of reaction; *i.e.*, it shows how to obtain the reaction under the most varied circumstances. The importance of this result is still greater if the student has made his own deductions and obtained the conditions of reactions himself. He must nevertheless prove, by a confirmatory test, in which he compares the physical or chemical properties of the two, that his deductions were correct, and the body sought for actually the one produced. To simplify the formation and solution of such problems, the first two groups are in this regard thoroughly discussed. The remaining groups are given a more concise and systematic treatment, under the assumption that the student has become fairly proficient in his work by the time they are reached.

The study of the general and special characteristics of the metals of the first group should be followed by a series of exercises involving the detection of all its members in the presence of each other. This requires a combination of the properties of various compounds and of the conditions of many reactions. The detection of potassium in presence of sodium and ammonium, for instance, necessitates that several reactions be combined into a systematic course of analysis, in which their order is consistent with the properties of the metals, and the latter are isolated and detected one by one. The student, aided by the hints given at the close of each group, must elaborate this systematic course himself. The separation of any metal must also be followed by a confirmatory test, to prove the correctness of the reaction. The student can test the system which he has devised by following it in the analysis of a known mixture of the metals of the first group. After this substantiation he may use it in the analysis of unknown mixtures. The study of the first group is followed by that of the second and third, etc., in which the combination of reactions extends not only to single elements, but also to entire groups, and is much more complicated. A systematic course of analysis for all the metals of all groups is thus finally derived. After the metalloids have been studied in the same manner, the analysis of insoluble compounds, the most difficult of all, is to be taken up. The third section of this book contains rules and methods for this purpose, which are likewise derived from observation of the properties of compounds. With this the exercises in qualitative analysis terminate.

Since in this way the entire course of work is arranged in exercises, the performance of which is left to the student, it should be remarked that the path to the correct solution of the problems is sharply defined. This accuracy and the systematic solution of the exercises have great instructive value. The student becomes accustomed to compare the properties of the different compounds, to derive the right conditions of reaction, and to combine them. The mental processes involved can be expressed by two words: Analytical chemistry teaches the art of *chemical thought*, which is the most important object of practical work. The accuracy of the methods, that is, their relative simplicity, has a greater or less disadvantage in often leading the student into the habit of mechanical instead of thoughtful work. Mechanical study affords no benefit whatever; nor can it in a single instance teach how to make a correct analysis, to say nothing of developing the faculty of chemical thought.

After the analytical methods have been observed in qualitative analysis, the student may turn to the quantitative branch. The latter, the passage to which must be governed by his progress, is chiefly valuable as a means of giving him the experience in exact work which qualitative analysis may not afford.

SECTION I

THE METALS

§ 5. Division of the Metals into Groups. — Analytical chemistry classifies the elements according to certain reactions in the formation of their sulphides, and with regard to the stability or instability of these compounds when acted upon by water. By the term "Metals" we indicate the elements, the sulphides of which are not decomposed by water, but are either soluble or insoluble in it. Sulphides of the latter class are formed by the action of hydrogen sulphide or ammonium sulphide upon any soluble compounds of the metals. To the metals proper we add the elements which are precipitated as oxides by ammonium sulphide, although they form no sulphides through its action. The metals are divided, according to the solubility of their sulphides, into two classes: the first comprising those the sulphides of which are soluble in water; and the second, those which give insoluble precipitates with sulphuretted hydrogen or ammonium sulphide. No salts of the first class are thrown down by these reagents.

A. **Metals, the Sulphides of which are soluble in Water.**—The division of this class into groups is based, not upon the sulphides, but upon the properties of their carbonates and phosphates.

First Group: Potassium, Sodium, Ammonium, Rubidium, Cæsium, and Lithium.—The sulphides of this group of metals are soluble in water, and there is no general reagent by which they are precipitated in the form of insoluble compounds.

Second Group: Barium, Strontium, Calcium, Magnesium.—Their sulphides are soluble and their carbonates insoluble in water. Ammonium carbonate is the general reagent of the group. It throws down all these metals as their carbonates.

B. **The metals, the sulphides of which are insoluble in water,** form three groups. To distinguish them, we use the behaviour of their sulphides (or hydroxides) toward weak acids and ammonium sulphide.

Third Group: Aluminium, Chromium, Beryllium, Yttrium, Zirconium, Thorium, Cerium, Lanthanum, Didymium, Erbium, Titanium, Tantalum, Niobium; Iron, Manganese, Zinc, Nickel, Cobalt, Uranium, Indium, Thallium, Gallium.—As far as, and including, niobium, they form no sulphides by the wet way, but from iron on they have sulphur compounds which dissolve in dilute acids to the salts of the acid used. They are not precipitated from an acid solution by hydrogen sulphide, but ammonium sulphide throws down the sulphides or oxides, and these are insoluble in excess of the reagent. Ammonium sulphide is the general reagent of this group.

Fourth Group: Silver, Mercury, Lead, Bismuth, Copper, Cadmium, Palladium, Ruthenium, Rhodium, Osmium.—The sulphides are insoluble in dilute acids, are precipitated from acid solution by hydrogen sulphide, and are insoluble in ammonium sulphide. Hydrogen sulphide in acid solution is the general reagent of this group.

Fifth Group: Gold, Arsenic, Tin, Antimony, Platinum, Iridium, Vanadium, Tungsten, Molybdenum, Selenium, Tellurium.—The sulphides of this group are likewise insoluble in dilute acids, and are thrown down from an acid solution by hydrogen sulphide. They are distinguished from the sulphides of the fourth group by their solubility in ammonium sulphide,—to thio-salts soluble in ammonium sulphide (compounds of ammonium sulphide and metallic sulphides).

GROUP I

POTASSIUM, SODIUM, AMMONIUM (CÆSIUM, RUBIDIUM, LITHIUM)[1]

The analytical definition of the metals of this group is as

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[1] Metals of this and the following groups in parentheses are the rare elements. In the general scheme they will be only slightly considered, but are especially described in the Supplements.

follows: The metals of the first group are distinguished by the solubility of their sulphides and carbonates. This group has no general reagent.

§ 6. **The Alkali Metals and their Compounds.**—Let us first recall the most important properties of these metals, in order to be able to choose from among the compounds described below those to be used for their qualitative recognition.

The metals of the first group, metals of the alkalies, or the alkali metals, are distinguished by their extraordinary affinity for other elements. They unite directly with the halogens, and displace other metals, and some metalloids, in their compounds. (This is the case with aluminium, magnesium, silicon, boron, uranium, etc.) The difficulties presented in separating them from their compounds do not permit us, however, to apply these properties to their detection.

The oxides.—The alkali metals decompose water at the ordinary temperature, setting hydrogen free and forming hydroxides (caustic alkalies) soluble in water. Their solutions show an alkaline reaction, turn red litmus paper blue, and turmeric paper brown.[1]

The Salts.—The alkali metals displace the hydrogen of acids atom for atom, and thus give for every acid as many series of salts as there are atoms of metallic hydrogen in the acid. With polybasic acids they form either neutral or acid salts, the latter term denoting compounds in which the hydrogen is not completely displaced by the metal. In relation to litmus paper, we say that the saturation of the acid in an alkali salt is complete —the salt neutral—when blue litmus paper, treated with a very weak acid, and thus changed to violet, undergoes no alteration in colour in its solution; as, for instance, in that of potassium chloride, or sulphate. If a drop of a weak solution of caustic alkali be added to that of a neutral salt, the paper will become blue; if a drop of weak acid, the paper changes to red. In some cases we use litmus tincture instead of the

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[1] Litmus contains a certain organic acid (litmus acid), which dissolves in water to a red liquid, but the salts of which are blue. Litmus paper is coloured with the red solution of litmus acid, or with the blue solution of one of its salts. The effect of any acid upon the blue paper is to redden it, and this is therefore used to detect acids; while, by the action of alkalies upon the red paper, a blue salt is formed. The cause of the colouring of turmeric by alkalies is not yet fully understood. Many other substances have of late been applied in testing for alkalies and acids, such as cyanine, rosalic acid, phenolphthalein, etc.

paper. If weak sulphuric acid is added to a solution of caustic alkali which is coloured blue by litmus, the colour will remain unaltered until a sufficient amount of acid has been added to form the neutral sulphate; at this point the blue solution becomes violet (neutral reaction), and on the addition of a single drop more the liquid becomes red (acid reaction). This reaction is very delicate. The salts of the alkali metals with weak acids, such as the carbonates, acetates, etc., show an alkaline reaction, turning red or violet litmus paper blue. Almost all salts of the alkali metals are soluble in water, and some of them are very characteristic. The sulphates unite with other sulphates, of the general formula $R_2(SO_4)_3$, where R equals Al, Cr, Fe, Mn, to form double salts called alums: these usually crystallise in octahedra, and contain twelve molecules of water. The formula for aluminium alum, for instance, is $KAl(SO_4)_2 + 12H_2O$. The double salts of the chlorides with platinum chloride, having the general formula R_2PtCl_6, in which R signifies an alkali metal, also crystallise well. The acid tartrates, of the formula $C_4H_4O_4(OH)(OR)$, are also characteristic. The ammonium salts are sharply distinguished from those of the alkali metals, in being volatile at a relatively low temperature (300°-400°) and easily generating ammonia through the action of oxides.

We now turn to the study of the compounds of the alkali metals which are used in analysis. Following the methods given in §§ 2, 4, and 5 of the Introduction, let us begin with the study of the properties of these compounds, and observe the conditions which the single reactions require. Having finished the study of these reactions, both general and special, we will take up their combination, in order to form a scheme for analysis. Before we apply ourselves to the practical consideration of the general and special reactions, the student should be advised to make himself acquainted with them by reading and thinking, and to go to the laboratory desk with the plan for his day's work already formed. Every experiment must be made with the view of attaining a definite end, an answer to the questions suggested by the experiments. Aimless experiments are absolutely harmful; and it is only when the student works as independently as possible that the study of analytical chemistry can bring the returns which will enable him to attain the higher aims of our science.

Remark.—All the reactions described below are brought about between dissolved salts of the alkali metals and the reagents, both being used, as a rule, in 10 per cent solutions. It is still better for beginners to employ what are known as "Equivalent Solutions," *i.e.*, those which hold in a liter equivalent quantities of the acid and alkali respectively. The advantage of using such solutions lies in the fact that equal volumes of the interacting liquids are requisite for the reactions, and the student can thus judge correctly respecting the amount to be taken, and not, as is usually the case otherwise, employ an undue excess of the precipitant. The action of the reagent is observed in a test-tube ; and before a test the tube must be washed with distilled water, and be absolutely clean. The use of reagents for the qualitative investigation of metals is founded, in the great majority of cases, upon the formation of insoluble or difficultly soluble compounds, which are thrown down as *precipitates* by the action of the reagent upon the solution of the given metal. These precipitates are distinguished from each other either by their colour or their physical properties. We call a precipitate *crystalline* when it forms in fine granules and settles rapidly to the bottom of the vessel: a precipitation of this kind may not occur at once, but occasionally takes some time. It may, in some cases, be hastened by stirring the solution with a glass rod, or scratching the latter against the sides of the vessel, and by certain other operations. Placed under the microscope, crystalline precipitates show a regular construction, while *amorphous* precipitates, on the contrary, exhibit no definite form, are thrown down immediately, and in most cases settle more slowly than those of the first class. The characteristics of the third class, *gelatinous* precipitates, are fully indicated by their name. If but a slight precipitate is formed, and this is so fine that it does not deposit, though at the same time the solution is not quite opaque, we speak of it as being *turbid.*

General Reactions

To learn the general reactions, let us study the properties of those corresponding compounds of the alkali metals which enable the separation of the metals from one another and their recognition.

§ 7. The Acid Tartrates.—The composition of tartaric acid is expressed by the formula $C_4H_6O_6$. Since metals can be substituted for only two of its hydrogen atoms, it is dibasic, and contains two acid hydroxyl groups, possessing, more exactly, the formula $C_4H_4O_4(OH)_2$. Two classes of its alkali salts are known, one of them neutral, as $C_4H_4O_4(OK)_2$, and one acid, as $C_4H_4O_4(OH)(OK)$. Although the neutral salts are easily soluble and cannot be obtained as precipitates, of the other variety the salts of potassium and ammonium, $C_4H_4O_4(OH)(OK)$ and $C_4H_4O_4(OH)(ONH_4)$, dissolve less readily than the acid sodium and lithium salts. We are thus in position to detect potassium and ammonium in presence of sodium and lithium by means of the acid tartrates.

Properties of acid potassium tartrate.—The use of tartaric acid as a reagent for potassium is based upon the formation of the acid salt, $C_4H_4O_4(OH)(OK)$. The reaction takes place according to the following equation:

$$KCl + C_4H_4O_4(OH)_2 = C_4H_4O_4(OH)(OK) + HCl.$$

The salt is usually obtained in the reaction as a white crystalline powder, a result of its rapid formation (by slower crystallisation it is procured in prismatic crystals of the rhombic system). We must make ourselves acquainted with those of its properties which find an application in analysis. In consideration of the fact that we are at first to be engaged with the simplest analyses, those of solutions, and that these can show an alkaline, neutral, or acid reaction, let us turn to the study of the relations which acid potassium tartrate bears to water, alkalies, and acids. It may not be superfluous to remark that we must, for the same reasons, learn in every reaction the relations to these substances. At the usual temperature (exactly at 10° C.) one part of acid potassium tartrate requires 250 parts of water, but at 100° only 15 parts, for its solution. Alkalies and their carbonates dissolve the precipitate, forming easily soluble neutral salts:

$$C_4H_4O_4(OH)(OK) + KOH = C_4H_4O_4(OK)_2 + H_2O,$$
$$2C_4H_4O_4(OH)(OK) + K_2CO_3 = 2C_4H_4O_4(OK)_2 + H_2O + CO_2.$$

By the action of the carbonates, as we find from the equation, carbon dioxide is liberated. Mineral acids also dissolve the salt, decomposing it with formation of free tartaric acid and the salt of the acid employed:

$$C_4H_4O_4(OH)(OK) + HCl = C_4H_4O_4(OH)_2 + KCl.$$

REMARK.—The properties of acid potassium tartrate described must be studied by experiment. Dissolve a little tartaric acid in a small flask: heat can be used for its solution, but the experiments, on the contrary, must be made with the well-cooled acid. Partly fill a number of test-tubes with the solution of a potassium salt (KCl, KNO_3), and then add to each an excess of tartaric acid. The formation of the precipitate can be hastened, if necessary, by mixing with a glass rod. Having observed the external form of the acid potassium tartrate obtained, make the following tests:

1. Warm one of the test-tubes, to examine the solubility of the precipitate in hot water. It dissolves.
2. Add to one portion of the cold solution, alkali, and to another, potassium carbonate. The precipitates dissolve in each case.
3. Test with an acid, such as hydrochloric. The precipitate dissolves.

The conditions of the reaction between tartaric acid and a potassium salt are, as we see, determined by these experiments.

Conditions of reaction.—(1) Having observed the solubility of acid potassium tartrate in water, we know that the experiment must be made with concentrated solutions, both of the tartaric acid and the substance to be examined. If the solution at hand is dilute, therefore it must be strongly concentrated. The precipitation may sometimes be aided by stirring with a glass rod, and, further, in result of the greater insolubility of the acid potassium salt at the ordinary temperature, the test must be made in the cold. (2) Since both alkalies and acids dissolve the precipitate, the reaction should take place in a neutral solution, and therefore the reaction with litmus paper must first be tried. If the solution proves to be alkaline, it is to be made neutral by carefully adding hydrochloric or acetic acid before the tartaric acid is applied: if, on the contrary, the test with litmus shows that it is already acid, the free acid must either be cautiously neutralised with sodium hydroxide, or, if volatile, as hydrochloric acid, etc., it can be removed by evaporation. (3) Since an acid salt is to be formed, a relatively large amount of tartaric acid must be added.

The normal conditions for the reaction are thus derived. The student must also seek to obtain the reaction when unfavourable conditions are present, trying to satisfy these according to the hints given above. For this purpose let him make the following experiments: (1) detection of potassium in the solution of a potassium salt which is acidified with hydrochloric acid; (2) in presence of sodium hydroxide; and (3) in very dilute solution.[1]

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[1] Before performing these experiments, the student must be made acquainted with certain general operations and with the Bunsen's burner.

The Bunsen's Burner has the following form:—Into the middle of a solid cast

We will now observe how the detection of potassium is accomplished in the presence of sodium. If tartaric acid be added in excess to a concentrated solution of sodium hydroxide or carbonate, and the solution, which becomes heated by the chemical reaction, allowed to cool, a precipitate of acid sodium tartrate will form. The compounds of sodium named possess an alkaline reaction, but the neutral salts, on the contrary, such as the chloride, give no precipitate with tartaric acid. Since the detection of potassium depends upon the neutrality of the solution (that is, if it is alkaline it must be made neutral), the possibility of the formation of acid sodium tartrate and the consequent error are prevented.

In the reaction between potassium salts and tartaric acid, the acid previously united to the potassium is set free; hydrochloric acid, for example, is liberated from its chloride according to the equation:

$$KCl + C_4H_4O_4(OH)_2 = C_4H_4O_4(OH)(OK) + HCl.$$

The solvent action of the free mineral acid influences the delicacy of the reaction, and to overcome its effect and make the test as delicate as possible the acid must be neutralised. We accomplish this by substituting for tartaric acid a

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iron rest is fastened a small brass burner, which is perforated by three holes, or by an irregular slit, for the escape of the gas. Over this burner an iron cylinder is screwed, which at its base is provided with two large openings and a ring, by turning which the latter can be reduced in size or entirely closed. As the gas rushes from the burner it draws air through the openings. It is lighted at the mouth of the cylinder, where, being mixed with air, it burns with a non-luminous flame which is free from soot. The air-openings at the bottom of the cylinder must be closed or reduced whenever a small flame is to be used, as an explosive mixture of air and gas forms if the current of the latter be too weak, and the flame in consequence recedes to the base of the burner, the whole cylinder then becoming heated. The burner is connected with the gas-pipe by a piece of caoutchouc tubing. To secure a proper flame the gas must be allowed to flow through the burner for a few seconds before being lighted, to avoid the recession of the flame to the bottom of the cylinder. The flame is protected by a cap of iron plate, which rests on a star-shaped support screwed to the top of the cylinder.

Evaporation.—Liquids are evaporated in porcelain (or platinum) dishes or casseroles, which are placed over a flame. The water of aqueous solutions boils and escapes as vapour, and volatile acids pass off at the same time. Evaporation over an open flame is effected at the temperature at which the solution boils (usually slightly over 100° C.) The ebullition is apt, however, to cause the loss of more or less substance from spirting, and to prevent this a water-bath is sometimes employed. The water-bath is a metallic vessel, the cover of which is a set of rings of varying diameters. The vessel is filled with water, the dish containing the liquid to be evaporated set in a ring of suitable size, and the water boiled. The solution is thus heated by steam instead of a direct flame. Acids must be evaporated under a hood—a large case in which a draught can be secured.

solution of acid sodium tartrate,[1] by the action of which no free mineral acid is set free, but the sodium salt is formed:

$$KCl + C_4H_4O_4(OH)(ONa) = C_4H_4O_4(OH)(OK) + NaCl.$$

Tartaric acid gives the reaction with almost all potassium salts, though those of acids which are rich in oxygen form an exception (for instance the chromate, permanganate, etc.) These do not show the reaction, because, in the presence of chromic or permanganic acids, the tartaric acid undergoes decomposition. If, after the complete reduction of the oxygen acids in the solution, however, an excess of undecomposed tartaric acid still remains, the acid potassium salt can then be formed.

The formation of the precipitate results according to the equation,

$$KX + C_4H_4O_4(OH)_2 = C_4H_4O_4(OH)(OK) + HX.$$

(X is the acid radical, the salt of which is used for the reaction.) As this equation shows, we have learned the influence of all four members upon the reaction, or, which is the same thing, the influence of the compounds which enter into and result from the reaction. Other important reactions should also be learned in the same way as much as possible. The importance of the subject has induced us to give an example of this in full in the reaction of tartaric acid with potassium salts.

The confirmatory tests for the tartrate are: solution of the precipitate on warming, and in either alkalies or acids. They are, as we see, directly opposed to the conditions under which the experiments are carried out.

Acid ammonium tartrate is very similar in its properties to the potassium salt. We shall not treat of it fully (comp. § 13), as tartaric acid is a poor reagent for ammonium, and is not employed in the detection of this body.

§ 8. **Platinichlorides.**—Platinum chloride, $PtCl_4$, is capable of entering into compounds, the so-called platinichlorides, with the chlorides of the alkali metals. Some of these compounds dissolve in water, and these are usually soluble, like platinum chloride itself, in alcohol or ether.[2] The others are difficultly soluble in water and insoluble in alcohol and

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[1] This salt can be prepared by dividing a solution of tartaric acid into two parts, neutralising one of them with sodium hydroxide, and adding the remaining portion to the neutral solution.

[2] Alcohol, C_2H_5OH, boils at 78° C. In the laboratory we usually use alcohol containing water (90-95 per cent); it can be obtained in the anhydrous state by

ether. The latter are especially important. Potassium and ammonium (cæsium and rubidium) form difficultly soluble platinichlorides, while the sodium and lithium salts dissolve easily in either water, alcohol, or ether. The general formula of platinichlorides is $R_2PtCl_6 = 2RCl . PtCl_4$, in which R is an alkali metal. The best method of separating potassium from sodium is by the use of these salts.

Platinichlorides of potassium and ammonium.—By the action of platinum chloride upon the salts of potassium or ammonium, yellow crystalline precipitates are obtained (orange-coloured octahedra by slower crystallisation). These precipitates are more difficultly soluble in cold than in hot water (the potassium salt needs 110 parts, the ammonium salt 170 parts, at 10°, while at 100° the former dissolves in 19 and the latter in 50 parts). They are hardly soluble in alcohol, the potassium salt needing 12,000 parts and the ammonium salt 26,000 parts of anhydrous alcohol, while in a mixture of alcohol and ether (3 parts alcohol, 1 part ether) they are absolutely insoluble.

Conditions of the reaction.—For the formation of the platinichlorides the potassium or ammonium must be present as its chloride. It is possible, in fact very often the case, that neither chlorine nor a chloride is present in the solution to be examined. The solution of platinum chloride, as a rule, contains free hydrochloric acid, however, and it is therefore usually unnecessary to add more, but in case the solution is alkaline this must be done. The platinichlorides can be formed even when free hydrochloric acid is not present:

$$3PtCl_4 + 4KNO_3 = 2K_2PtCl_6 + Pt(NO_3)_4.$$

The addition of free hydrochloric acid and sufficient concentration of the aqueous solution—the reaction is still more delicate in alcohol—are the conditions which ensure the reaction with platinum chloride.

§ 8a. Behaviour of the Salts of the Alkali Metals at

treating with anhydrous calcium oxide and distillation. The anhydrous alcohol takes up moisture from the air very easily.

Ether, $C_4H_{10}O = (C_2H_5)_2O$, is formed from two molecules of alcohol by the abstraction of one molecule of water:

$$2C_2H_5 - OH = (C_2H_5)_2O + H_2O.$$

It is obtained by the action of strong sulphuric acid upon alcohol, whence it is sometimes called "Sulphuric ether," an incorrect name. It boils at 35° C.

a High Temperature.—The alkali salts of most inorganic, though not organic, acids are exceedingly stable at such a temperature as we can reach by heating a porcelain crucible or evaporating dish with an ordinary flame. This is at about 600° C. At a higher temperature, however, they can be volatilised. Their stability at 600° C. permits their separation from ammonium salts, which are decomposed and, for the most part, volatilised at temperatures little higher than 350° C. This separation of ammonium from sodium or potassium, a very important one in qualitative analysis, is described among the special reactions of the ammonium salts.

§ **9. Flame Coloration.**—If we bring the salts of the alkali metals into the flame of a gas-burner, or into any non-luminous flame, such as that of alcohol or hydrogen, in quantities which are small enough to attain the high temperature of the flame, they volatilise. The volatilisation is marked by the colouring of the flame, and this coloration is very important as a qualitative test for the salts of the alkali metals.

The temperature in the flame of a gas-burner is very unequal, and in experiments with the flame reactions it is necessary to know its variations. In the flame we distinguish two cones. The inner dark blue one has a low temperature, and is hardly sufficient for the decomposition of the constituents of the gas. The oxidation proper takes place in the outer cone, and this has, in consequence, a higher temperature. The dark inner cone forms the lower third of the flame; in the outer, the temperature is unequally divided, the greatest heat, about 2300° C., being, according to the experiments of Bunsen, a little above the first third of the flame and halfway between the tip of the dark cone and the outer edge of the flame. The substance to be investigated is brought into this section of the flame. In lieu of a gas-burner, flame tests can be carried out with a spirit-lamp, or by igniting alcohol in a dish which contains the substance. The temperature of the alcohol flame is not as high as that of gas, however, and the flame colorations are not obtained as easily by its means.

The rate of volatilisation of the salts of the alkali metals is variable, as we see from the table below, which was prepared by Bunsen. In the heat of the gas flame, at about 2300° C., and with the rate of volatility of sodium chloride taken as the unit, the sulphates volatilise the most slowly, and the chlorides with the greatest rapidity:

$Na_2SO_4 = 0{\cdot}66$ $Na_2CO_3 = 0{\cdot}133$ $NaCl = 1{\cdot}000$
$K_2SO_4 = 0{\cdot}127$ $Li_2CO_3 = 0{\cdot}114$ $LiCl = 0{\cdot}739$
$K_2CO_3 = 0{\cdot}310$ $KCl = 1{\cdot}288$

Difficultly volatile or non-volatile salts, such as silicates, borates, and, to a certain extent, phosphates, hardly cause the flame coloration. In these cases we decompose the salts in the heat of the gas flame itself, forming volatile from non-volatile compounds, but since we shall not make such experiments immediately, their description may be postponed.

All volatile salts of one and the same metal, as well as the metal itself, give the same colour, the coloration being in all probability due to the reduction of the metal from its salts in the flame of the gas-lamp, and caused by the vapour of the element alone (comp. Section III. Spectrum Analysis).

Performance of the experiment.—The substance to be tested in the flame of the gas-burner, whether in solution or a dry salt, is held in the flame by means of a platinum wire, the end of which forms a small loop. The observation is more easily made, and the colour more lasting, when solid salts are employed, as more substance can thus be used than the solutions would contain. When solutions are under examination, therefore, they must be evaporated before the test is made. As regards the choice of volatile salts for the experiment, it is best, as experience has taught us, to apply the sulphates, the reaction proceeding more smoothly with these salts, because, as we see from the table, they are the least volatile. Potassium salts colour the flame violet, sodium yellow, and lithium carmine-red (for the ammonium salts this reaction is not important). The characteristic flame of each metal is discussed in connection with the special reactions. The colour is easily distinguished by the eye if a single element is present, but varies in a mixture of two or more, and then necessitates a thorough examination of the flame. The flame reactions of the alkali metals are exceedingly delicate, being caused by the most minute particles of the substance. Their efficiency can be illustrated by the fact that ordinary dust, which contains only a minimum quantity of sodium, always tinges the flame yellow.

Stas was the first experimenter to remark that dust invariably contains sodium. As the metal is therefore distributed about in the air, the colour imparted to the flame by other metals in ordinary experiments is influenced by its presence. The potassium flame, for instance, appears violet only because and when the test is made in presence of sodium. If chemically pure potassium salts (Stas experimented with the chloride, chlorate, and perchlorate) be examined in an atmosphere which contains no sodium, the flame is seen to be blue, varying from a dark to a light shade according to the salt volatilised.

§ 10. Examination of the Coloured Flame.—When caused by two or more alkali metals, the flame coloration is not the same as if only one were present. Sodium, even if present in minute quantities, completely hides the colour of potassium and lithium, and the flame is tinged yellow; that is, it shows only the colour caused by sodium. If but one part of sodium is mixed with two hundred of potassium or one thousand of lithium, the colorations due to the latter metals are entirely imperceivable. In order to apply the colour reactions to the detection of the alkali metals, more than one being present, we pass the rays of light through a blue glass, or, better still, through a blue solution of indigo in sulphuric acid. The yellow rays of sodium are by these means entirely absorbed, and only the violet and carmine-red of potassium and lithium are transmitted. The apparatus for carrying out the experiment is called an *Indigo Prism* (Bunsen). The latter is a wedge-shaped bottle, the great advantage of which lies in the fact that it presents a gently-increasing layer of indigo solution. If the non-luminous flame of gas be observed no colour is noticeable; seen through the layer of indigo, however, the flame appears tinged with violet, the shade of which must not be mistaken for that of potassium. Observing through the indigo prism a flame tinged by sodium, the light violet colour of the flame itself is seen through the thin layer, while the yellow due to the metal is entirely absorbed. The carmine-red of lithium is visible only through a thin layer, its rays growing gradually darker, and finally, at a certain thickness of the liquid, disappearing entirely. The point where the lithium rays vanish is accurately marked in each apparatus. The flame of a potassium compound appears blue (and therefore like the colour caused by potassium in an atmosphere free from dust) through the thin layer, changes, in proportion to the layer which it pierces, to blue-violet, violet, or violet-red, and in very thick layers becomes a carmine-red. It is difficult, however, to detect potassium in the presence of lithium with such an apparatus, and, to avoid mistakes, a second flame should be placed near the one in which the substance is being volatilised. A potassium salt alone is introduced into this additional flame, a pure potassium flame thus being obtained for comparison. The difference in the colour due to the presence of lithium is easily seen, and the metal cannot be overlooked if present. The potassium is detected by observing the flame through so thick a layer of the solution that the lithium rays are not transmitted. In order to show the presence of all three alkali metals, we make two experiments: (1) the mixture of the salts is brought into the flame, and the yellow colour observed shows the presence of sodium; (2) the presence of potassium and lithium is shown by investigating the flame with the prism. The alkalies can be much more exactly distinguished by examining a flame coloured by their salts through the spectroscope (Sec. III.) This is the only means for the qualitative detection of cæsium and rubidium.

It must be remembered that the flame reactions are not to be confused with the reactions previously learned. The latter are a means of separation, and allow us to judge, according to the measurement by the eye and the quantity of the precipitate, whether much, little, or only traces of this or that metal are present in the solution. The colour reactions, not only of the flame, but in general, which can be caused by an extremely small quantity of the respective elements, can give no indication as to how much of the metal the substance under investigation contains.

SPECIAL REACTIONS

We have learned in the general reactions the methods of separating the alkali metals. The special reactions, to the study of which we now turn, serve as confirmatory tests for the compounds obtained by the methods of separation, the thoroughness of the latter thus being ascertained.

Potassium

§ 11. Reactions of Potassium Salts.—All the characteristic reactions of potassium salts have already been mentioned; from their number let us again refer to the following:

Acid potassium tartrate, $C_4H_4O_4(OH)(OK)$ (§ 7).—Tartaric acid, or acid sodium tartrate, throws down from a cold concentrated and neutral solution of a potassium salt a white crystalline precipitate of the acid salt, which is soluble in acids or alkalies.

Potassium platinichloride, K_2PtCl_6 (§ 8).—Platinum chloride gives in a concentrated solution a yellow crystalline precipitate of potassium platinichloride. The reaction is more delicate in alcoholic solution.

Potassium silicofluoride, K_2SiF_6.—Hydrofluosilicic acid, added to a neutral or acid solution of a potassium salt, causes a half-transparent precipitate of K_2SiF_6, which is distinctly visible only when it has settled. It is decomposed to potassium fluoride and silicon fluoride on heating, and by alkalies with formation of silica.

The colouring of the non-luminous flame (§ 10).—Potassium salts colour the flame violet. This reaction is important for the qualitative detection of the metal. The dry salt or the solution is brought into the flame of the gas-burner by means of a platinum wire. The spectrum of potassium is described in Section III. Sodium salts hide the flame coloration.

Sodium

§ **12. Reactions of Sodium Salts.**—The salts of sodium, as well as sodium itself, are less volatile than those of potassium. Because of their great solubility in comparison with potassium salts, characteristic reactions of sodium are very difficult to find. The solubility of acid sodium tartrate in water, and that of sodium platinichloride in either water, alcohol, or ether, have already been mentioned. Potassium pyroantimonate is almost the only reagent which precipitates sodium salts.

Sodium pyroantimonate, $Na_2H_2Sb_2O_7 + 6H_2O$, is formed as a white crystalline precipitate (quadratic octahedra on slower crystallisation) through the action of potassium pyroantimonate upon the sodium salts:

$$K_2H_2Sb_2O_7 + 2NaCl = Na_2H_2Sb_2O_7 + 2KCl.$$

Fremy, who discovered this salt, called it the metantimonate, hardly a correct name. Antimonic acid is, in a certain degree, analogous to phosphoric acid :

Phosphoric Acid. H_3PO_4.	Antimonic Acid. H_3SbO_4.
Pyrophosphoric Acid. $2H_3PO_4 - H_2O = H_4P_2O_7$.	Pyroantimonic Acid. $2H_3SbO_4 - H_2O = H_4Sb_2O_7$.
Metaphosphoric Acid. $H_3PO_4 - H_2O = HPO_3$.	Metantimonic Acid. $H_3SbO_4 - H_2O = HSbO_3$.

The sodium salt has, without doubt, the composition $Na_2H_2Sb_2O_7$, *i.e.*, it is a salt of pyroantimonic acid, and Fremy used the prefix "meta" only to distinguish it from the salts of the common, or "ortho," antimonic acid (as we say stannic and metastannic acids). The reagent, the potassium salt, probably has a similar composition. The product of the fusion of potassium nitrate with antimony ore, or of antimony potassium tartrate, has, in all likelihood, the formula $K_4Sb_2O_7$, and by treatment with water it is changed to $K_2H_2Sb_2O_7$ and 2KOH. It must be noticed that the pyroantimonate is sometimes mistaken for the salt of metantimonic acid, $2NaSbO_3 + 7H_2O$, and also for that of antimonic acid, $2NaH_2SbO_4 + 5H_2O$; the question obviously depends upon the amount of water of crystallisation, the determination of which in this case is very difficult.

Sodium pyroantimonate is difficultly soluble in either cold or hot water (requiring at 100° C. 300 parts H_2O). The sodium salt acts as all other salts of pyroantimonic acid, being decomposed by acids with separation of a white amorphous precipitate of metantimonic acid, $HSbO_3$. Excess of potassium carbonate hinders the reaction, perhaps through the formation of a soluble double salt of potassium and sodium. The condition of the reaction is the presence of a neutral or slightly alkaline solution; too alkaline solutions must be neutralised by dilute hydrochloric or acetic acid; acid solutions, with potassium hydroxide (ammonia cannot be used, as ammonium pyroantimonate is difficultly soluble). It is still better to drive off free acid by evaporation and ignition. It must be remembered that in this case, where a crystalline precipitate is involved, its formation may not immediately take place, though it can be hastened by scratching with a glass rod, and it is therefore convenient to make the test upon a watch-glass. In weak solutions rubbing is insufficient, and we must wait. If, after quietly standing for twelve hours, no precipitate be formed, it is safe to say that no sodium is present. We emphasise again that the precipitate of sodium pyroantimonate must be crystalline; if an amorphous precipitate results which does not become crystalline on standing, it is impossible to decide the presence of sodium by its means.

The *yellow coloration of the flame* is exceptionally characteristic of sodium. The test is described in § 10. An orange-coloured crystal of potassium dichromate, $K_2Cr_2O_7$, becomes colourless and transparent under the influence of these rays; paper which is coloured red by mercuric iodide appears white, and when observed through a green glass the flame seems orange-yellow. It is a most delicate reaction.

Ammonium

Review of the Ammonium Derivatives.—Ammonia unites with acids to form salts. Before passing to the description of the characteristics and properties of ammonium salts, let us cast a glance at those of its compounds which occur in analysis. By the action of ammonia upon the solutions of certain neutral metallic salts, an ammonium salt results, which, uniting with that of the metal, forms a double salt, such as the compound $MgCl_2 . 2NH_4Cl$. The ability to give such soluble double salts with ammonia is characteristic of magnesium (Group II. Div. 2); of ferrous iron, manganous manganese and zinc (Group III. Div. 2); of nickel and cobalt (Group III. Div. 3); and of silver, copper, and cadmium (Group IV.) In addition to these double salts, which possess in many respects the properties of the simple ammonium salts, metallo-ammonium compounds are formed by the action of ammonia or ammonium carbonate upon the salts of certain metals. In these compound ammonias one or more atoms of the hydrogen of the ammonia is displaced by metals. Such ammonias can form salts; the latter can also be considered as a product of the direct union of ammonia with metallic salts. So, for instance, $(NH_3Hg)_2Cl_2$ is the formula of a compound ammonia, while $Hg_2Cl_2 + 2NH_3$ represents the same compound as a product of the union of ammonia with mercurous chloride. The metallo-ammonium compounds usually give off ammonia on boiling with alkalies. Soluble metallo-ammonium compounds are characteristic of cobalt, silver, cadmium, copper, platinum, etc. Mercury forms compounds insoluble in water.

§ 13. Reactions of Ammonium Salts.—*Their volatility.*—The salts of ammonium are very similar to those of potassium and sodium (their crystals are in most cases isomorphous), but are easily distinguished from the latter by their extreme volatility. They begin to volatilise even at a low temperature (about 350° C.), some without apparent decomposition (the chloride, sulphate, carbonate), and some being decomposed (nitrate, phosphate).

It may be well to study these reactions more carefully. As already mentioned, the ammonium salts volatilise with the following phenomena:

(1) Without visible decomposition taking place. Under the influence of a high temperature ammonium salts of volatile acids dissociate into ammonia and acid, but these products immediately reunite upon cooling, with formation of a white cloud. As an example let us mention the chloride or carbonate:

$$NH_4Cl = NH_3 + HCl.$$

(2) The salts of non-volatile acids dissociate, ammonia being given off and the non-volatile acids remaining behind. For example, ammonium phosphate:

$$(NH_4)_3PO_4 = 3NH_3 + H_3PO_4.$$

(3) The ammonium salts of acids rich in oxygen (nitric, chromic, chloric, etc.) are decomposed on heating, ammonia oxidising to water and nitrogen or its oxides:

$$NH_4NO_3 = N_2O + 2H_2O.$$

Upon this property of volatilisation is based the separation of ammonium salts in both qualitative and quantitative estimations. In qualitative analysis we evaporate the solution from which an ammonium compound is to be separated to dryness in a porcelain dish and then ignite in the same vessel. The ammonium salts volatilise in the form of a thick, white cloud, and when the evolution of the fumes ceases the salts can be considered as completely driven off. This operation should be carried out only under a hood.

The similarity of the ammonium salts to those of the alkali metals permits the use of the same reagents for the detection of all. The volatilising ammonium salts give a slight violet tinge to the gas flame, but this reaction is not important.

Acid ammonium tartrate, $C_4H_4O_4(OH)(ONH_4)$, (§ 7), has the same properties as the corresponding potassium salt. Tartaric acid produces a crystalline precipitate, though with difficulty, and only in very concentrated solutions; with acid sodium tartrate the reaction is more easily secured. It is not used as a test for ammonium salts.

Ammonium platinichloride, $(NH_4)_2PtCl_6$, (§ 8).—Platinum chloride produces in the solutions of ammonium salts a yellow precipitate with properties similar to those of potassium platinichloride.

Generation and Reactions of Ammonia.—The chief characteristic of ammonium compounds is their power of easily evolving ammonia when acted upon by the alkalies or hydroxides of the alkaline earths:

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

Although the reaction goes on in solution even at the ordinary temperature, it nevertheless proceeds slowly, and some time is needed for its completion; warming hastens it. Potassium hydroxide or calcium hydroxide is added in a test-tube to the ammonium salt, or to the solution to be investigated, and the mixture warmed. Ammonia is immediately given off.

The *test for free ammonia* is made by bringing the proper reagent into the neck of the test-tube in which the ammonium salt is being decomposed by the alkali. If the test-tube be joined to a tube for leading off the gas, the test is made at the end of the latter. The ammonia evolved is easily detected, possessing a strongly-marked odour. This characteristic can be made use of only if sufficient ammonia is formed, however, and there are many still more delicate reactions. When dissolved in water, ammonia gives, as we know, a strongly *alkaline reaction;* if moistened litmus or turmeric paper be held over the vessel while the experiment is being made, the observation of an alkaline reaction, in which litmus paper turns blue or turmeric paper brown, indicates the presence of ammonia in the substance investigated. This method is applicable even in cases where only traces of ammonia are present. The test is made either at the ordinary temperature or at a gentle heat. The vessel is covered by a watch-glass, to the under side of which is fastened a previously moistened piece of litmus paper; if the vessel be allowed to stand for a short time, the alkaline reaction of the paper becomes visible in the presence of even traces of ammonia. A glass rod moistened with any volatile acid, such as hydrochloric, nitric, or acetic, and held over the vessel in which the gas is being evolved, will be surrounded by a thick, white cloud, which consists of an *ammonium salt non-volatile at the ordinary temperature.* It is advisable to use acetic acid in the experiment, as concentrated hydrochloric acid itself fumes in the air. Paper which is moistened with mercurous nitrate becomes gray or almost black in the vapour of ammonia gas, owing to the formation of a di-mercuro-ammonium salt which is black. With an excess of ammonia it easily passes over into mercuric oxide, whereupon metallic mercury separates out and the precipitate becomes gray:

$$Hg_2(NO_3)_2 + 2NH_3 = Hg_2NH_2(NO_3) + NH_4(NO_3).$$

In this experiment caution must be taken that no drops of the boiling liquid come upon the paper; if this occur, the potassium hydroxide which sets free the ammonia will likewise stain the paper, through the formation of black mercurous oxide:

$$Hg_2(NO_3)_2 + 2KOH = Hg_2O + 2KNO_3 + H_2O.$$

For ordinary analyses the given reactions amply suffice; but in some cases, such as the testing of natural waters, we use mercuric chloride, $HgCl_2$, for detecting ammonia, with which it forms a white precipitate even in very dilute solutions:

$$4NH_3 + 2HgCl_2 = (NH_2Hg_2)Cl_2 + 2NH_4Cl.$$

In such cases the double salt of mercuric iodide and potassium iodide, HgK_2I_4 (Nessler's reagent; in preparing it an excess of potassium iodide is to be avoided), may also be used. In the presence of potassium hydroxide this reagent produces a brown precipitate of dimercuriammonium iodide, $NHg_2I . H_2O$, with either free ammonia or ammonium salts:

$$2HgK_2I_4 + 3KOH + NH_3 = NHg_2I . H_2O + 7KI + 2H_2O.$$

Traces of ammonia give no precipitate, but the solution assumes, according to the quantity of ammonium salts present, a yellow or an orange-red colour of various shades.[1]

SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS FOR METALS OF THE FIRST GROUP

§ **14.** Having learned the general and special reactions, we now turn to their combination, in order to work out a systematic course of analysis. In the following groups this task will be left to the student himself.

Let us first see, in general, whether it is necessary to combine reactions for this so simple a group. The need of a combination results from the insufficiency of the colour-reactions alone, which, although pointing out the presence of the alkali metals without a separation, still do not answer all the questions of analysis. We usually make a qualitative examination with the view of utilising the results in quantitative analysis. In

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[1] It is recommended to the beginners not to study practically the reactions which are printed in small type, since they relate only to special cases. They are for this reason not fully described, but noticed merely that he may better understand more important tests.

this case the former becomes of the utmost importance, in giving an insight into the relative quantities of the several constituents of which the compound is made up. These questions cannot be answered by the colour reactions, and the latter alone are therefore insufficient. They are chiefly used for confirming the results of the examination. The questions are decided by observing the precipitation, from which, according to the quantity of the precipitate, the amount of the constituent (more, less, or traces) can be determined by the eye.

As precipitation methods are therefore necessary, we cannot do without their combination, because of the similarity of the salts of all the alkali metals in this regard. If we turn our attention to the reactions to be employed, we see that both tartaric acid and platinum chloride give precipitates with either potassium or ammonium salts: potassium pyroantimonate throws down the sodium and ammonium compounds; and we also notice that a potassium salt is here used as a reagent. No matter how we apply these reagents, it is impossible to recognise any one metal without its previous isolation; and the necessity of separating some one of the group, and thus simplifying the question next to be solved, is clear.

Since, if we apply the reactions mentioned above, the correctness of the analysis is not affected by the choice of the metal to be separated (this the student must determine for himself), we get rid of the one which can be separated the most *easily*, viz., ammonium. As this separation is to be made before all others, we must satisfy ourselves as to whether ammonium salts are present in the substance to be analysed. The first operation is, therefore, to test for ammonia by liberating it, if present, in a separate portion of the substance, as explained in § 13. A special portion must be used, in order to be able to employ any desired base for the liberation of the ammonia. If the entire solution is taken, neither sodium nor potassium hydroxide is available, as their use would introduce into the solution elements which must be looked for in the following steps of the analysis. The use of barium or calcium hydroxide is rendered troublesome by the necessity of removing the excess; and this is unavoidable, as both metals form insoluble salts with either tartaric acid or sodium pyroantimonate. All of these difficulties are surmounted by using a separate portion for the detection of ammonium, and this plan is often used in analogous cases in qualitative analysis. If ammonia is found, it must be removed by evaporating the original solution to dryness and igniting the residue (§ 13).

The ignited residue is dissolved in a small quantity of water. As, when ammonium salts in the dry state are ignited with the alkali metals, double decomposition often ensues (compare Group I., Supplement 3), the solution obtained after ignition can show any one of the three possible reactions—acid, neutral, or alkaline. A neutral solution will be obtained if the original solution contained only similar compounds (such as the chlorides, sulphates, etc.); an alkali solution, either if alkali salts which on ignition decompose with the formation of their carbonates were present, or if it contained neutral salts and an excess of ammonium carbonate. An acid solution, finally, will result from the presence of a large quantity of the ammonium salts of a non-volatile acid (phosphate, borate, etc.), and also from that of free acids or acid salts. After testing the solution with litmus paper and, if necessary, neutralising, one separate portion is examined for potassium with tartaric acid, and another for sodium with potassium pyroantimonate, the conditions given in §§ 7 and 12 being carefully observed. The necessity of dividing the solution results from the fact that if tartaric acid be first added as a test for potassium, the subsequent use of potassium pyroantimonate is forbidden, since the latter is decomposed by acids; on the other hand, should we wish to begin with the sodium test, it would be impossible to detect potassium, as a salt of that metal has already been employed as a reagent. With the precipitates confirmatory tests are made, in which the properties of the compounds explained in the special reaction of the metals are examined.

The systematic scheme of analysis is thus naturally arranged. As we see, there is no other choice of reactions, and, indeed, their arrangement cannot be modified without influencing the correctness of the results. The systematic course is not only a method of analysis practically worked out, but is the necessary result of the properties of the compounds reacting upon each other and resulting from the reaction. The need of grasping and understanding the correct methods for elaborating a systematic scheme gives rise to one of the chief objects for which we strive in the practice of analytical chemistry.

The application of platinum chloride in qualitative analysis is seldom necessary, and we have, therefore, not considered this reagent in the scheme developed. We may mention here that in the second group a slight variation from the course of analysis is necessitated if the metals of the second group occur together with those of the first in the substance to be examined.

The student is advised to prepare himself mixtures of the salts of the first group metals, and, after their analyses have been rightly made, to test his knowledge with unknown mixtures of the same group.

SUPPLEMENT

1

RUBIDIUM, CÆSIUM, LITHIUM

§ 15. **Reactions of Rubidium and Cæsium Salts.**—The alkali metals are always accompanied in nature (sometimes in minerals, as lepidolite, sometimes in springs) by very small quantities of rubidium and cæsium. The latter occurs in significant amounts only in the mineral pollux (aluminium-cæsium silicate). These metals and their compounds show a great similarity to those of the alkalies; their acid tartrates are likewise difficultly soluble, though the cæsium salt dissolves more easily than that of potassium, and the platinichlorides are also thrown down as yellow precipitates, being, in fact, less soluble than potassium platinichloride. They are detected by means of the spectrum analysis of the flame coloured by their salts, this being the only method by which these metals can at present be distinguished from others of the same group. (The description of their spectra occurs in Section III.) The salts of rubidium colour the flame violet, and those of cæsium, blue-violet. Accurate methods for separating them either from each other or from potassium are unknown. The methods of preparing their salts depend upon the difference between the solubility of the latter and that of the analogous potassium compounds.

The *preparation of rubidium and cæsium salts.* For their separation from other metals, for example, in the mother-liquors of springs or in lepidolite, the alkali metals are precipitated by platinum chloride. On methodical digestion of the precipitate with water the platinichlorides of rubidium and cæsium, which are less soluble than the potassium salt, remain behind in a fairly pure state, and are then converted to the chlorides by gentle ignition (100 parts of water dissolve at 100° C. 5·13 parts

K_2PtCl_6, 0·46 parts Rb_2PtCl_6, and only 0·077 parts $CsPtCl_6$). Instead of the platinichlorides the alums can be employed, as potassium alum is less soluble and the first to crystallise from the solution. The disappearance of the potassium salt is shown by the spectroscope. The separation of cæsium from rubidium was based, in former methods, upon the solubility of cæsium carbonate and the insolubility of rubidium carbonate in alcohol. A new means is the precipitation of cæsium in the form of a double chloride with antimony chloride, $CsSbCl_4$; this compound is insoluble in strong hydrochloric acid (like the ammonium compound), while the rubidium salt is soluble. This last reaction can be used as a qualitative test for cæsium when occurring with rubidium.

Lithium

Reactions of Lithium Salts.—Lithium also accompanies the alkali metals (chiefly in the minerals lepidolite, spodumene, petalite, and triphylite). The most common lithium mineral is lepidolite (lithium mica). In its chemical character lithium forms the connection between the alkali metals and those of the second group. As has been previously remarked, the acid lithium tartrate is easily soluble in water, and the platinichloride in both alcohol and ether. The difficult solubility of lithium oxide, carbonate, and phosphate in water is the chief characteristic of this metal. The carbonate, thrown down from a cold concentrated solution by sodium carbonate, is a white precipitate. The phosphate, Li_3PO_4, is precipitated as a white crystalline powder on boiling with sodium phosphate. This salt, as well as the solubility of lithium chloride and nitrate in alcohol and ether, is made use of as a means of separating this metal from the other alkalies. The colour of its flame is carmine-red, and affords a very characteristic reaction for lithium. Its spectrum is described in Section III.

2

Analysis of the compounds of the alkali metals found in nature.—Potassium and sodium are very widely spread in nature, chiefly as complicated compounds, the analysis of which will be more accurately described later. Thus we find in silicates both potassium (in feldspar, mica) and sodium (albite, labradorite). Both are found among the products of the gradual decomposition of rock systems. Potassium also occurs in clay, in soils, and in the ashes of plants. The analysis of these complicated substances will be considered later (among the silicates). Sea water contains chiefly sodium chloride, but also small quantities of potassium salts, and salt deposits have been derived from this source. In Stassfurt, in the upper layers of rock salt, we find one of the few simple minerals of potassium, viz., carnallite, $KMgCl_3$. All of these compounds are soluble in water, and can therefore be analysed according to the method given for the first group. The analysis of cryolite, $NaAlF_4$, is described under Fluorine (Section II.)

3

Application of the alkali metals in analysis.—As the alkali hydroxides and salts are soluble in water, they are much used as a means of forming insoluble compounds of the other metals (oxides and salts). The reaction is obtained by double decomposition:

$$CuSO_4+2KOH=Cu(OH)_2+K_2SO_4,$$
$$ZnSO_4+K_2CO_3=ZnCO_3+K_2SO_4.$$

We should mention, concerning the reactions of the hydroxides, that in the precipitation of the oxides of any metals which can form compounds with the alkalies, the oxide thrown down dissolves in excess of the reagent to a compound soluble in water:

$$KOH+Al(OH)_3=KAlO_2+2H_2O.$$

This class of oxides is composed of Al_2O_3, Cr_2O_3, ZnO, PbO, SnO, SnO_2, Sb_2O_3, Sb_2O_5, Au_2O_3, PtO_2. The reactions of the hydroxides and the carbonates can also serve other purposes, viz., to convert insoluble salts of any acid into salts (of alkalies) which are soluble:

$$SrSO_4+K_2CO_3=SrCO_3+K_2SO_4.$$

The insoluble salts are treated with the alkali carbonate either in solution or by fusion: by boiling the salt with an alkali carbonate the sulphates of barium, strontium, and calcium, which are insoluble in water, and the insoluble oxalates, chlorides, iodides, and bromides can be decomposed; silicates, phosphates, borates, sulphides, etc., are decomposed by fusion. In the last case we employ a mixture of potassium and sodium carbonates, which fuses more easily than sodium carbonate alone. The sodium salt is in all reactions preferable to that of potassium because of its greater purity. The carbonates are more rarely used in the preparation of elements (such as mercury), sometimes mixed with carbon (copper), or with potassium cyanide (bismuth, tin, arsenic, antimony). The use of "Berthollet's salt," $KClO_3$, as well as of the nitrates, as an oxidising agent is described under the corresponding acids. The other salts of the alkali metals, almost all of which are soluble in water, are employed in the preparation of salts insoluble in water, or of other metals.

Since ammonia and its carbonate show great similarity to the compounds of the alkali metals, they are often substituted for these, especially in quantitative work, on account of the ease with which they are purified and driven off by ignition. Ammonium carbonate is used in the estimation of the alkalies as their sulphates. The acid salts are thus readily converted to the neutral salts, the ammonium carbonate being partially decomposed at the same time, with formation of the likewise volatile ammonium sulphate:

$$2KHSO_4+(NH_4)_2CO_3=K_2SO_4+(NH_4)_2SO_4+CO_2+H_2O.$$

By the action of ammonium carbonate, at high temperatures, the oxides of certain metals (those of the second group) are easily converted into carbonates (comp. Determination of calcium):

$$CaO + (NH_4)_2CO_3 = CaCO_3 + 2NH_3 + H_2O.$$

For the same purpose, and under the same conditions, a few other ammonium salts are used; for example, NH_4NO_3, to convert basic magnesium nitrate into the neutral salt. We have still to mention the application of ammonium sulphide as a precipitant for the metallic sulphides, and its power of forming thio-compounds, soluble in water, with the sulphides of gold, arsenic, antimony, tin, platinum, etc.

GROUP II

MAGNESIUM, CALCIUM, STRONTIUM, BARIUM

§ **16.** The solubility of the sulphides and the insolubility of the carbonates in water characterise this group of metals. Ammonium carbonate is its general reagent.

This group embraces metals dissimilar in their properties; the chemical nature of magnesium is very different from that of the three other elements. Magnesium belongs to the natural group of which zinc, cadmium, etc., are members. Reserving till later the discussion of the properties of the single metals, I may here point out their variations, some of which form regular series. The solubility of the hydroxides is the greatest in barium, and, gradually diminishing through strontium and calcium, becomes almost *nil* in magnesium hydroxide. Magnesium sulphate and chromate dissolve easily in water; the solubility becomes less in the calcium and strontium salts; and barium sulphate and chromate are insoluble. The carbonates form a like series in regard to the ease with which they lose carbonic acid, from the exceptionally great instability of the magnesium salt to the almost absolute stability, even at a white heat, of that of barium. The nitrates and chlorides are all easily soluble in water.

Determination of the Divisions.—Magnesium is sharply distinguished from the other three members by its power of forming soluble double compounds with ammonium salts. In presence of ammonium salts in general, for example, in that of ammonium chloride and ammonia, ammonium carbonate does not precipitate magnesium as its carbonate. This important reaction will be more fully considered under magnesium; it forms the basis for the separation of this group into divisions. Remembering the general definition given above for the group, we formulate the divisions as follows:

1st Division: Barium, Strontium, Calcium.—These metals are precipitated as carbonates by ammonium carbonate in the presence of ammonium chloride and ammonia.

2nd Division.—Magnesium is not thrown down by ammonium carbonate in the presence of ammonium chloride and ammonia, forming soluble ammonium magnesium double salts.

Remark.—Test-tubes can be used for most of the reactions which are employed in the study of this group. The examination of the compounds obtained, however, is much more complicated than that of the salts of the metals of Group I., and requires familiarity with a greater number of operations.

Precipitation, in case the precipitate is apt to be bulky, is performed in a beaker; if the solution must be boiled at the same time a porcelain casserole is still better.

Filtration.—By this operation the solution is separated from the insoluble precipitate. The liquid is allowed to run through a *filter*, made of unsized paper, which retains the precipitate. If the latter is to be subsequently examined, a smooth filter, prepared by folding a circular piece of filter paper into a quadrant, is used. The filter is inserted into a glass funnel, where it is opened out so that three thicknesses of paper remain on one side, and only one on the other. It is then thoroughly moistened and pressed tightly against the sides of the funnel. The latter must be of such a size that the edge of the filter will be at least half an inch below its rim. "Ribbed filters" can be employed only when the filtrate alone requires examination, since precipitates cannot be washed upon them. They are, nevertheless, convenient whenever their use is permitted, as the filtration thus proceeds much more rapidly than when the smooth sort is employed. The funnel is held in a ring attached to a standard. The filtration must not be commenced before the precipitate has fully subsided.

The washing of the precipitate.—After the filtration proper has been completed, the precipitate still retains a portion of the liquid from which it was deposited, to remove all traces of which the precipitate must be washed. The water, or the liquid in general, with which the washing is effected, is delivered from a so-called wash-bottle; the filter is filled to its edge and the liquid added allowed to pass through the precipitate; this operation being repeated until the washing is finished. Washing a precipitate is one of the most important operations of analytical chemistry. It must not be considered thorough until the filtered liquid has been examined. If the precipitate is insoluble, as is usually the case, a drop from the end of the funnel is caught on a piece of platinum foil and evaporated to dryness; if no residue remains the washing is complete. In case such a test cannot be made the thoroughness of the washing must be judged from the quantity of water or liquid used. If the above directions are followed the filter need usually be filled only five or six times.

Decantation.—If the precipitate subsides quickly after being thrown down, decantation may be substituted for filtration. The supernatant liquid is here simply poured off by inclining the vessel or through a syphon. Water (or the proper liquid) is then added, the precipitate vigorously stirred about and allowed to subside again, and the liquid again decanted, the operation being repeated as many times as is necessary. Decantation is sometimes resorted to in connection with filtration.

GROUP II., DIVISION 1

BARIUM, STRONTIUM, CALCIUM

The solubility of the sulphides and the insolubility of the carbonates mark the metals of the second group. Its first division is especially characterised by the fact that it forms no soluble double salts with ammonium compounds, the carbonates being precipitated by ammonium carbonate in the presence of ammonium chloride and hydroxide.

GENERAL REACTIONS

§ **17.** In this group, and to a still greater extent in the following groups, the reactions become more complicated and the properties of the compounds used in analysis more varied. In beginning their study we must, before all, ascertain the analytical importance of the reactions, since not all have the same weight. The most important reactions must be thoroughly studied. The importance of a reaction is determined by its employment in analysis. The reactions can be divided into two classes: those by which the qualitative characteristics of the chemical compound are tested, and those used for the separation of single elements, or of entire groups, from one another. Qualitative reactions are studied only with the view of being able to apply them under all circumstances, without requiring that the whole of the chemical compound be involved. Reactions used in separations, however, must be complete, that is, all the substance taken must enter into the reaction. They would otherwise be uselessly employed. The completeness of the reaction must be ascertained by a confirmatory test in each and every experiment. The student obtains in this way both a thorough knowledge of the reactions and confidence in the methods of separation. The character of the various reactions and, when necessary, the proper confirmatory tests will be explained throughout the description of Group II.; in subsequent groups it will be left to the student's judgment. We state again that the study of general reactions has for its purpose the separation of whole groups as well as of single metals.

The Carbonates.—Reactions used in separating Group II. Division 1 from Group I. Since the metals of Group II. form many insoluble salts, several of these may be used to separate them from Group I. We give the carbonates the preference, since they are not only insoluble in water and easily formed, but dissolve without difficulty in acids, and can thus be easily converted into soluble salts. The carbonates of barium, strontium, and calcium are thrown down as white, amorphous precipitates, which become crystalline upon long standing in water. They dissolve easily in acids, such as hydrochloric, nitric, acetic, with formation of soluble salts and liberation of carbon dioxide:

$$BaCO_3 + 2HNO_3 = Ba(NO_3)_2 + CO_2 + H_2O.$$

Although insoluble in water itself, the carbonates dissolve somewhat in water containing carbon dioxide.

Let us now observe the use of these compounds in the separation from the metals of Group I. For the precipitation we use ammonium carbonate; the potassium and sodium salts are unavailable, while ammonium salts, as we know, can be easily driven off from the compounds of the alkali metals. We do not have the neutral ammonium carbonate in the laboratory, as this salt decomposes in aqueous solution to ammonia and the acid carbonate. The aqueous solution of the commercial salt contains the acid salt, NH_4HCO_3. Carbon dioxide is given off when the metals of Group II. are precipitated by this salt:

$$2NH_4HCO_3 + BaCl_2 = BaCO_3 + 2NH_4Cl + H_2O + CO_2.$$

The possibility of the carbonates of barium, strontium, and calcium being held in solution through the formation of free carbon dioxide is prevented by precipitating in slightly warm solution and in presence of a small quantity of free ammonia. Some time is necessary for complete precipitation. In exact analyses the absence of ammonium salts, especially of the chloride, is required.

The confirmatory test for complete precipitation consists in filtering and adding to the filtrate some fresh ammonium carbonate, upon which no precipitate should appear. The washing of the precipitate on the filter should be very carefully performed; in the separation of the metals of the first group, the latter are found in the filtrate.

§ 17a. **The chromates** serve for the separation of barium from strontium and calcium. All three metals form with chromic acid only the salts of the formulæ $BaCrO_4$, $SrCrO_4$, $CaCrO_4$. Barium chromate is a yellow precipitate, almost absolutely insoluble in water (1:87,000, at the ordinary temperature), especially in the presence of ammonium chromate, but soluble in nitric acid: it is obtained by precipitating the solution of a barium salt with a soluble chromate. Strontium chromate also forms a crystalline yellow precipitate which is soluble, though difficultly so, in water (1 : 840); acetic acid greatly increases its solubility. Calcium chromate is easily soluble in water. As the separation of barium from strontium and calcium is rendered difficult by the sparing solubility of the strontium salt, it must be performed with careful observance of the necessary conditions. The well-washed precipitate of the carbonates, as obtained by the method described in the foregoing paragraph, is removed from the filter into a small beaker by means of the wash-bottle, and with gentle warming dissolved in the least possible amount of acetic acid. (The excess of the latter must be a minimum.) The precipitation is made with ammonium chromate. This reagent is prepared by carefully adding ammonia to a solution of ammonium dichromate until the latter has attained a pure yellow colour, though still remaining slightly acid. The reagent is first slowly added to a small portion of the solution of the acetates, and the mixture slightly warmed if the precipitate does not appear at once. If barium is thus detected, the entire solution is precipitated in the same manner and, after a short time, filtered; barium chromate remains on the filter, and calcium and strontium in solution. This separation of barium is accurate. The confirmatory tests for barium chromate are described under the special reactions of the metal.

§ 18. **The sulphates** of the metals of Group II. are formed as white precipitates on the addition of dilute sulphuric acid, or of a soluble sulphate, to solutions containing these metals. They are at first amorphous, but become crystalline:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl,$$
$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl.$$

In the amorphous state these precipitates pass through the pores of the filter, and to prevent this they must be thrown down from a boiling solution, allowed some time to settle, and only then filtered. The study of the properties of the sulphates may be arranged under the following heads:—

1. *Solubility in water.*—Barium sulphate is almost insoluble in water (1:800,000); strontium sulphate sparingly soluble (1:7000); and calcium sulphate relatively easily dissolved (1:430). As a result of the unequal insolubilities, even traces of barium can be detected by sulphuric acid, *i.e.*, a precipitate is obtained in extremely dilute solutions of barium salts. To afford the precipitation of strontium, the solution must be more concentrated, as no precipitate will appear if it contain more than 7000 parts of water to one of strontium sulphate; while to throw down calcium sulphate, it must be more concentrated still, no precipitation occurring in a solution which contains more than 430 parts of water. Strontium sulphate and calcium sulphate can therefore be used to detect barium and strontium respectively. A saturated solution of strontium sulphate contains only 7000 parts of water, and can therefore precipitate barium from barium salts, while strontium and calcium cannot thus be thrown down, as their sulphates are soluble in this amount of water. A saturated calcium sulphate solution contains but 430 parts of water, and therefore precipitates either barium or strontium from their solutions, while calcium salts remain unprecipitated. (We may mention that calcium sulphate cannot throw down *strontium sulphate* from a *strontium sulphate* solution.) These reactions are only qualitative, and made in the following manner: To a portion of the solution of the metals of Group II. we add a solution of strontium sulphate; the formation of a precipitate points directly to the presence of a barium salt. (In the systematic course the test can be made with a small portion of

the hydrochloric acid solution of the carbonates, to ascertain whether it is necessary to separate barium as its chromate.) If no precipitate results, and barium is therefore absent, another separate portion is tested for strontium with calcium sulphate. In the presence of barium the strontium cannot be distinguished, since calcium sulphate precipitates the salts of both metals, and this test is therefore omitted if barium has been detected. In performing this experiment it must be borne in mind that the formation of the precipitates takes more or less time, according to the concentration of the solution; to definitely confirm the presence or absence of strontium or barium, therefore, the solution tested must be allowed to stand for about an hour. It must, further, be remembered that the presence of a quantity of the calcium salt hinders in a great degree the reaction of strontium.

2. *Behaviour toward acids.*—Barium sulphate is also insoluble in the strongest acids, and its treatment by acids is used as a confirmatory test.

3. *Behaviour of the sulphates toward a solution of ammonium sulphate* (separation of calcium from strontium).—Calcium sulphate dissolves in a large excess (about 300 parts) of a concentrated solution of ammonium sulphate (1 part salt to 4 parts water) on standing for twelve hours at the ordinary temperature. Strontium sulphate, on the contrary, is only slightly soluble in this medium (1 part in 17,000 parts of the solution).

The test is made with the solution of the carbonates in hydrochloric acid (§ 17); if barium has been found and separated as the chromate, strontium and calcium must be reprecipitated as their carbonates from the filtrate. The hydrochloric acid solution, which must contain only the least possible amount of free acid, is treated with a large excess of ammonium sulphate, allowed to stand for twelve hours, and filtered. The residue is washed with ammonium sulphate and subjected to the confirmatory tests mentioned in § 20. For the detection of calcium, the filtered solution of ammonium sulphate is precipitated by ammonium oxalate, when calcium oxalate separates as a fine white powder. The confirmatory tests for this salt are described in § 21. Since calcium oxalate is somewhat soluble in ammonium sulphate, the test may fail if only traces of calcium are present, and in this case it is necessary to evaporate the ammonium sulphate solution to dryness, ignite, and examine the residue thus obtained.[1]

Flame coloration—The salts of the metals of Group II. which volatilise in the flame of a gas-burner (the chlorides, but not the carbonates or sulphates) colour the flame in a very characteristic manner. These colorations are described among the special reactions. By means of the spectroscope (see Section III.) the single metals can be distinguished in the presence of each other, and for the recognition of strontium when calcium is present this method is the best known.

SPECIAL REACTIONS

Barium

§ 19. Reactions of the Barium Salts.—The majority of barium salts of inorganic acids are insoluble in water, but the insoluble salts, with the exception of the sulphate and silicofluoride, dissolve in dilute acids. The halogen salts, as well as the nitrate and chlorate, are soluble. The difficult solubility of barium chloride in hydrochloric acid, and of the nitrate in nitric acid, should be mentioned; this is especially characteristic of the nitrate, which is even precipitated if concentrated nitric acid be added to its solutions or, indeed, to that of barium salts in general. Barium chloride and nitrate are also insoluble in alcohol and ether.

Barium sulphate is precipitated as a white granular powder on the addition of dilute sulphuric acid, or of the solution of a sulphate to barium salts; strontium sulphate also throws down the salts of barium after some time. Barium sulphate is insoluble in water or dilute acids, is not transformed into the carbonate by boiling with potassium carbonate, and does not dissolve in ammonium sulphate.

Barium carbonate.—The carbonates of the alkali metals and of ammonium throw down barium salts in the form of a

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[1] Although this method has been proved by the experiments of R. Fresenius to be not entirely accurate, the beginner must still be content with it. An exact separation of calcium from strontium is obtained through the action of a mixture of alcohol and ether upon their nitrates, previously dried at 130° C. The solvent extracts the calcium and leaves the strontium undissolved. Although for the beginner there is some danger of fire in using this method, we shall give a more complete description of its details in explaining the course of analysis of this group.

white, amorphous precipitate of barium carbonate which is insoluble in water, but dissolves easily in dilute acids, and to a slight degree also in ammonium chloride.

Barium silicofluoride, $BaSiF_6$, is fairly insoluble in water (1 : 4000). It is precipitated by hydrofluosilicic acid, in the crystalline state, and settles rapidly to the bottom of the vessel; in dilute solutions the reaction requires some time. The salt is absolutely insoluble in alcohol. Although the silicofluorides of calcium and strontium are easily soluble in water, the separation of these metals from barium by means of this salt is accurate only under very complicated conditions.

Barium chromate, $BaCrO_4$.—Potassium chromate precipitates this salt, yellow, soluble in nitric acid, but separating again on neutralisation. To make the confirmatory tests, the barium chromate obtained in the course of analysis is transformed to the carbonate by sufficient boiling with potassium carbonate; after filtering and washing, the carbonate is dissolved in the least possible quantity of hydrochloric acid, and the characteristic reactions of barium made with the solution.

Flame coloration.—The volatile salts of barium, such as the chloride or nitrate, colour the non-luminous flame of gas or alcohol a yellowish green. The phosphate does not show this reaction itself, but does so after being moistened with hydrochloric acid, or fused with sodium carbonate. The experiment is made as described under the alkali metals (§ 9). Seen through a green glass the rays of the coloured flame appear blue. Its spectrum is given in Section III. (§ 111). As there are many other characteristic reactions of barium this test is seldom used for its detection.

Strontium

§ 20. Reactions of Strontium Salts.—The salts of strontium are very similar to those of barium, the chief difference being shown in the silicofluoride and chromate, which are much more soluble; a further variation is found in the behaviour of strontium chloride toward absolute alcohol, by which it is dissolved. The nitrate is insoluble in alcohol or ether.

Strontium sulphate.—Obtained as a white, crystalline precipitate by the action of dilute sulphuric acid or soluble sulphates. Strontium salts are not precipitated by a solution of strontium sulphate, but are thrown down by calcium sulphate. The presence of an excess of hydrochloric or nitric acids, as well as of calcium salts, materially hinders the reaction. The sulphate is somewhat soluble in dilute acids, and is completely decomposed on boiling with alkali carbonates, even in presence of other sulphates. Its slight solubility in ammonium sulphate affords a method for its separation from calcium (§ 18).

Strontium carbonate is a white, amorphous precipitate, easily soluble in acids.

The *flame coloration* is a very characteristic reaction. Brought into the flame of the gas-lamp on a platinum wire, strontium salts colour the flame a carmine-red. In cases similar to those mentioned under Barium, the salt must be moistened with hydrochloric acid or ignited with sodium carbonate. Blue glass alters the strontium rays to a rose-red or purple-red. The spectrum of the metal is described in Section III. The flame coloration of strontium salts is an important reaction in distinguishing this metal from the other members of the group. Strontium is usually obtained in analysis as the sulphate, a compound which does not show the flame coloration which, in lieu of other reactions, must be obtained as a confirmatory test. If sufficient of the sulphate is at hand, it is transformed to the carbonate by boiling with potassium carbonate or, better still, igniting with sodium carbonate; after being treated with water and washed, it is dissolved in hydrochloric acid, and the test made with the chloride thus obtained. If too little of the sulphate is found for this process, as is usually the case, the precipitate is washed and dried together with the filter; the dry paper is folded up, and first charred and then ignited upon a platinum wire until the combustion of the carbon is complete. The flame is then made luminous and the salt further ignited, whereupon the sulphate becomes reduced to the sulphide. The ash is moistened (preferably in a small porcelain crucible) with a drop of hydrochloric acid, and again cautiously introduced into the flame. The flame coloration will depend upon the amount of strontium chloride formed; with small quantities it very quickly passes away.

Since strontium shows no other characteristic reactions, the above tests prove its presence only when the impossibility of other metals being present is assured. This fact must be remembered. The student must decide for himself whether this condition is complied with.

Calcium

§ 21. Reactions of the Calcium Salts.—Calcium, though in general more similar to the foregoing metals, occupies an intermediate position between these and magnesium. It forms a hydroxide, $Ca(OH)_2$, more difficultly soluble than those of barium or strontium, and which easily parts with its water upon ignition; a more easily soluble sulphate, and a soluble silicofluoride and chromate. These salts, and the solubility of the nitrate and chloride in alcohol, distinguish calcium from barium and strontium.

Calcium oxalate, CaC_2O_4, is a characteristic salt, and oxalic acid a characteristic reagent for calcium.[1] Ammonium oxalate precipitates calcium oxalate as a white, crystalline powder, which is thrown down immediately from concentrated solutions, or on warming, as $CaC_2O_4 + H_2O$; from cold and dilute solutions the salt separates out only after some time, and then has three molecules of water, $CaC_2O_4 + 3H_2O$. *It does not dissolve in water,* is soluble in mineral acids, but not in acetic acid. This is an important characteristic. The salt cannot be used as a means of separating calcium from barium and strontium, as the oxalates of the latter are also difficultly soluble and show the same behaviour toward acetic acid. This reaction establishes the presence of calcium, therefore, only when it is certain that barium and strontium are absent. This is also an important fact.

Calcium sulphate.—On the addition of sulphuric acid to the concentrated solution of a calcium salt the sulphate separates immediately as a white precipitate; from dilute solutions it is precipitated only after some time, or, indeed, not at all. It dissolves in a concentrated solution of ammonium sulphate (§ 18), and is easily transformed to calcium carbonate by boiling with potassium carbonate. Calcium sulphate solution precipitates barium and strontium salts. It is insoluble in alcohol.

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[1] Oxalic acid, a dibasic acid, $C_2O_2(OH)_2$, is obtained through the oxidation of sugar by nitric acid, and also occurs in sorrel.

Calcium carbonate is obtained as an amorphous, voluminous precipitate on addition of ammonium carbonate or that of an alkali. It becomes crystalline after remaining in water for some time at the ordinary temperature, and more quickly on boiling. When freshly precipitated and amorphous, it is somewhat soluble in ammonium chloride, but separates out almost completely if the solution be boiled.

The *flame coloration* is rarely employed for the detection of calcium. The flame is coloured orange-yellow upon the introduction of a calcium salt, and seen through a blue glass it becomes sulphur-yellow. The method of making the experiment is explained under Strontium (§ 20). The spectrum of the flame is described in Section III.

SYSTEMATIC COURSE OF ANALYSIS FOR THE METALS OF GROUP II. DIVISION 1

§ 22. Detection of the Metals of Group II., Division 1.—We remember that in § 14 the systematic course was formed after consideration of the following questions:—Which reactions are to be chosen for the detection of the elements studied? Is the use of the reactions selected possible in the presence of many elements of the given group, or must these be previously separated? Which metal must be separated? If we choose the reaction with ammonium chromate for barium, with sulphuric acid for strontium, and with ammonium oxalate for calcium, it is obvious that the respective metals must be isolated, since the chosen reagents exert a more or less similar action upon all. Barium is the most easily to be separated.

Since, therefore, the course of analysis is dependent upon the presence or absence of barium, the first operation is the addition of strontium sulphate solution to *a portion* of the solution to be investigated, and allowing it to stand for some time. If the chromate is to be employed for this test, a portion of the solution is diluted, acidified with a few drops of acetic acid if neutral, and precipitated with ammonium chromate. In case barium is found it must be separated, and this is most easily accomplished in the form of the chromate, as explained in § 17. Calcium and strontium are precipitated from the filtrate as carbonates by ammonium carbonate, and, after filtering and washing, dissolved in hydrochloric acid. The separation of calcium from strontium depends upon the insolubility of strontium sulphate in ammonium sulphate (§ 18). To control the separations the characteristic reactions of the respective metals must be made, the flame coloration being used for strontium, and calcium recognised by precipitating the ammonium sulphate filtrate with ammonium oxalate (§ 20 and § 21). As regards these confirmatory tests, it has been mentioned in §§ 20 and 21 that they are conclusive only in the certain absence of the other metals of this group; we point this out to the student that he may give it his attention, although the exigency is satisfied in the given course of analysis.

As an exact means of distinguishing between the metals of this division, R. Fresenius recommends the following method:—The well-washed carbonates are dissolved in dilute nitric acid, and the solution evaporated to dryness in a small porcelain dish. The dry residue is then pulverised and digested with about 10 c.c. of a mixture of equal volumes of absolute alcohol and ether. The insoluble residue of barium and strontium nitrates is brought upon a filter and washed with a small quantity of the same mixture. If calcium was present, it is contained in the filtrate, where it can be readily recognised by the addition of a few drops of dilute sulphuric acid. The barium and strontium nitrates are next dissolved in water, and a few drops of acetic acid and some potassium monochromate added to the solution, which is then boiled. The precipitate of barium chromate is filtered off, the filtrate treated with ammonium carbonate, and the precipitated carbonate examined for strontium in the usual manner.

Metals of Groups I. and II. Separation from the first group.—In this case, for the first time, the reactions of *separate groups* must be combined. The alkali metals cannot be detected unless barium, strontium, and calcium have been previously removed, as these metals form insoluble compounds with both tartaric and pyroantimonic acids. The second group is distinguished from the first by its members having many insoluble salts, of which the carbonates are the most suitable for the purposes of separation, not only because the separation can be made with accuracy by their means, but also since the salts themselves possess properties which simplify the rest of the analysis.

The separation is accomplished by a general reaction; the precipitation of barium, strontium, and calcium in warm solution by ammonium carbonate and ammonia (§ 17). The precipitate is filtered off (leaving the metals of Group I. in the filtrate), washed, and dissolved on the filter in dilute hydrochloric acid. A solution of the chlorides is thus obtained, in which the metals are detected by the methods given in this paragraph. A confirmatory test of the completeness of precipitation is absolutely indispensable here, since if it, and in consequence the separation, is imperfect, the reactions of the metals of Group I. cannot be obtained. As a confirmatory test the filtrate from the carbonates is again tested with ammonium carbonate and gently heated, upon which no precipitation must occur; the analysis of the first group can be proceeded with only when this has been done. The ammonium salts are next separated by evaporation and ignition (§ 13), and the residue tested for potassium and sodium according to § 14. It must be remarked that, as ammonium salts have been used in searching for the metals of the second group, ammonia cannot be tested for in this solution. This alkali is detected in a separate portion of the original solution by the method given in § 14.

Practical experience in the analysis of the metals of this division should be gained by the plan recommended for Group I., first by the study of mixtures known to the student, and then of those which are unknown.

GROUP II., DIVISION 2

MAGNESIUM

Magnesium is characterised as a metal of Group II. by the solubility of its sulphate and the insolubility of its carbonate; it is at the same time distinguished from the metals of Division 1 by its power of forming soluble double salts with ammonium compounds.

Magnesium is a silver-white metal of specific gravity 1·75. It is very soft, and is usually found in commerce as "Magnesium ribbon." It is stable in the air at ordinary temperatures, but if lighted, burns with a blinding bluish white flame. The metal begins to decompose water even at the ordinary temperature, but is protected from further oxidation by the crust of oxide formed. Magnesium is extremely soluble in dilute acids.

The magnesium salts corresponding to those which characterise the metals of Division 1, viz., the sulphate, chromate, and silicofluoride, are all readily soluble in water. The reagents, therefore, by means of which the calcium, strontium, and barium salts are obtained, do not precipitate magnesium.

The salts with volatile acids are often partially decomposed even by evaporation, and completely so by ignition.

§ 23. Reactions of Magnesium Salts.—*Magnesium hydroxide,* $Mg(OH)_2$, is thrown down from the solutions of magnesium salts by alkali hydroxides as a white, amorphous, voluminous precipitate which is slightly soluble in water (about 1:55,000). Warming accelerates its separation. In the presence of chlorides, or the sulphates of the alkalies, the precipitation is not complete unless a great excess of the reagent be used. The behaviour of magnesium salts toward the alkalies is also influenced by the presence of ammonium salts, as will be described below. Magnesium hydroxide is easily transformed to the anhydrous oxide, MgO, by ignition. It can be precipitated by the hydroxides of barium or calcium, or with mercuric oxide (used in the separation of magnesium from the alkalies):

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2.$$

Magnesium carbonate.—Sodium and potassium carbonates precipitate in the cold the basic carbonate, $4(MgCO_3) . MgO + 10H_2O$, according to the reaction:

$$5MgCl_2 + 5K_2CO_3 = 4(MgCO_3) . MgO + CO_2 + 10KCl.$$

A portion of the salt is retained in solution by the liberated carbon dioxide. This is deposited on boiling, however, as the normal salt, $MgCO_3 + H_2O$. This reaction is likewise influenced by the presence of ammonium salts (comp. below). As qualitative reactions, the formation of magnesium hydroxide and carbonate is not important. They are explained here to give the student a better insight into the following reactions.

Ammonium Magnesium Double Salts.—Magnesium salts easily form double compounds with those of ammonium. The majority of these double salts—such, for instance, as $2NH_4Cl . MgCl_2$, or $(NH_4)_2SO_4 . MgSO_4$—dissolve readily in water; but there are also difficultly soluble salts, such as NH_4MgPO_4.

The formation of the soluble double salts is employed in the separation of magnesium from the metals of the first division of this group. The insoluble salt, NH_4MgPO_4, is extremely characteristic of magnesium, and is important.

Soluble double salts.—Let us consider the formation of these salts in acid, neutral, and alkaline solutions, or, in other words, under all the conditions which may occur in analysis. The simplest case is presented in neutral solutions, where the magnesium salt unites directly with that of ammonium: thus, on the addition of an ammonium chloride solution to one of a magnesium salt, the corresponding double salt will be obtained. In considering the formation of double salts in alkaline solution, it is especially important to study cases where ammonia or ammonium carbonate is the alkali present.

The action of ammonia upon a neutral solution is to form a soluble double salt with one-half of the magnesium, while it precipitates the other half as hydroxide; this is illustrated by the following examples:

$$2MgCl_2 + 2NH_3 + 2H_2O = MgCl_2 . 2NH_4Cl + Mg(OH)_2,$$
$$2MgSO_4 + 2NH_3 + 2H_2O = MgSO_4 . (NH_4)_2SO_4 + Mg(OH)_2.$$

This reaction depends upon the fact that the ammonia, whatever its excess, can only form sufficient ammonium salt to unite with half of the magnesium, and the other half must therefore be precipitated.

Ammonium carbonate at first produces no precipitate in a *neutral* solution of magnesium salts, other ammonium salts being absent; after some time, however, a salt separates out which, according to the quantity of the reagent added, has either the composition $MgCO_3 + 3H_2O$ (incomplete precipitation), or with excess, and in the presence of ammonia, that of the double salt, $MgCO_3 . (NH_4)_2CO_3 + 4H_2O$. The latter is difficultly soluble in water.

On acid solutions of magnesium salts ammonia has a different effect. In the cases cited above, the hydroxide was precipitated because an insufficient amount of ammonium salt was formed to unite with that of the metal. If the solution is acid, on the contrary, an excess of an ammonium salt will obviously be formed by the ammonia, and the hydroxide cannot be precipitated. Ammonia does *not*, therefore, precipitate the acid solution of a magnesium salt:

$$MgSO_4 + H_2SO_4 + 2NH_3 = MgSO_4 . (NH_4)_2SO_4.$$

The ammonium salt will be formed at the moment of the reaction. The same result will occur if ammonium salts are already present. *Ammonia does not precipitate magnesium hydroxide in presence of ammonium salts.* No precipitate results, therefore, if ammonia be added to a magnesium sulphate solution in presence of ammonium chloride. To better understand the reaction, it may be divided into two parts:

I. $2MgSO_4 + 2NH_3 + 2H_2O = MgSO_4 . (NH_4)_2SO_4 + Mg(OH)_2.$
II. $Mg(OH)_2 + 4NH_4Cl = MgCl_2 . 2NH_4Cl + 2NH_3 + 2H_2O.$

No precipitate can result, since two ammonium double salts are formed.

In the presence of ammonium salts ammonium carbonate does *not* precipitate magnesium, a double salt being formed in the reaction.

The separation of magnesium from the metals of Division 1 rests upon the combination of all the reactions cited above. This separation is especially described in the systematic course of analysis, and it is sufficient to mention here that it is accomplished by means of ammonia and ammonium carbonate, in presence of ammonium chloride. Too great an excess of ammonium chloride is to be avoided, as the error due to the solubility of the carbonates of Division 1 in this medium may otherwise be increased.

The action of alkalies in presence of ammonium salts is not important. A precipitate is not caused; but as ammonium salts are decomposed by alkalies (when the latter is in large excess, even in the cold, and rapidly on boiling), magnesium hydroxide will in time be deposited because of this action.

$$MgSO_4 . (NH_4)_2SO_4 + 4KOH = Mg(OH)_2 + 2K_2SO_4 + 2NH_3 + 2H_2O.$$

Insoluble ammonium magnesium double salts.—We shall study only the phosphate.

Ammonium magnesium phosphate. — The phosphates, $Mg_3(PO_4)_2$ and $MgHPO_4$, which are thrown down from the solution of magnesium salts by soluble phosphates as amorphous white precipitates, are not very characteristic of this metal, and are unimportant for analytical purposes. Ammonium-magnesium phosphate, $Mg(NH_4)PO_4$, is the most important salt of magnesium, being a white *crystalline* precipitate. It is somewhat soluble in water, but absolutely insoluble in ammonia; and while it dissolves in acids, even in acetic, it is reprecipitated on neutralisation with ammonia. To obtain this salt several conditions must be observed, some of which result from the general character of magnesium compounds, and some from the special properties of the magnesium ammonium phosphate itself. It is formed by precipitating magnesium salts with sodium phosphate or, better, with $Na(NH_4)HPO_4$, in presence of ammonium chloride and ammonia. Ammonium chloride is added to prevent the precipitation of magnesium hydroxide by the ammonia. The latter must be present in sufficient quantity to impart a strong odour to the solution, serving partly to aid the formation of this trimetallic phosphate, and partly to render it more insoluble. If these conditions are satisfied, sodium phosphate will precipitate a *crystalline* ammonium magnesium phosphate. (The student should especially notice this characteristic.) It is advisable to add the reagent by drops and, after shaking, to ascertain the crystalline nature of the precipitate.

SYSTEMATIC COURSE OF ANALYSIS FOR GROUP II. OF THE METALS

§ 24. **Magnesium and the Metals of Division 1** (barium, strontium, and calcium).—The properties of the magnesium compounds, and the impossibility of directly precipitating them as magnesium ammonium phosphate, prevent the detection of this metal before its complete isolation from the members of the first division. As a means of separation, ammonium carbonate in the presence of ammonium chloride and ammonia is used (§§ 17 and 22). Enough ammonium chloride must be added to prevent precipitation on the subsequent addition of ammonia. The solution is precipitated by a slight excess of ammonium carbonate, and heated gently, but not to boiling. The carbonates of barium, strontium, and calcium separate, while the ammonium magnesium double salt remains in solution (together with traces of barium and calcium). It must be remembered here, as in § 22, that it is necessary to ascertain whether a quantity of ammonium carbonate sufficient for the complete precipitation of barium, calcium, and strontium has been added. This is best seen by testing the filtrate from the carbonates again with ammonium carbonate; if the experiment has been correctly made, no precipitate should appear. The well-washed precipitate of barium, strontium, and calcium carbonates is next treated according to § 22. In the filtered solution magnesium is tested for by precipitation with sodium phosphate (§ 23). The student must remember that only a crystalline precipitate indicates the presence of magnesium.

In accurate analyses it is necessary to be attentive of any traces of barium and strontium which may have been held in solution together with magnesium, by the interaction between the carbonates of these metals and the ammonium chloride. The removal of these traces is very important if but little magnesium is present. In this case barium is previously separated with dilute sulphuric acid (two to four drops), and calcium with ammonium oxalate, as small a quantity of the reagents as possible being used. The test for magnesium is made after filtering from the precipitates.

Metals of Groups I. and II.—We have noticed the separation of barium, strontium, and calcium from magnesium. The course of analysis is not altered by the additional presence of the alkali metals, and therefore only the separation of magnesium from the alkalies remains to be discussed. This is necessary because the detection of the alkali metals is impossible if magnesium is still present, as magnesium tartrate and pyroantimonate are also insoluble in water. Magnesium is distinguished from the metals of Group I. by the insolubility of its oxide, carbonate, and phosphate; in qualitative analysis it is more conveniently separated as its hydroxide. After barium, strontium, and calcium have been removed, as above, magnesium and the alkali metals remain in the solution. A separate portion is tested for magnesium with sodium phosphate; to the remainder, from which the ammonium salts must be previously separated by evaporation and ignition, an excess of milk of lime is added, and the liquid boiled in a porcelain dish. The lime must be in excess, which is the case if, after boiling for some time (about $\frac{1}{4}$ hour), the solution turns turmeric paper brown. On filtering, the magnesium hydroxide and the excess of lime remain on the filter, while the alkali metals are in solution together with the calcium salt formed.

To test for magnesium it is first necessary to separate the lime from the precipitate by dissolving in hydrochloric acid, neutralising the solution with ammonia, and precipitating with ammonium oxalate. (The precipitate may contain traces of magnesium ammonium oxalate.) The calcium oxalate having been filtered off (it must be carefully and completely precipitated in the heat and allowed to stand until it has fully subsided), the magnesium chloride remains in solution and is detected by means of a soluble phosphate.

The solution containing the alkali metals is likewise treated with ammonium oxalate to separate calcium, filtered and evaporated to dryness. The ammonium salts having next been driven off, the alkali metals are tested for according to § 14.

Barium hydroxide can be used for the separation of magnesium as well as lime milk. In this method a solution of barium hydroxide is added until a precipitate ceases to form, and the solution boiled and filtered. The barium can be separated from the magnesium hydroxide in the precipitate by means of sulphuric acid, and is thrown down from the filtrate which contains the alkali metals by ammonium carbonate and ammonia.

A separate portion of the original solution is tested for ammonia (§ 14).

SUPPLEMENT TO GROUP II

1

Analysis of the compounds of the metals of Group II. which occur in nature.—Barium, strontium, and calcium are found in nature chiefly as their sulphates or carbonates. $BaSO_4$ (heavy spar), $SrSO_4$ (celestine), and $CaSO_4$ (gypsum and anhydrite) are insoluble in water and acids. They are transformed to soluble compounds by fusion with alkali carbonates. $BaCO_3$ (witherite), $SrCO_3$ (strontianite), and $CaCO_3$ (calc-spar, marble) are soluble in acids. Calcium also occurs as a phosphate (apatite, phosphorite, etc.), as calcium fluoride (fluor spar); and likewise in silicates (comp. Section III., Examples). Magnesium is a constituent of many minerals (augite, hornblende, serpentine, talc, olivine, etc.), the analysis of which is described in Section II. It also occurs as carbonate (magnesite, bitter-spar, dolomite). These minerals are soluble in acids. Carnallite, $KMgCl_3$, and a few other potassium and magnesium double salts (such as the sulphate, kainite) which are found in the upper layers of rock salt in Stassfurt, are soluble in water

2

Application of the compounds of the metals of Group II. in analysis.—Both barium and calcium compounds are used in analysis. Their oxides are employed in the same cases as those of the alkalies, but with the advantage of being more easily removed afterward. The precipitation of magnesium and separation of ammonia with barium or calcium hydroxides have already been mentioned in §§ 24 and 13. We have still to notice the use of barium oxide as an absorbent for carbon dioxide, and the analysis of silicates by fusion with the oxides, carbonates, or chlorides of barium or calcium (Section II.) Barium carbonate is also employed in precipitating oxides of the formula R_2O_3.

GROUP III

ALUMINIUM, CHROMIUM, IRON, MANGANESE, ZINC, NICKEL, COBALT (BERYLLIUM, YTTRIUM, CERIUM, DIDYMIUM, LANTHANUM, ZIRCONIUM, THORIUM, TITANIUM, TANTALUM, NIOBIUM, URANIUM, INDIUM, THALLIUM).

§ **25.** With the exception of the first two metals (and the majority of those in parentheses), which form no sulphides in the wet way, the members of Group III. possess sulphides of the general formula RS; these salts are soluble in acids, and therefore are not precipitated from acid solution by hydrogen sulphide. They are thrown down, however, by ammonium sulphide (or other soluble sulphides), that is, by hydrogen sulphide in alkaline solution. Ammonium sulphide is the general reagent of this group. Aluminium and chromium (and a greater part of the rare metals) are precipitated by ammonium sulphide as oxides of the formula R_2O_3.

Characteristics of the Divisions.—Although the third group of metals contains elements varying in their chemical properties, the characteristics which are used in analysis facilitate their classification into divisions comprising chemically similar elements. Such a classification may be based upon our acquaintance with some of the properties of the oxides and sulphides.

The oxygen compounds of the metals under discussion are of various kinds. It is sufficient, for our purpose, to notice those of the formulas R_2O_3 and RO:

— — FeO, MnO, CoO, NiO, ZnO,
Al_2O_3, Cr_2O_3, Fe_2O_3, Mn_2O_3, Co_2O_3, Ni_2O_3. —

The first row consists of oxides of the general formula RO, or monoxides. They easily give salts, to which are applied the termination *-ous*, in distinction from those of the higher oxides, which end in *-ic* (ferrous sulphate, ferric chloride). Since the metals of the first row unite with one atom of oxygen to form monoxides, they combine in this series with two atoms of a halogen, their chlorides thus being represented by the formula RCl_2. In forming salts they displace two atoms of hydrogen in the acid, the sulphate, for example, being RSO_4. This degree of oxidation is unknown in aluminium, and though we are acquainted with the corresponding compounds for chromium (for example, $CrCl_2$), they are so unstable that they cannot exist under the usual conditions, and pass into the higher series.

The second series of oxides consists of the sesquioxides, of the general formula R_2O_3. Such an oxide is for zinc alone unknown. They show, as far as their stability and the power of forming salts are concerned, great variability in their chemical character. One property, however, is possessed by all, viz., that of being precipitated from their solutions in the cold by barium carbonate. The oxides of aluminium, chromium, and iron are easily transformed to the corresponding chlorides, such as ferric chloride, $FeCl_3$, and also form salts with oxyacids, as ferric sulphate, $Fe_2(SO_4)_3$. The sesqui-salts of these metals are all well defined and are stable; of aluminium they are the only ones known. Manganic chloride, $MnCl_3$, is very unstable, and the salts of oxyacids with manganese sesquioxide are almost unknown. The cobalt compound, $CoCl_3$, exists only in a cold solution, though the cobaltamine compounds and cobaltic nitrite are relatively stable. Nickel sesquioxide is incapable of forming salts. As a result of the variable stability of the chlorides, the sesquioxides do not all show the same behaviour toward hydrochloric acid. Those of aluminium, chromium, and iron do not evolve chlorine, and their chlorides are stable, while the sesquioxides of manganese, cobalt, and nickel decompose hydrochloric acid, at the same time being transformed to salts of the monoxides:

$$Ni_2O_3 + 6HCl = 2NiCl_2 + 3H_2O + Cl_2.$$

If peroxides be defined analytically as those oxygen compounds which generate free chlorine when acted upon by hydrochloric acid, these oxides may be called peroxides. In this relation they are analogous to the higher oxides of the same metals; thus, manganese peroxide, MnO_2, manganic acid, H_2MnO_4, permanganic acid, $HMnO_4$, and chromic acid, H_2CrO_4, all afford a like reaction in evolving chlorine with hydrochloric acid. As a result of the study of the oxides, aluminium, chromium, and the ferric compounds of iron are placed in a separate division (Division 1). Sulphides of these metals are not formed in the wet way.

The remaining metals are separated into divisions according to the behaviour of their sulphides toward weak acids. The sulphides of ferrous iron, manganese, and zinc, are easily soluble in hydrochloric acid, with evolution of hydrogen sulphide and formation of chlorides. Nickel sulphide and cobalt sulphide are not decomposed by, but almost insoluble in, dilute hydrochloric acid.

The third group of metals is thus arranged in three divisions. The general characteristics of (1) precipitation by ammonium sulphide, and (2) non-precipitation by hydrogen sulphide, being retained for them all, the divisions can be characterised as follows:—

Division 1: Aluminium, Chromium, Ferric Iron.—The sesquioxides, R_2O_3, are precipitated by barium carbonate in the cold. They are not thrown down from aqueous solutions as sulphides.

Division 2: Ferrous Iron, Manganese, Zinc.—The monoxides, RO, are precipitated neither by barium carbonate nor as basic acetates. The sulphides, RS, are soluble in dilute acids.

Division 3: Nickel and Cobalt.—The monoxides, RO, are precipitated neither by barium carbonate nor as basic acetates, and their sulphides, RS, are insoluble in dilute hydrochloric acid.

Remark.—Before taking up the study of the metals of Group III. the student must become acquainted with certain new operations. The term "Ignition" denotes the heating of a substance to a very high temperature, whether the operation causes a change in the ignited substance or not. Ignition is used for several different purposes, and therefore performed by various methods. In its application to qualitative analysis (testing the stability at a high temperature, fusibility, etc., of the given compounds) the operation is carried out in a glass tube which is sealed at one end. Usually, however, a substance is ignited in a crucible. When a substance melts on ignition (either alone or on the addition of another body) the operation is called a "Fusion." This is rarely employed in order to bring the compound into a molten state, but more often to induce certain chemical reactions.

GROUP III., DIVISION 1

ALUMINIUM, CHROMIUM, AND FERRIC IRON

These metals are placed in the third group because of their non-precipitation by hydrogen sulphide from acid solutions and of their behaviour toward ammonium sulphide, by which they are thrown down as hydroxides. The characteristics of the first division are these: The oxides of the formula R_2O_3 are precipitated in the cold by barium carbonate; aluminium and ferric iron form basic acetates insoluble in water.

§ 26. The Compounds of the Metals of Division 1.—This division embraces metals which are to a high degree similar in their chemical natures. The properties of the *metals* themselves are described under the Special Reactions, and their *oxides* are fully treated under the General Reactions. Their *sulphides* are known, but are formed only in the absence of water, and are decomposed by the latter to the oxides.

The salts.—The oxides, being weak bases, do not unite with weak acids. Sulphides (in the wet way), thiosulphates, and sulphites are unknown; carbonates are formed only by iron and chromium, and even these are basic. With the strong acids, however, they form well-defined salts: the normal acetates, sulphates, and nitrates are easily soluble in water. The majority of the salts lose their acid when heated, the anhydrous oxides being formed from the nitrates even at 250° C., and from the sulphates on ignition. The sulphates, of the formula $R_2(SO_4)_3$, unite with those of the alkali metals and of ammonium to form double salts, or alums, as $KAl(SO_4)_2$,

$KCr(SO_4)_2$, $KFe(SO_4)_2$. These salts crystallise in octahedra, and contain twelve molecules of water (manganic sesquioxide also forms such a compound). The chlorides, RCl_3, are soluble in water, but on evaporation of the solutions to dryness they partially or wholly give off their hydrochloric acid. The anhydrous chlorides are volatile at a higher temperature (the facts noted concerning the chlorides of the various metals should be compared with the statements made under the Special Reactions). The oxides, phosphates, and the basic salts of many acids, the neutral salts of which are soluble, are insoluble in water. All of these compounds are, with a few exceptions, dissolved by acids.

As the oxides are weak bases, their salts are easily decomposed by water, with loss of acid. In the case of complete decomposition by water, the hydroxide results, *e.g.*:

$$Al(C_2H_3O_2)_3 + 3H_2O = Al(OH)_3 + 3C_2H_4O_2.$$

If it is incomplete, basic salts are formed:

$$Al(C_2H_3O_2)_3 + H_2O = Al(OH)(C_2H_3O_2)_2 + C_2H_4O_2.$$

The formulæ of the simplest basic salts correspond to those of the hydroxides, but have one or more of the hydroxyl groups replaced by acid radicals. To these simplest basic salts belongs the above basic aluminium acetate. It often happens that no formula can be assigned to basic salts formed in certain reactions, since from every neutral salt compounds of widely varying basicity may be derived, and their composition depends entirely upon the conditions under which they are obtained, *i.e.*, the temperature, amount of water present, etc. It follows from the above that when basic salts are to be formed, free acid must not be present.

As the oxides of aluminium and chromium are weak bases they have the power of uniting with other bases. The oxides of aluminium and potassium, for instance, form the compound, potassium aluminate, $KAlO_2$; those of chromium and zinc, the compound $ZnCr_2O_4$. These compounds are decomposed by acids; they are not formed by iron, or at least there are none of definite composition known.

In spite of the similarity in the properties of the compounds, there are still a few differences in the characters of the different metals of Group III., Division 1, which may serve for their qualitative distinction and quantitative estimation. These variations are found in the existence of only one oxide of aluminium, while for iron and chromium more than one are known. Chromium forms a higher oxide in chromic acid, CrO_3, which suffices both for its detection and separation. Oxidation is, therefore, an important reaction for chromium. Iron forms both the sesquioxide and a monoxide, and the corresponding salts, being thus distinguished from both aluminium and chromium. Reduction, therefore, is an important reaction for the ferric compounds of iron.

We will now turn to the study of the compounds of iron, aluminium, and chromium, the properties of which are made use of in analysis.

General Reactions

§ **27**. The hydroxides, of the general formula $R(OH)_3$, are very important in both qualitative and quantitative analyses. The hydroxides are insoluble in water, but dissolve in acids to form salts. They are obtained as gelatinous, voluminous precipitates, which can be washed only with difficulty. Aluminium hydroxide is white, chromium hydroxide gray-green or gray-violet, according to the variety of the chromic salt from which it is deposited—the green or violet (§ 32). Ferric hydroxide is red-brown. As already mentioned, in addition to the usual reactions for obtaining the insoluble hydroxides, *e.g.*, the precipitation by alkalies or ammonia, those of aluminium and chromium are also thrown down by carbonates, sulphites, thiosulphates, and soluble sulphides, as they are incapable of forming the corresponding salts. We shall now consider each of these reactions in which hydroxides are formed.

Conditions for the complete precipitation of the hydroxides.—Under the conditions mentioned below, the suitable reagents throw down the hydroxides either incompletely or not at all. Non-volatile organic acids, such as tartaric, citric, oxalic, etc., can hinder the reaction more or less, according to the quantity in which they are present; or, if this be large, they may even entirely prevent precipitation. This fact is explained by the properties of the salts of these organic acids. Aluminium tartrate and citrate are both easily soluble in water; they are not precipitated from solution as hydroxides by the action of the alkalies, ammonia, or carbonates, but form soluble double salts instead (*e.g.*, a double salt of aluminium and potassium), of which the tartrate, $KAl(C_4H_4O_6)_2$, and others are known. This property of forming double salts explains why the precipitation results incompletely or not at all when aluminium, ferric, and chromic salts are thrown down in presence of such organic acids. Not only non-volatile acids, but also non-volatile organic substances in general, such as sugar, cellulose, and filter paper, hinder more or less the precipitation, especially that of aluminium hydroxide. The cause of this is likewise the formation of soluble double compounds. To obtain a complete precipitation all organic substances which may be present must first be decomposed.

In taking up the consideration of the general reactions, the student should remember the statements made concerning this class of reactions in the first part of § 17, and study them in accordance with the importance which they attain.

§ **28. Formation of the Hydroxides.**—A. *Reaction with barium carbonate.*—This reaction, one of the most important for the salts of the metals under consideration, results according to the following equation, in which aluminium chloride is used as an example:

$$2AlCl_3 + 3BaCO_3 + 3H_2O = 2Al(OH)_3 + 3BaCl_2 + 3CO_2.$$

The reaction with barium carbonate is used exclusively for the separation of this division from the second and third of this group, and the conditions necessary for complete separation and for complete precipitation must therefore be carefully considered.

The solution to be investigated must contain no sulphuric acid. The separation is impossible if the metals of Group III. are present as sulphates, since these decompose barium carbonate. If nickel sulphate be taken as an example,

$$NiSO_4 + BaCO_3 = NiCO_3 + BaSO_4;$$

it is seen that the insoluble nickel carbonate would be formed by the reaction and found, together with the hydroxides of Division 1, in the precipitate. A separation under these conditions is therefore impossible, and sulphuric acid must first be tested for and removed if found. In the systematic course of analysis this condition is satisfied by precipitation with ammonium sulphide. As the solutions which the student generally uses for examining the metals of this group are those of alums, these compounds must be changed to the chlorides before the reaction can be studied. The student should also have his attention called to another point, viz., that as barium carbonate is a general precipitant for the oxides of the formula R_2O_3, it throws down Mn_2O_3 and Co_2O_3 as well as the oxides of this division. The separation of the first division from the others can be accurately accomplished in spite of this fact, as in the systematic course neither the salts of cobaltic nor manganic sesquioxide can remain in solution, having been reduced, if present, by the hydrochloric acid and hydrogen sulphide previously used. The above are the theoretical requisites for the application of barium carbonate in separations. Let us now consider the conditions necessary for complete precipitation.

Since the reaction occurs between a solid body and a solution, the barium salt must be freshly precipitated, and shaken with water to a milk without previous drying; it should not be kept long under water, as the amorphous barium carbonate gradually becomes crystalline, and in this state precipitates the oxides with greater difficulty. The barium carbonate must (in being prepared from barium chloride and ammonium carbonate) be thoroughly washed. The solution from which the hydroxides are to be precipitated must have a slightly acid or neutral reaction. In order to avoid using too much barium carbonate without purpose, the solution, if acid, is first neutralised with sodium carbonate, drop by drop being added until a permanent turbidity is obtained; this is then dispelled by a few drops of hydrochloric acid. The barium carbonate, suspended in water, is then added, and the solution allowed to stand in the cold for at least twelve hours.[1] If an insufficient quantity of the carbonate be added, the precipitation will not be complete. Chromium solutions are precipitated much more slowly than those of aluminium or iron. The reaction is not as simple as the equation given in the first part of this paragraph indicates, the composition of the precipitate being very complicated. In addition to the hydroxides, which make up the greater portion, it contains a mixture of basic carbonates, basic salts of the acid the salt of which was decomposed, and the excess of barium carbonate which has had

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[1] Barium carbonate often has a different action on hot solutions from that caused in the cold; for instance, it has no effect on zinc salts in the cold, although on boiling the solution the latter are precipitated.

no action. The examination of the precipitate is explained under the Separation of Division 2 from Division 1, § 40 B. In studying this reaction, the student should make it with each single metal. It is left to him to find out and to make, after experiments with each metal, a confirmatory test of the completeness of the precipitation.

B. *The action of alkaline hydroxides.*—The formation of the hydroxides by this reaction and their behaviour to an excess of the reagent are important, both as a qualitative reaction and, to a certain degree, in separations. The hydroxides of aluminium and chromium are soluble in alkalies, aluminium forming a potassium aluminate, $KAlO_2$. Ferric hydroxide does not dissolve in alkalies. The application of these reactions to the detection of the single metals will be noticed under the Special Reactions.

As for the usefulness of these reactions in separation, it must be noticed that they vary in presence of the salts of more than one of the metals. Thus, in the presence of chromium and iron hydroxides, potassium hydroxide does not dissolve all the chromium, while on the other hand, some of the ferric hydroxide passes into solution. Chromium oxide is even more difficultly dissolved, if lead, zinc, magnesium, calcium, nickel, or cobalt are present; this is due to the formation of compounds of these oxides with chromic oxide, similar to the aluminates (for example, $MgCr_2O_4$; ferrous chromic oxide, $FeCr_2O_4$—the native chrome-iron ore—also belongs to this class), which are insoluble in alkaline hydroxides. The formation and insolubility of these compounds can be readily observed by means of the following experiments:—Zinc oxide dissolves in caustic potash; if such a solution be mixed with one of chromium oxide, also in caustic potash, a compound insoluble in the alkali will be precipitated. When the foreign oxides stand in certain proportions to that of chromium, they will in part be carried into solution with the latter. The reaction with the alkali hydroxides cannot be employed in separating iron from aluminium, either in presence of metallic oxides of another group, or in that of chromium alone, and the absence of chromium must be established before its use is permitted. The oxides are treated in the cold with an excess of alkali, and then filtered; ferric hydroxide remains on the filter, and the filtrate contains potassium aluminate, from which aluminium hydroxide is separated as explained in the Special Reactions. The precipitate of ferric hydroxide must at first be washed by decantation, since caustic potash acts upon the filter paper and renders filtration difficult. The washing is finished on the filter.

C. *Action of ammonia.*—Ammonia precipitates the respective hydroxides from the solutions of aluminium, chromium, and ferric salts. Aluminium hydroxide is hardly soluble in ammonia, chromic hydroxide slightly more so, and ferric oxide absolutely insoluble (see Special Reactions).

D. *Action of the carbonates of potassium, sodium, and ammonium.*—The basic salts or, more correctly, a mixture of the hydroxide and basic carbonates, are formed, with evolution of carbon dioxide. The excess of the carbonate added is converted to an acid carbonate. The behaviour of the precipitates to an excess of the reagent varies (see Special Reactions).

E. *Ammonium sulphide* precipitates the hydroxide from aluminium and chromium salts, hydrogen sulphide being at the same time set free. Let us take, as an example, the reaction with aluminium sulphate:

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S.$$

Sulphides of these metals are not formed. Ferric salts, which usually resemble those of aluminium, are reduced by the action of ammonium sulphide, and a new addition of the reagent produces a black precipitate of ferrous sulphide:

$$2FeCl_3 + (NH_4)_2S = 2\ FeCl_2 + 2NH_4Cl + S,$$
$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl.$$

This reaction serves for the separation of this division from the metals of Group II. The solution is first treated with a sufficient quantity of ammonium chloride, and the ammonium sulphide then gradually added until it ceases to cause a precipitate. The solution is then placed aside for an hour in a closed vessel and finally filtered. The addition of ammonium chloride has been empirically found beneficial; it has in all probability an influence on the composition of the precipitate (see § 31). The precipitation is complete. The further treatment of the precipitate is explained under the systematic course of analysis. All operations with ammonium sulphide, as well as the washing of the precipitates, should be carried on in a room especially designated for such purposes.

F. *Sodium sulphite and thiosulphate*, Na_2SO_3, and $Na_2S_2O_3$, likewise precipitate aluminium and chromium hydroxides, since their sulphites and thiosulphates cannot exist. Sulphur dioxide is liberated in the reaction with either of these reagents. (Thiosulphates decompose with formation of sulphur and sulphur dioxide):

$$2AlCl_3 + 3Na_2SO_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3SO_2,$$
$$2AlCl_3 + 3Na_2S_2O_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3SO_2 + 3S.$$

Iron solutions are not precipitated by these reagents, the sulphur dioxide released being oxidised to sulphuric acid, and the ferric iron reduced to a ferrous salt (compare § 34 B):

$$2FeCl_3 + Na_2S_2O_3 + H_2O = 2FeCl_2 + 2NaCl + H_2SO_4 + S.$$

§ 29. **The anhydrous oxides** of aluminium, chromium, and iron, are distinguished in many ways from the hydroxides. The reactions by which they are formed consist mainly in ignition of the hydroxides or of the salts which easily part with their acid, such, for example, as the nitrates, salts of organic acids, etc. Aluminium oxide forms, according to the degree of heat to which it is subjected, either a white powder or a porous mass. Chromic oxide is a green, ferric oxide a brown powder. The anhydrous oxides, even if but slightly ignited, are extremely difficultly soluble in acids, and as it often happens in analysis that they must be ignited before their solution, the latter becomes an important operation. Hydrochloric acid is sufficient for the solution of well-ignited ferric oxide. The operation is performed by pouring fuming hydrochloric acid over the ignited oxide, warming for some time on the water-bath, and treating with water, whereupon ferric chloride passes into solution. Aluminium and chromium oxides cannot be dissolved in this way, since when in the anhydrous state they are much less readily attacked by acids than iron oxide. Alumina is treated with concentrated sulphuric acid (3 parts acid to 1 part water) in the manner described above, *i.e.*, it is warmed on the water-bath and taken up with water. Chromium oxide is brought into solution most easily by ignition with sodium carbonate and potassium nitrate, an easily soluble alkali chromate being thus formed (see Special Reactions, § 32).

§ 30. **The Acetates.**—Acetic acid, $C_2H_3O(OH)$, is a monobasic acid. The neutral acetates of the formula $R(C_2H_3O_2)_3$ are easily soluble in water (the formation of ferric acetate as a qualitative test for ferric iron is described in § 34). The basic salts of iron and aluminium are insoluble (chromium has no insoluble basic acetate) and, in the *absence of chromium*, they are used as a means of separating iron and aluminium from the metals of Group III., Division 2.

Before taking up the practical methods, it may be well to say a few words concerning this complicated reaction. The basic salts are formed by the action of water upon neutral solutions of acetates (§ 26). The composition of the basic salt of aluminium is $Al(C_2H_3O_2)_2(OH)$, its formation from the neutral salt being expressed by the following equation:

$$Al(C_2H_3O_2)_3 + H_2O = Al(C_2H_3O_2)_2(OH) + C_2H_4O_2.$$

The reactions are complicated by the fact that from the solutions of their acetates soluble aluminium and ferric hydroxides can be separated (*e.g.*, by dialysis), the solutions of which deposit the insoluble hydroxides, either when heated or on the addition of salts:

$$Fe(C_2H_3O_2)_3 + 3H_2O = Fe(OH)_3 + 3C_2H_4O_2.$$

The composition of the precipitates as they are obtained in analysis is therefore very complicated. That of the ferric compound consists chiefly of ferric hydroxide.

The reaction is obtained as follows: the solution is neutralised by sodium carbonate, until the turbidity caused does not disappear on stirring; hot water and a sufficient quantity of sodium acetate are then added, and the whole boiled for a short time. Precipitates of basic salts hereupon separate, which are red-brown of iron, white of aluminium. The solution is filtered hot, and washed with a dilute solution of sodium acetate. The further treatment of the precipitate is given in the Systematic Course, § 40, and we remark, here, only that these basic salts are decomposed by alkalies, the aluminium hydroxide formed dissolving in excess of the alkali.

SPECIAL REACTIONS

Aluminium

§ **31.** Aluminium is a white, light metal, of sp. gr. 2·6, melting at 625° C., and non-volatile. It does not decompose water, even on boiling. Hydrochloric acid dissolves it easily, with evolution of hydrogen and formation of aluminium chloride. Sulphuric and nitric acids have only a slight action upon it, the layer of hydrogen formed in the first case, and of nitric oxide in the second, protecting the metal from further attack, although both aluminium sulphate and nitrate are easily soluble in water. It also dissolves in the alkalies, especially potassium hydroxide, with evolution of hydrogen and formation of an aluminate:

$$KOH + H_2O + Al = KAlO_2 + 3H.$$

The alloys of aluminium worthy of mention are aluminium iron and aluminium bronze; their analyses will be considered under the respective metals. All the general statements made concerning the salts of the metals in this Division can be applied expressly to those of aluminium (§ 26).

Reactions of Aluminium Salts.—The properties made use of for analytical purposes have nearly all been mentioned under the General Reactions. Let us turn again to the most important.

Aluminium hydroxide is a white, gelatinous precipitate, insoluble in water, but soluble in acids. It is thrown down from solutions of aluminium salts by the following reagents:—

Ammonia produces a precipitate consisting of the hydroxide and basic salts, soluble in great excess of the reagent (ammonium salts lessen the solubility). In testing for small quantities of aluminium this behaviour to ammonia should always be kept in mind. If the solution be boiled for a short time the precipitation is complete: on protracted heating in presence of ammonium salts a portion of the hydroxide redissolves, probably in the acid liberated through the decomposition of the ammonium salts. The precipitated hydroxide is gelatinous, difficultly washed with water, and has the composition of the normal hydrate, $Al(OH)_3$.

Alkali hydroxides (§ 28 B).—Aluminium oxide dissolves easily in excess of caustic alkalies, forming a soluble potassium or sodium aluminate. The reprecipitation of the hydroxide from this solution is important as a qualitative indication of aluminium salts. The aluminate solution being stable on heating, precipitation must be effected by neutralising the alkali; it can be brought about by the action of acids, even that of hydrogen sulphide or carbonic acid, as the hydroxide is insoluble in either potassium sulphide or carbonate. The direct use of a stronger acid, such as hydrochloric or sulphuric, is inadvisable, as the accidental addition of an excess would redissolve the precipitate. It is preferable to neutralise the solution by means of an ammonium salt, as an excess of the latter has no effect upon the subsequent course of analysis (see above); the salt usually chosen is ammonium chloride. If this reagent be added to the solution of the aluminate, the precipitation begins even in the cold if the solution is concentrated, and is complete on boiling. In this reaction the caustic alkali decomposes the ammonium salt, setting free ammonia and forming potassium chloride, and the hydroxide is precipitated as soon as the alkali has become neutralised. The precipitate thus obtained is denser and more easily washed than the normal hydroxide. It has the formula $Al_2O_3 . 2H_2O$, which may be written $(OH)_2Al—O—Al(OH)_2$, and is a semi-anhydride of the normal aluminium hydroxide:

$$2KAlO_2 + 2NH_4Cl + H_2O = Al_2O_3 . 2H_2O + 2KCl + 2NH_3.$$

This is a very characteristic reaction of aluminium salts. Barium hydroxide can be substituted for the alkalies used.

The *alkali carbonates* precipitate a mixture of the hydroxide and basic carbonates, which dissolves slightly in an excess of the reagents. From boiling solutions the precipitation is complete.

Barium carbonate (§ 28 A) completely precipitates aluminium hydroxide from cold solutions.

Ammonium sulphide throws down aluminium hydroxide. The addition of ammonium chloride (in separations, § 28 E) is beneficial, apparently influencing the composition of the precipitate.

The formation of aluminium hydroxide by precipitation with a salt of sulphurous or thiosulphuric acid is employed only for the quantitative separation of aluminium from iron. It is described under that head (§ 122).

Non-volatile organic acids, such as citric or tartaric, when present in large quantities completely prevent the precipitation of aluminium hydroxide by the above reagents (§ 27). Other organic substances, *e.g.*, sugar, cellulose, pieces of filter paper, etc., are also detrimental to its formation.

Anhydrous aluminium oxide (§ 29) has different properties. Its difficult solubility in acids is especially characteristic. When moistened with a drop of a cobalt nitrate solution on a platinum wire and ignited, a blue coloration is obtained which becomes especially apparent on cooling: it is due to the formation of a cobalt aluminate (Thenard's Blue). As many other substances show the same coloration with cobalt nitrate the test does not absolutely establish the presence of aluminium.

The *basic acetates* of aluminium are described in § 30. They are important only in separations.

Chromium

Metallic chromium, which is very rare, can seldom be met with in the course of an analysis. Chrome-iron ore, one of its alloys, is used in the arts (see Iron). Chromium differs from aluminium and iron, as we have already shown, chiefly in the formation of a higher oxide, chromic acid. The reactions of this compound are used in the separation of chromium. Under chromium, therefore, we must consider both the oxide and its derivatives, and chromic acid, and also the conversion from the oxide to the acid and *vice versâ*.

§ **32.** *Chromic salts.*—The remarks made in § 26 may all be applied to the salts of chromic oxide. The salts with volatile acids lose their acid and pass into the oxide on ignition. The anhydrous chloride, $CrCl_3$, is a violet, volatile compound, insoluble in water or acids, and formed only in reactions in which the presence of water is excluded. Chromic hydroxide dissolves readily in hydrochloric acid, however, the resulting solution containing the hydrated chloride. The chromic salts are remarkable in that almost all of them exist in two modifications, one green and the other violet. Several varieties of the hydroxide are also known.

The green and violet solutions of chromic salts.—Crystalline salts can be obtained directly only from the violet solutions. The green solutions leave on evaporation a sirupy liquid from which (if sufficient water be present) violet crystals separate in time. The distinction in the colour of the precipitate excepted, there is no great difference between the reactions of the two varieties of chromic salts. Precipitates obtained from green solutions are grayish green, from the violet they are gray-violet. To a certain extent a difference exists in the formation of chromic phosphates in the one or the other solution,—the violet being precipitated by sodium phosphate immediately, the green, only after some time. One more important point is to be considered: from a green solution of chromic sulphate barium salts do not throw down the whole of the sulphuric acid as barium sulphate (only two-thirds of it); silver salts, likewise, do not precipitate all the chlorine from the green chromic chloride solutions as silver chloride. The violet solutions, on the contrary, are completely precipitated. Either variety can be converted into the other, the violet being transformed to the green in the course of time on standing, more quickly on being boiled; and on the other hand, the green changing to the violet on crystallisation, as we have already noticed. As a rule, chromic alum is the salt used for laboratory experiments; prepared in the cold, its solution is violet, but in the course of time it becomes green. As a very long period, however, is necessary for the complete transformation, some of the violet solution always remains, and thus a mixture of the two varieties is usually employed in the reactions. These phenomena are caused by the action of water upon the neutral chromic salts, the green solutions containing basic compounds.

The reactions of chromic salts consist, like those of aluminium, in the formation of the hydroxide by different methods.

Chromic hydroxide is a gelatinous precipitate, in colour gray-green or gray-violet, according to the variety of solution from which it is deposited; it is insoluble in water, but soluble in acids. The most important means of obtaining it are as follows:—

Caustic alkalies, added in excess, dissolve the chromic hydroxide at first formed and yield an emerald-green solution. As the presence of any one of several other oxides greatly influences the solubility of the hydroxide in alkalies (§ 28 B), this characteristic reaction cannot be employed for the separation of chromium from the other metals. On prolonged boiling the chromic hydroxide is completely deposited from the alkaline solution. It can also be precipitated, in the same manner as aluminium hydroxide, by neutralising the alkali (with ammonium chloride).

Ammonia precipitates the hydroxide, slightly soluble in excess to a violet solution. The precipitation is made complete by boiling.

Barium carbonate completely precipitates from a cold solution a mixture of hydroxide and basic salts. Complete precipitation is obtained only after some time (12 hours); for the conditions of reaction, see § 28 A.

Ammonium sulphide likewise precipitates the hydroxide (§ 28 E).

Non-volatile organic acids influence or completely hinder the precipitation of chromic hydroxide (§ 27).

Anhydrous chromic oxide is obtained by igniting the hydroxide. As it is insoluble in acids, in order to get it into solution it must be treated according to the directions in § 29. Solution of the anhydrous oxide by oxidation is described more fully below.

In analyses of compounds of this Division the presence or absence of chromium must be positively established, in order to enable the selection of a correct method of separation. The following is an important reaction employed for this purpose: Anhydrous chromic oxide (like the oxides of many other metals) dissolves in molten microcosmic salt or borax to an emerald-green bead. The experiment is made as follows: The loop of a platinum wire is brought to a red heat and dipped into the vessel of borax or so-called microcosmic salt (NH_4NaHPO_4). The salt clinging to the loop is then introduced to the flame of the gas-burner. When the water of crystallisation has been driven off, a transparent fused bead is obtained. Some care is required in fusing the microcosmic salt, as when in the molten state it runs easily and may drop from the loop. The chromic oxide is then placed upon the bead and the whole again heated in the flame. The oxide dissolves in the molten salt, imparting to it a blue colour which is very plain as soon as the bead has cooled off. Both chromic oxide and its compounds in general show this bead coloration. Aluminium and ferric oxides are not detrimental to this reaction, especially if it be made in the reduction flame (see below, Remark).

It may be well to discuss the theory of this reaction. The acid ammonium-sodium phosphate changes on being heated in the gas-flame to sodium metaphosphate:

$$Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O.$$

Borax, $Na_2B_4O_7$, does not change its composition on fusion. Both salts are compounds of anhydrohydrates of phosphoric or boric acids. Salts of such acids are transformed on fusion with a base into salts of the ortho-acids (ortho-phosphoric, ortho-boric) which in the experiment remain fused:

$$NaPO_3 + MnO = MnNaPO_4.$$

It is thus explained why only bases dissolve in molten borax or microcosmic salt, in which the acid anhydrides, such as silica, stannic oxide, etc., are insoluble. The stability of boric anhydride and phosphoric acid at a high heat also explains why the experiment succeeds with most salts; the acids contained in the latter being displaced, at a high temperature, by the less volatile phosphoric or boric acid.

REMARK.—When a metal has more than one oxide, variously coloured beads may be obtained, according to the conditions under which the fusion takes place. The properties of the flame of the gas-burner have already been partly considered (in relation to the variations in temperature, § 9). We will now notice its other characteristics. If (by turning the ring) the opening through which the gas is supplied with air be somewhat reduced, a small, luminous point can be distinguished, in addition to the inner cone and the outer cone above the former. The dark cone, and especially the luminous point, contain unburned hydrocarbons of the gas, and possess at the same time a temperature sufficiently high for the reduction reactions. These two sections of the flame are called "*the reducing flame.*" The outer cone contains the products of oxidation of the gas and air; in this part of the flame, "*the oxidising flame,*" the oxidation reactions are made. These relations will be more fully discussed in the Supplement of Section III. The coloration of the bead has been sufficiently explained above, but mention should be made in addition of the sections of the cones in which these experiments are to be made. If the oxidation flame is to be used, the bead is introduced into the outer edge of the outer cone, at a point opposite the tip of the dark inner cone, but not higher, as the heat in the upper portion is not so great. In reduction experiments the bead is brought into the upper part of the dividing line between the inner and outer cones. As the dimensions of the gas-flame are not great the experiments should be made with a small bead and thin platinum wire. As has been mentioned above, the colouring of the bead by some metals varies according to the section of the flame in which the bead is held. Manganese, for example, gives an amethyst-coloured bead in the oxidation flame, a colourless one in the reduction flame.

The oxidation of chromic oxide to chromic acid is an important reaction, serving for the separation of chromium from the metals of Groups II. and III., and is at the same time characteristic. As chromium hinders the detection and separation of aluminium and iron salts, it is itself removed, both in qualitative and quantitative analysis, by oxidation to chromic acid. This characteristic of undergoing oxidation distinguishes chromic oxide from those of iron and aluminium.

1. *Oxidation by means of nitric acid and potassium chlorate.*—Moist chromic hydroxide is dissolved in hot, concentrated nitric acid, and small pieces of potassium chlorate then added to the solution. The success of the operation depends essentially upon the amount of water present, and if the chromic hydroxide contained a great deal the oxidation cannot be effected. The nitric

acid solution, to which the crystals of potassium chlorate are added one by one, must be heated under the hood. If the necessary conditions are satisfied the solution becomes brown. To ascertain when the reaction is finished, a few drops of the liquid are added to water in a test-tube; a pure yellow colour indicates that the oxidation is completed, the solution otherwise having a green tinge. The reaction has not been sufficiently studied to enable an explanation of its steps. It is mostly employed for the oxidation of chromic oxide in separations. The confirmatory tests are given below.

2. In alkaline solution chromic oxide is easily oxidised to chromic acid by chlorine or bromine water (or a hypochlorite):

$$Cr_2O_3 + 3KBrO + 4KOH = 2K_2CrO_4 + 3KBr + 2H_2O.$$

If it be necessary to remove the chromium by oxidation, this can be conveniently effected, also, with bromine in a neutral solution, in presence of sodium acetate (see Course of Analysis). This reaction, however, is incapable of a general application, as manganese is precipitated by halogens as its dioxide. Hydrogen peroxide in alkaline solution has recently been employed in oxidising chromic oxide; the oxidation is readily effected by its means, but the objections just given likewise prevent its use in separations. The following reactions are less important in qualitative analysis.

3. *Oxidation with sodium carbonate and potassium nitrate.*—Six parts of a mixture of these salts (1 part KNO_3 and 2 parts Na_2CO_3) are rubbed together with one part of chromic oxide in a mortar, and ignited in a crucible until the evolution of gas ceases and the mass melts. On treatment of the fused residue with boiling water an alkali salt of chromic acid is obtained in solution:

$$Cr_2O_3 + 3KNO_3 + K_2CO_3 = K_2Cr_2O_7 + 3KNO_2 + CO_2.$$

The sodium carbonate must be anhydrous, and the chromic oxide well dried at 100° C. The application of potassium nitrate is subject to a certain inconvenience, viz., that on treating the fusion with water and acids, the nitrous acid (formed from the potassium nitrate which results from the incomplete decomposition of the nitrate) reduces a part of the chromic acid again to chromic oxide, and the yellow solution obtained changes to green. The oxidation can be performed with sodium carbonate and potassium chlorate under the same conditions as when potassium nitrate is used; it should be mentioned that potassium chlorate is very quickly decomposed at a high temperature, and an explosion may thus easily ensue. The mixture must contain six parts of sodium carbonate and one part of potassium chlorate.

4. Hempel has recently proposed to convert chromic oxide to chromic acid by fusing it in a silver crucible with one part of sodium peroxide and two of sodium carbonate.

§ 33. Reactions of Chromic Acid and its Salts.—Chromic acid, CrH_2O_4, is not known in the free state. Its anhydride, CrO_3, crystallises in red needles. The chromates of Groups I. and II. are, with the exception of the barium salt, soluble in water. Those of other metals are insoluble in water, but usually dissolve in acids. The insoluble salts are rendered soluble by converting them to alkali chromates, by fusion with sodium carbonate; some of them, indeed, are transformed to the alkali salts merely on boiling with sodium carbonate solution. The reactions of chromic acid consist either in the production of characteristic insoluble salts, or in oxidation reactions which are caused by the chromic acid, the latter being at the same time reduced to chromic oxide.

Barium chromate.—Barium salts produce in the solutions of chromates a yellow precipitate, soluble in nitric acid and reprecipitated from this solution by alkalies (§ 17).

Lead chromate is a yellow precipitate, insoluble in nitric acid, but soluble in caustic alkalies. It is reprecipitated from this solution by acids.

Mercurous chromate, $Cr(Hg_2)O_4$, is a brick-red, and *silver chromate* a dark red precipitate. Both are soluble in acids.

Hydrogen peroxide is one of the most delicate and characteristic reagents for chromic acid. The latter is oxidised by the hydrogen peroxide, apparently being transformed to the so-called perchromic acid, $HCrO_4$ (the composition of which, owing to its instability, is not yet accurately determined):

$$2CrH_2O_4 + H_2O_2 = 2HCrO_4 + 2H_2O.$$

The compound has of late been variously regarded as $CrO_3 . H_2O_2$ (Moissan), or $Cr_2O_7 . 2H_2O_2$ (Berthelot), and therefore, as a union of hydrogen peroxide with chromic or perchromic anhydride. It is not necessary to use a solution of pure hydrogen peroxide, that prepared by the action of *very dilute* hydrochloric acid upon barium dioxide being sufficient. If a drop of a potassium dichromate solution be transferred on a glass rod to the solution of hydrogen peroxide and free acid thus obtained, the latter receives a blue tint from the perchromic acid which forms. This blue colour is still more distinctly seen if ether be added and the solution shaken, the ether dissolving the perchromic acid, and, as it is lighter than water, floating above the latter as a beautiful blue layer. An excess of potassium dichromate hinders the reaction; free chromic acid acts upon the perchromic acid with formation of chromic oxide and evolution of oxygen. With an excess of potassium dichromate, therefore, the colour is not obtained:

$$2CrHO_4 + 2CrH_2O_4 + 3H_2O = 4Cr(OH)_3 + O_7.$$

Reduction of the chromic acid to chromic oxide (oxidation reactions at the expense of the oxygen in the chromic acid). The reduction of chromic acid is employed, in qualitative analysis, chiefly as a confirmatory test. In the above reactions chlorides or bromides are obtained together with the chromic acid, and may hide the reactions of formation of characteristic chromates. The chromic acid must, therefore, be subjected to reduction as a confirmatory test. The reduction is usually accomplished with alcohol in presence of hydrochloric acid, the alcohol becoming oxidised to aldehyde, C_2H_4O, at the cost of the oxygen in the chromic acid, and the latter undergoing conversion to chromic chloride or the salt of whatever acid was employed:

$$2CrO_3 + 3C_2H_6O + 6HCl = 2CrCl_3 + 3C_2H_4O + 6H_2O.$$

Concentrated hydrochloric acid and alcohol are added to the concentrated solution of chromic acid (dilute solutions must be strongly evaporated). The reduction is hastened by warming the solution, and is easily recognised by the green colour to which the liquid changes, the penetrating odour of aldehyde being noticed at the same time. Upon further oxidation the aldehyde is changed to acetic acid, and, if the latter is formed in sufficient quantity, a violet solution of chromic acetate is often obtained.

We must mention, from among the remaining reactions, the following:

Hydrogen sulphide easily reduces chromic acid in acid solutions, with separation of sulphur: the chromic hydroxide formed, being soluble in acids, is not precipitated:

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

In the general course of analysis the separation of sulphur, when unaccompanied by the formation of any other precipitate, is an indication of chromic acid (or ferric iron). Ammonium sulphide throws down from acid solutions a mixture of chromic hydroxide and the brown dioxide, CrO_2.

Sulphurous acid likewise reduces chromic acid, being at the same time converted to sulphuric acid. Since chromic acid readily parts with its oxygen it acts as a peroxide; when heated with hydrochloric acid it evolves chlorine and is converted to chromic chloride:

$$2CrH_2O_4 + 12HCl = 2CrCl_3 + Cl_6 + 8H_2O.$$

Chromic acid is also reduced by many other substances, such as stannous chloride, non-volatile acids (tartaric), etc.

Ferric Iron

§ **34.** The properties of metallic iron will be considered in the second Division. Here we shall confine ourselves to the compounds of ferric oxide. These differ from those of aluminium and chromium in their reducibility, *i.e.*, in the power which they possess of changing from the ferric to the ferrous state.

A. *Ferric salts.*—The remarks made in § 26 apply to these salts; it may again be noticed that the salts of volatile acids (organic salts, the nitrate, etc.) decompose on ignition, with formation of ferric oxide. The solutions of ferric salts are yellow or brown. Those of neutral salts are often decomposed to basic compounds by the action of water. Ferric chloride splits up very readily into ferric hydroxide and hydrochloric acid, the decomposition being most rapid in concentrated solutions (soluble ferric oxide remains in solution). Almost all neutral ferric salts become basic when their solutions are boiled.

Reactions of Ferric Salts.—Ferric hydroxide is a brown precipitate very soluble in acids. The anhydrous oxide is much less soluble in acids than its hydroxide.

Alkalies and ammonia throw down the hydroxide, which is insoluble in an excess of the reagents (§ 28 B). Organic acids prevent the precipitation (§ 27).

Barium carbonate precipitates from cold solutions a mixture of the hydroxide and basic carbonates, which forms rapidly; for the conditions see § 28 A.

Ammonium sulphide produces a black precipitate of ferrous sulphide, FeS, a derivative of ferrous oxide (§ 28 E). Hydrogen sulphide also has a reducing action on ferric compounds, the conversion being accompanied by separation of sulphur:

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

Acetate.—The addition of sodium acetate to the solution of a ferric salt causes a red-brown coloration, due to the formation of the neutral acetate, $Fe(C_2H_3O_2)_3$. The basic acetate obtained on boiling the solution of the neutral salt forms a red-brown precipitate insoluble in water, but easily soluble in hydrochloric acid. The use of this salt in analysis is described in § 30. The above reactions are important for separations; as delicate qualitative tests for ferric salts, the following are preferable:—

Ferric sulphocyanate, $Fe(CNS)_3$, is a salt soluble in water to a dark red colour, and formed by the action of potassium sulphocyanate on ferric solutions. A very slight amount of this compound suffices to colour a large quantity of water red, and the reaction is therefore unusually delicate (see below). In case the coloration is slight, it may be more easily seen by placing a piece of white filter paper under the test-tube and looking down upon the liquid, a thicker layer thus being examined. Ether may also be used with advantage: it extracts ferric sulphocyanate from the aqueous solution, and as it floats above the latter the red colour imparted to it is easily seen. A large excess of free nitric acid decomposes the sulphocyanate and therefore hinders the reaction. The presence of undue quantities of foreign salts is also detrimental to its delicacy. Ferrous salts show no such reactions.

The action of potassium sulphocyanate upon ferric chloride presents a case of "Chemical equilibrium." In incomplete reactions such as this, which is built up from two opposite reactions in which ferric sulphocyanate is formed and again decomposed by potassium chloride, equilibrium sets in at a point determined by the conditions present. The sign of equilibrium is $\rightleftarrows$

$$FeCl_3 + 3KCNS \rightleftarrows Fe(CNS)_3 + 3KCl.$$

In cases of chemical equilibrium in general, an excess of one of the factors has the effect of making one of the reactions the more prominent. In this case the colour becomes more intense if an excess of potassium sulphocyanate be used, since a greater quantity of ferric sulphocyanate will thus be formed. G. Krüss and H. Moraht assert that double salts of ferric and potassium sulphocyanates, *e.g.*, $Fe(CNS)_3 + 9KCNS$, are in this way formed.

Ferric ferrocyanide (Prussian Blue).—Ferric ferrocyanide, $Fe_4(FeCy_6)_3 = 4FeCy_3 . 3FeCy_2$, is formed as a dark blue precipitate on the addition of potassium ferrocyanide, K_4FeCy_6, to the solution of a ferric salt. The reaction is delicate. If the iron is only present in traces a green solution is at first obtained, from which a blue precipitate slowly separates. As ferric ferrocyanide is slightly soluble in potassium ferrocyanide to a colourless liquid, the reagent must be added to the iron solution drop by drop. The reaction involved is as follows:

$$3K_4(FeCy_6) + 4FeCl_3 = F_4(FeCy_6)_3 + 12KCl.$$

The salt is characterised by its insolubility in hydrochloric acid, and its solubility in caustic alkalies with separation of ferric hydroxide. The latter reaction is analogous to the action of the alkali hydroxides upon ferric salts in general, potassium ferrocyanide being again formed:

$$Fe_4(Cy_6Fe) + 12KOH = 3K_4(Cy_6Fe) + 4Fe(OH)_3.$$

It is not advisable, in testing for ferric compounds, to allow the acid solutions to be exposed to the air for any length of time after the addition of the reagent, since ferric ferrocyanide may be formed by the oxidation of hydroferrocyanic acid alone, although no iron be present in the solution examined. In washing a precipitate of ferric ferrocyanide it will be observed that the precipitate commences to pass into solution in the colloidal state as soon as all foreign salts have been removed. The student is also reminded that none of the above reagents can serve for the detection of the iron in ferro- and ferricyanic compounds. They can be used for this purpose only after the decomposition of the cyanogen compounds by sulphuric acid (*v.* Sec. II. Hydrocyanic Acid). This behaviour of the ferrocyanides explains why, for the detection of iron, we can use compounds which themselves contain iron, but it also requires the experiments to be made in special portions of the liquid under analysis.

Ferricyanide of potassium, K_3FeCy_6, produces no precipitate with ferric salts, but the solution becomes dark brown.

Tannic acid (infusion of galls) produces in neutral solutions of ferric salts a blue-black precipitate (ink); an excess of the reagent should be avoided.

B. *Reduction of ferric compounds to the ferrous state.*—The reactions in reduction of ferric oxide are chiefly important in quantitative analysis. The ferric compound is usually warmed with zinc and dilute hydrochloric acid, and thus reduced by the hydrogen evolved. A solution of sulphurous anhydride in water answers equally well; in this reaction the reduction takes place at the expense of the hydrogen of the water, the oxygen of which unites with the sulphurous acid to form sulphuric acid. The equations for the two reactions are as follows:

$$FeCl_3 + H = FeCl_2 + HCl.$$
$$2FeCl_3 + 2H_2O + SO_2 = 2FeCl_2 + 2HCl + H_2SO_4.$$

The reduction can also be accomplished with sodium thiosulphate, in place of sulphurous acid. Thiosulphuric acid, as is well known, decomposes into sulphur and sulphurous acid (in acid solution; in neutral solution it forms tetrathionic acid):

$$2FeCl_3 + Na_2S_2O_3 + H_2O = 2FeCl_2 + 2NaCl + H_2SO_4 + S.$$

The addition of sodium thiosulphate to a solution of a ferric salt produces a deep violet colour, and on being warmed the liquid appears opalescent, through the separation of sulphur. When the thiosulphate is in excess sulphurous acid is set free (in quantitative analysis this reaction is used for separating iron and aluminium). The reduction of ferric salts can, lastly, be effected with stannous chloride, according to the reaction:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

SYSTEMATIC COURSE OF ANALYSIS FOR THE METALS OF GROUP III., DIVISION 1

§ **35.** If the student be guided by the methods of combining the reactions explained in §§ 14, 22, and 24, we believe that he is in condition to work out a systematic course of analysis for this Division himself, and a detailed discussion of the subject will therefore be unnecessary. Though following a somewhat different plan from that of the previous groups, nevertheless, the requirements to be fulfilled in choosing the reactions, as well as their application in the succession indicated in the proposed course of analysis, may be briefly explained.

A. *The metals of Group III., Division* 1.—The detection of the metals of this Division requires their previous separation; the analysis is based upon the properties of their hydroxides. The solution is precipitated by ammonia, an excess of the reagent being avoided (in the systematic course and in separations, ammonium sulphide is to be used, see below), heated, filtered, and the precipitate well washed. As the course of analysis is dependent upon the presence or absence of chromium (§ 28 B), the behaviour of the hydroxides obtained toward the microcosmic salt or borax bead is tested (§ 32). Should an emerald-green bead be obtained, this is a sign of the presence of chromium, which must next be separated by conversion to chromic acid. The still moist hydroxides are for this purpose dissolved in concentrated nitric acid and treated with potassium chlorate according to § 32. After complete oxidation has ensued, the greater portion of the free nitric acid is removed by evaporation, and the solution then reprecipitated by ammonia. The hydroxides of aluminium and iron are found in the precipitate, and must be separated by treatment with caustic alkalies according to § 32, confirmatory tests being made with each oxide. The chromic acid remains in solution; the best confirmatory test is its reduction to chromic oxide. If negative results in regard to chromium were obtained on fusion with the borax bead, the separation of the ferric iron and aluminium by caustic alkalies can be directly undertaken.

The oxidation of the chromium and separation of aluminium from iron by the following method is also convenient:—The acid solution is neutralised by sodium carbonate, bromine and an excess of sodium acetate added, and the solution heated, its neutrality being at the same time maintained by the further addition of soda. When the oxidation is complete the aluminium and iron are found in the precipitate as their basic acetates, while the alkali chromate remains in solution (§ 32).

A more roundabout method for separating chromium consists in the fusion of the precipitated and *well-dried* oxides with sodium carbonate and potassium nitrate (§ 32), and treatment of the fused mass with water. We observe that, in proportion to the quantity of soda taken, either part or the whole of the aluminium can go into solution as an aluminate, together with the chromic acid. The solution is acidified with nitric acid and the aluminium precipitated with ammonia (the precipitate requires confirmatory tests), the chromic acid being still kept in solution as a chromate. The portion of the fused residue insoluble in water consists of anhydrous ferric and aluminium oxides; they are dissolved in hydrochloric acid, etc. (§ 29), and subjected to the treatment above given.

B. *The metals of Groups I., II., and Group III., Division* 1.—For the separation of Group III., Division 1, from previous

Groups we employ the precipitation with ammonium sulphide. The conditions are explained in § 28 E (the completeness of the precipitation must be assured). The precipitate, consisting of the hydroxides of chromium and aluminium, and ferrous sulphide, FeS, must be well washed and dissolved in dilute hydrochloric acid. The iron, which goes into solution as a ferrous salt, is transformed to a ferric salt by boiling the liquid with nitric acid, which should be added drop by drop. The oxidation of ferrous compounds will be more closely observed in § 37 B. The detection of the single metals of Division 1 is accomplished by the methods described above (precipitation with ammonia, colour of borax bead, etc.) The metals of Groups I. and II. are found in the solution filtered from the hydroxides of the metals of this Division. The excess of ammonium sulphide in this filtrate is removed by boiling and adding hydrochloric acid; the separated sulphur having been filtered off, the detection of the metals of Groups I. and II. is accomplished by the methods given in § 24.

GROUP III., DIVISION 2

IRON (FERROUS COMPOUNDS), MANGANESE, ZINC

§ **36.** The metals of this Division are marked by the following characteristics:—1. Ammonium sulphide precipitates sulphides of the formula RS, which are easily soluble in acids. 2. The monoxides, RO, are not thrown down in the cold by barium carbonate. 3. They form no basic acetates (distinction from Division 1).

The metals of this Division are easily soluble in acids, with generation of hydrogen and formation of salts. The majority of their salts, *e.g.*, the nitrates, sulphates, and chlorides, are soluble in water, and most of the insoluble salts dissolve in acids. Zinc unites with oxygen to form only the monoxide, and is thus distinguished from iron and manganese, which easily form higher oxides (basis for a method of separation). As ferrous compounds are always transformed to the ferric state, in qualitative as well as quantitative analysis, the separation of iron is based upon the properties of the metals of Group

III., Division 1, and we shall therefore consider only the reactions of manganese and zinc in the General Reactions.

GENERAL REACTIONS

A. **The Sulphides** are obtained in analysis either as the so-called hydrates or in the anhydrous state.

The sulphides are salts of hydrogen sulphide. The latter can form with divalent metals (Me) the following salts:—

MeS; the neutral salt, sulphide.

$Me(SH)_2$ or $MeS.H_2S$; the acid salt of hydrogen sulphide. Such compounds are not at present known.

$Me(OH)(SH)$ or $MeS.H_2O$. The hydrated sulphides are basic salts of hydrogen sulphide. By the abstraction of water from several molecules of such compounds, basic salts of various composition can be formed; for instance:

$$3Zn(OH)(SH) - H_2O = 3ZnS.2H_2O.$$

As is true of all basic salts, the composition of the basic sulphide obtained depends upon the conditions under which the experiment is made (§ 26).

The hydrates of the sulphides are formed, almost exclusively, by precipitation of the solutions with ammonium sulphide or hydrogen sulphide. As was stated above, they are insoluble in water, but dissolve easily in acids, and undergo oxidation with extreme ease. The colour of these sulphides is important as a characteristic qualitative indication of the respective metals. Hydrated ferrous sulphide is deposited as a black precipitate which turns brown when exposed to the air, owing to its oxidation to ferric oxide (accompanied by separation of sulphur). The hydrate of manganese sulphide is a yellowish white or flesh-coloured precipitate which quickly changes to brown in the air, being oxidised to the mangano-manganic oxide, Mn_3O_4 (with separation of sulphur). Hydrated zinc sulphide is a white precipitate, insoluble in caustic alkalies, and much more stable in the air than the foregoing salts. (It changes to the oxide with generation of hydrogen sulphide.) The reactions involved in the formation of hydrated sulphides, *i.e.*, the action of ammonium sulphide and hydrogen sulphide, must be more closely considered.

Action of ammonium sulphide.—This reagent precipitates the hydrated sulphides from neutral and acid solutions; the reaction is important as a means of separating the metals of this Group from those of Groups I. and II. Complete separation is obtained by neutralising the acid solution with ammonia, adding ammonium chloride,[1] and precipitating the solution with ammonium sulphide.

The experiment is made in a flask, which, after the addition of ammonium sulphide, is closed by a cork and permitted to stand for some time (the longer the time allowed, the more complete the reaction; precipitation is entirely finished only after twenty-four hours.) The precipitate is then filtered and well washed. Its further treatment, when the whole of Group III. is to be separated from Groups I. and II., will be more fully discussed below. The same reaction may serve as a separation of zinc from manganese, as manganese sulphide dissolves in acetic acid, in which zinc sulphide is insoluble. In employing this method, the precipitates are poured into a small beaker and treated, while hot, with acetic acid; manganese sulphide goes into solution, while zinc sulphide remains unaffected. Confirmatory tests for both of these compounds will be described below.

Action of hydrogen sulphide.—Hydrogen sulphide precipitates from the neutral solutions of mineral acid salts, such as the chlorides and sulphates, either no sulphide at all or but small quantities; the mineral acid set free in the reaction hinders further precipitation by instantly dissolving the sulphide formed. The neutral acetates, however, show a somewhat different behaviour toward sulphuretted hydrogen. Manganous acetate is not precipitated, and ferrous sulphide forms only in small quantities; zinc acetate, on the contrary, is completely decomposed, all of the zinc being thrown down as zinc sulphide. In presence of free mineral acids, none of the sulphides are deposited; *an acetic acid solution* of a zinc salt, however, is completely precipitated, while that of a manganese or iron salt is not affected. Manganese can therefore be separated from zinc by this method also. Hydrogen sulphide is passed through the solution under investigation, after the addition of some

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[1] The necessity of the presence of ammonium salts for the complete precipitation of the hydrated sulphides has been empirically determined. It probably exerts an influence upon the constitution of the precipitate, as in the precipitation of aluminium hydroxide. If the acid solution contains hydrochloric acid, the addition of ammonium chloride is superfluous.

free acetic acid and enough sodium acetate to completely transform the manganous and zinc salts present into acetates; acid solutions should be previously neutralised by sodium carbonate until a permanent turbidity is caused. In the systematic course of analysis of the metals of this Group, the method last described must be employed for separating manganese from zinc, since when cobalt and nickel are present, it is the only one by which the white zinc sulphide characteristic for this metal can be obtained.

It must be noticed that, in spite of the ordinary precautions, small quantities of cobaltous sulphide are usually obtained together with the zinc salt in the precipitate. An accurate separation is rendered possible only if we add ammonia to the solution, dissolve the precipitate in monochloracetic acid, treat with hydrogen sulphide at 50° C., and filter off the zinc sulphide immediately.

The anhydrous sulphides differ in their properties from the hydrates, and are employed only in quantitative analysis. They are formed on ignition of the sulphides, oxides, and carbonates of the metals with sulphur in a current of hydrogen. They are stable, and do not undergo oxidation in the air. Ferrous sulphide, thus obtained, possesses a metallic lustre. Manganous sulphide is green or almost black, according to the temperature at which it is obtained. (It is also sometimes formed in solutions, if manganous salts be precipitated at 100° C. by a great excess of ammonium sulphide, in presence of much ammonia.) Zinc sulphide is a white or yellowish white powder. To the anhydrous sulphides belong the mineral pyrites, FeS_2, etc. (see Supplement).

B. **Ammonium Double Salts.**—(Action of ammonia and of ammonium carbonate.) The metals of this Division are characterised by the ease with which they form double ammonium salts, such as $FeSO_4 . (NH_4)_2SO_4$, etc., and, in the presence of ammonium chloride, or of ammonium salts in general, therefore, precipitation by means of caustic alkalies, ammonia, or carbonates, is incomplete. Ammonia produces no precipitate in presence of ammonium salts, or in acid solutions. The fact should be mentioned, that in a solution containing free ammonia, the double salts of manganese (and to a lesser extent those of iron), are oxidised by the air and deposited as a brown precipitate of mangano-manganic oxide.

C. The monoxides, the carbonates, and, to a less degree, the sulphides can be completely precipitated only when non-volatile organic acids are absent. This is likewise explained by the formation of double organic salts of the metals of this Division with potassium, sodium, and ammonium compounds; *e.g.*, $K_2Mn(C_2O_4)_2$ etc. (*v.* § 27).

SPECIAL REACTIONS

Ferrous Iron

§ **37.** Metallic iron possesses a shining gray colour, and fuses at about 1500° C. (In the fused state it is white and has a powerful lustre.) When exposed to the air and moisture it becomes oxidised, or rusts, and burns in the air on being subjected to a white heat. Iron dissolves easily in acids, passing into the ferrous state if the dissolving acid is incapable of oxidising it. (Ferric compounds can be obtained by solution of the metal in nitric and similar acids.) The ferrous salts are compounds unstable in solution, or even in the dry state if they be exposed to the air, as they readily absorb oxygen and pass into ferric salts. The majority of ferrous compounds are easily soluble in water or acids. Iron precipitates several other metals from the solutions of their salts, being converted itself to the corresponding iron salt:

$$CuSO_4 + Fe = FeSO_4 + Cu.$$

Steel and cast iron.—Iron can be prepared from its compounds in a perfectly pure state only through its reduction by hydrogen. The purest iron found in the arts (wrought iron, piano wire) contains about 0·3 per cent carbon. Steel is still richer in carbon (from 0·9 to 1·9 per cent) than wrought iron, its hardness resulting from this fact (iron itself is soft). Cast iron is still richer (it may contain as much as 7·0 per cent), and in this variety the carbon is partly bound to the iron, partly in the state of graphite. When cast iron is dissolved in acids the graphite remains as an insoluble black residue, while the chemically-bound carbon forms gaseous hydrocarbons which impart to the hydrogen generated an unpleasant odour. Upon solution of cast iron or steel in metallic salts, such as copper sulphate, mercuric chloride, etc., all of the carbon remains behind as an insoluble residue. Such a residue was recently shown to contain titanium carbide, TiC.

Iron alloys.—Several different alloys of iron have of late been employed in the arts. Ferro-manganese is a general term for such compounds as contain more than 25 per cent (up to 80 per cent) of manganese; those which contain a smaller percentage of this metal are known as specular pig-iron. In chrome-iron we find chromium in varying, and often in significant amounts. Aluminium-iron usually contains about 10 per cent aluminium. All of these alloys are dissolved by acids without difficulty.

In its separation from other metals iron is always converted, when existing in the solution as a ferrous compound, into the more stable ferric salt. After having observed the qualitative reactions for ferrous compounds, therefore, we must become acquainted with the methods for bringing them into the ferric state.

A. **Reactions of Ferrous Salts.**—*Ferrous hydroxide* is thrown down by alkalies and ammonia as a white precipitate, which is almost instantly turned to green, and finally brown, as a result of its oxidation. It is insoluble in an excess of potassium hydroxide, and on boiling is converted to the black magnetic iron oxide, Fe_3O_4. When ammonium salts (§ 36 A) or organic acids (§ 36 C) are present the precipitation is incomplete (ammonia has no apparent action); if the solution is exposed to oxidation, ferric hydroxide is in time deposited.

Ferrous sulphide.—The black hydrate is thrown down by ammonium sulphide from either ferrous or ferric solutions. In the latter case the ferric compounds are first reduced (§ 34). The hydrate of ferrous sulphide dissolves easily in acids and absorbs oxygen from the air. Very dilute iron solutions are at first only coloured green by ammonium sulphide, but after some time deposit a black precipitate. Ammonium chloride assists complete precipitation.

Ferrous ferrocyanide and ferrous ferricyanide afford very characteristic reactions of ferrous compounds. Potassium ferrocyanide, $K_4(FeCy_6)$, produces a white precipitate, $K_2Fe_3(FeCy_6)_2$, which, like all ferrous salts, is quickly oxidised by the air, turning blue and changing to the ferric salt. It may likewise be oxidised by chlorine or nitric acid. The reactions involved in its formation and oxidation are as follows:

$$2K_4(FeCy_6) + 3FeCl_2 = K_2Fe_3(FeCy_6)_2 + 6KCl,$$
$$3K_2Fe_3(FeCy_6)_2 + 8Cl = 2Fe_4(FeCy_6)_3 + 6KCl + FeCl_2.$$

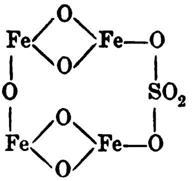
Potassium ferricyanide, $K_3(FeCy_6)$, produces a blue precipitate (Turnbull's blue), which cannot be distinguished by its colour from Prussian blue. Its composition, $Fe_3(FeCy_6)_2$, is also very similar to that of the latter body. If, to simplify the comparison, these compounds be regarded as double salts, the formula of the precipitate becomes $3FeCy_2 . 2FeCy_3$, and that of Prussian blue, $3FeCy_2 . 4FeCy_3$. The one salt is the ferricyanide of ferrous oxide, $Fe_3(FeCy_6)_2$, the second the ferrocyanide of ferric oxide, $Fe_4(FeCy_6)_3$. The two salts have almost the same characteristics. Turnbull's blue is likewise insoluble in hydrochloric acid. The reaction must be made under observance of all the precautions given in § 34; it is very characteristic of ferrous compounds.[1]

B. **Conversion of Ferrous Salts to the Ferric State.**—The reactions by which ferrous compounds become oxidised are very important in analysis. Ferrous salts undergo oxidation so readily that they cannot be used in separations, and they must therefore be converted to ferric compounds, to permit the use of methods based upon the characteristics of the latter. The oxidation can be accomplished in many ways; in qualitative analysis, chlorine or nitric acid is the most convenient agent for the purpose.

1. *Oxidation with nitric acid.*—Concentrated nitric acid is added, drop by drop, to the boiling solution of the ferrous salt until the liquid attains a yellowish brown colour (colour of ferric solutions). A portion of the nitric acid decomposes, with evolution of nitric oxide. The oxidation with nitric acid is accomplished more successfully and quickly if another free acid (sulphuric or hydrochloric) is present, as the molecule of a ferric salt contains more acid than that of a ferrous compound:

$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + NO + 2H_2O.$$

If no free acid is present, basic, and usually insoluble, ferric salts will be to some extent formed. Thus, for example, if ferrous sulphate be oxidised without the previous addition of sulphuric or hydrochloric acid, both the soluble ferric salt, $Fe_2(SO_4)_3$, and the insoluble basic salt, $2Fe_2O_3 . SO_3 =$



will be obtained. Weak solutions of the ferrous salts must be concentrated before the oxidation, and to properly effect the conversion nitric acid of some strength is wanted.

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[1] It may be mentioned that potassium ferrocyanide and ferricyanide produce precipitates with the majority of metallic salts, and that for this reason their reactions cannot be employed in separations. These reagents serve only for the detection of iron.

2. *Oxidation with chlorine.*—Instead of employing the free halogens (chlorine or bromine water), the solution of the ferrous salt, previously concentrated (if necessary), is acidified with strong hydrochloric acid, heated, and two or three small crystals (not more) of potassium chlorate, $KClO_3$, then added. The hydrochloric acid is thus decomposed to water and free chlorine, and the latter converts the ferrous salts to the ferric condition. The odour of chlorine in the solution indicates that the oxidation is completed:

$$2FeCl_2 + Cl_2 = 2FeCl_3,$$
$$3FeSO_4 + Cl_3 = Fe_2(SO_4)_3 + FeCl_3.$$

The oxidation reaction with hydrochloric acid and potassium chlorate is represented by the following equation:

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

Ferrous and ferric oxides, when present together, necessitate two experiments for their detection: (1) a test is made for ferrous compounds by means of potassium ferricyanide, and (2) for ferric compounds with potassium ferrocyanide. The formation of a blue precipitate in both tests indicates the presence of both ferrous and ferric salts.

Manganese

§ **38.** Manganese forms several series of compounds, the majority of which are of analytical value. The manganous compounds are chiefly important for the quantitative estimation of manganese. The higher oxidation products afford especially characteristic qualitative reactions of the metal, and, as compounds which distinguish it from many others, are often employed in quantitative reactions for the separation of manganese.

We shall study closely the reactions of manganous compounds alone, without entering more deeply into the consideration of the other oxides. Under the conditions obtained in complete analyses, the higher oxides of manganese cannot exist in the solution, the reactions performed in the systematic course of analysis (*e.g.*, the action of hydrochloric acid or of hydrogen sulphide), converting these compounds into manganous products. The study of the one oxide therefore suffices.

The manganous salts which are soluble in water do not oxidise on exposure to the air. The higher oxides of manganese are easily prepared from manganous compounds, and their formation is very characteristic of the metal, affording, indeed, its best qualitative reactions. To thoroughly understand these reactions, therefore, the student should turn his attention to the behaviour of the higher manganese oxides toward hydrochloric and nitric acids.

Hydrochloric acid decomposes all of the higher oxides of manganese on warming; free chlorine is generated and manganous chloride formed:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl,$$
$$MnHO_4 + 7HCl = MnCl_2 + 5Cl + 4H_2O.$$

Manganese sesquioxide, Mn_2O_3, is not decomposed by hydrochloric acid in the cold, manganic chloride, $MnCl_3$, being stable in its cold solution.

Nitric acid which contains no nitrous acid decomposes neither manganese dioxide nor permanganic acid. These two compounds are formed, as we shall see below, from the manganous salts, either by the action of nitric acid or in its presence. Manganic sesquioxide and mangano-manganic oxide are split up by nitric acid into manganous salts and the dioxide:

$$Mn_2O_3 + 2NHO_3 = Mn(NO_3)_2 + MnO_2 + H_2O.$$

As manganese dioxide and permanganic acid readily part with oxygen when acted upon by acids, they are powerful oxidising agents. For oxidising with permanganic acid the potassium salt, potassium permanganate, is usually employed.

Reactions of Manganous Salts.—*Manganous hydroxide*, $Mn(OH)_2$, thrown down by alkalies or ammonia, is a white precipitate, which quickly turns brown in the air, undergoing oxidation to mangano-manganic oxide. The presence of ammonium chloride hinders the reaction (see the ammonium double salts).

Manganous carbonate, $MnCO_3$, is a white precipitate.

Manganese ammonium double salts.—If ammonium salts, such as the chloride, be present, ammonia produces no precipitate with manganous salts (the precipitation by alkalies is also incomplete), in consequence of the formation of the soluble double salt, $MnCl_2 . 2NH_4Cl$. Manganous hydroxide (which has not been browned by the air) is easily soluble in ammonium chloride, though excess of ammonia precipitates mangano-manganic hydroxide from this solution. Ammonium carbonate in presence of ammonium chloride precipitates manganous carbonate.

Manganous sulphide.—Ammonium sulphide precipitates the hydrated manganous sulphide, yellow or flesh-coloured, and turning brown in the air through oxidation. It is characterised by its easy solubility in acids (the separation from zinc is based upon the readiness with which it dissolves in acetic acid, § 36 A). In presence of an excess of ammonia and ammonium sulphide, a green precipitate of the anhydrous manganous sulphide is sometimes formed, especially from hot solutions. For complete precipitation with ammonium sulphide the presence of ammonium chloride is necessary. Hydrogen sulphide does not precipitate manganous sulphide from acid solutions, even from that of acetic acid (for the use of this characteristic in the separation of manganese from zinc, see § 36 A).

In the systematic course of analysis manganese is separated as manganous sulphide. The confirmatory tests, however, should not be made directly with the manganous acetate obtained by dissolving the sulphide in acetic acid. It is better to precipitate this solution with sodium carbonate, and dissolve the well-washed manganous carbonate in nitric acid. The solution thus prepared is subjected to the following tests, which constitute the most characteristic reactions shown by manganese.

Manganic oxide, Mn_2O_3.—Manganous hydroxide, precipitated from manganous salts by an excess of potassium hydroxide and shaken until it has become brown, already contains mangano-manganic oxide. Addition of oxalic acid to this precipitate imparts to the solution a rose-red colour, owing to the formation of the double oxalate of manganese and potassium[1] (the more brown the oxidised solution is, the more successful the reaction). The oxalic acid is reduced to carbon dioxide and water on

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[1] The probable composition of this salt is analogous to that of the compounds of ferric iron, viz., $MnK(C_2O_4)_2$ or $MnK(C_2O_4)_2 . 2K_2C_2O_4$. The compound is too unstable to be analysed.

heating, and the colour then disappears. When oxalic acid is in excess, a white crystalline precipitate of manganous oxalate, MnC_2O_4, is formed.

Manganic acid, MnH_2O_4.—If any compound of manganese be fused in the gas-flame on platinum foil, with a mixture of from 2 to 3 parts of anhydrous sodium carbonate and a small quantity of potassium nitrate, a bluish green mass is obtained, which consists of the manganates of potassium and sodium. The cake turns brown on exposure to the air, often very quickly, but the bluish green colour again appears on fusion. It is a delicate reaction for manganese:

$$Na_2CO_3 + MnCO_3 + O_2 = MnNa_2O_4 + 2CO_2.$$

Permanganic acid, $MnHO_4$.—The solution of this acid has a deep carmine-red colour, and its formation is therefore a delicate reaction. If concentrated nitric acid (sp. gr. = 1·2) be heated to boiling with lead dioxide or minium, $Pb_2O_3 = PbO.PbO_2$, and a few drops of a dilute manganous solution be then added, a carmine-red coloration will be observed:

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O.$$

The colour may be seen as soon as the excess of lead dioxide has settled; the solution must not be filtered through paper, as the fibre of the latter would reduce the permanganic acid. To make the experiment successfully, it is absolutely necessary to add the manganese only in *dilute* solution, and but a few drops even of this. An excess of manganous salts has a reducing action and causes the nitric acid solution to lose its colour:

$$3MnO + Mn_2O_7 = 5MnO_2.$$

Manganous compounds impart to the borax or microcosmic salt bead a faint violet colour; in the reduction flame the bead remains colourless.

Zinc

§ **39.** Zinc fuses at 412° C., and boils at 940° C. When heated with access of air, it first fuses, and finally burns with a blinding flame, giving off white clouds of zinc oxide. Ordinary metallic zinc dissolves in alkalies and acids with evolution of hydrogen, though the chemically pure metal is passive toward most acids (see Aluminium, § 31). Its solution by nitric acid is accompanied by evolution of the fumes of nitrous or nitric oxide, according to the concentration of the solution, and also by the formation of ammonium nitrate. The majority of zinc salts are soluble in water, and those insoluble in this medium dissolve, for the greater part, in mineral acids. Metallic zinc precipitates many metals from their solutions. (For application of this reaction in analysis, see Copper, Antimony, etc.)

Reactions of Zinc Salts.—*Zinc sulphide* (§ 36).—Hydrogen sulphide does not completely precipitate zinc sulphide from neutral solutions. In the presence of acids it produces no precipitate at all, except in that of acetic; from acetic acid solutions the zinc is completely deposited. Ammonium sulphide (in presence of ammonium chloride) throws down zinc sulphide; the reaction is complete. The hydrated sulphide is white, and this colour, as well as the insolubility of the salt in acetic acid and alkalies, is strongly characteristic. Zinc sulphide is easily soluble in mineral acids. (Separation of zinc from manganese, § 36 A.)

Zinc hydroxide is thrown down by caustic alkalies as a white, gelatinous precipitate, soluble in excess of the alkali, with which it forms the compound K_2ZnO_2. If the alkaline solution is concentrated it suffers no change on heating, but in dilute solutions the oxide is almost completely deposited on boiling. The dissolving action of caustic potash upon zinc hydroxide is influenced by the presence of other oxides; in that of chromic oxide, for example, a compound of zinc oxide and chromic oxide results, which is insoluble in the alkali. An alkaline solution of zinc hydroxide is at first precipitated by ammonium chloride, but dissolves on further addition of the reagent, $ZnCl_2 . 2NH_4Cl$ being formed. The action of ammonia upon zinc salts is similar to that of the caustic alkalies. The precipitate formed is soluble in excess of the precipitant, and zinc hydroxide is entirely deposited from an ammoniacal solution on boiling only when the latter is very dilute. Ammonium salts render precipitation by caustic alkalies incomplete, as soluble ammonium zinc double salts are formed (§ 36). Ammonia produces no precipitate in presence of ammonium salts.

Zinc carbonate.—The carbonates of sodium and ammonium throw down a white precipitate of basic zinc carbonate, $2ZnCO_3 + 3Zn(OH)_2 + 5H_2O$, soluble in excess of ammonium carbonate. A large excess of an ammonium salt influences or hinders the precipitation, zinc ammonium double salts being formed.

Zinc cyanide.—Potassium cyanide produces with zinc salts a white precipitate of zinc cyanide, $ZnCy_2$, which dissolves in excess of the reagent to form the double salt, $2KCy . ZnCy_2$. Potassium sulphide throws zinc sulphide down from this double salt, though hydrogen sulphide and ammonium sulphide have no action.

Zinc oxide assumes a green colour if it be ignited after having been moistened with cobaltous nitrate. This experiment is performed, as a confirmatory test, in the following manner.—The precipitate of zinc sulphide is dissolved in the least possible quantity of nitric acid, and a few drops of cobaltous nitrate added to the resulting solution; a piece of filter paper is then moistened with the solution, dried and ignited; if zinc be present a green colour is imparted to the ash.

SYSTEMATIC COURSE OF ANALYSIS FOR THE METALS OF GROUP III., DIVISION 2

§ **40. A. Metals of Group III., Division 2.**—The detection of manganese and zinc requires the previous separation of ferrous iron. Ferrous salts, unlike the ferric compounds, possess no properties which can be used in separating them. If the addition of potassium ferricyanide to a separate portion of the solution to be tested indicates the presence of ferrous iron, the remainder of the solution must be oxidised according to § 37 A. The separation of the iron is then included in that of Division 1., and will be noticed below. We shall here consider only the separation of manganese and zinc. The simplest and, at the same time, the most accurate method is based upon the properties of their sulphides (§ 36 A). The solution is precipitated by ammonium sulphide, and the well-washed precipitate treated with acetic acid. When metals of Group III., Division 3, are present, the solution is first neutralised by sodium carbonate, and, after the addition of sufficient sodium acetate and a few drops of acetic acid, the zinc sulphide precipitated alone by hydrogen sulphide. Confirmatory tests must be made with the isolated metals, and for this purpose the zinc sulphide is dissolved in nitric acid (Reactions with caustic potash, etc.) The manganese is precipitated from the acetic acid solution by sodium carbonate (Reactions with sodium carbonate, lead dioxide, etc.)

B. *Metals of Group III., Divisions* 1 *and* 2.—A test for ferrous compounds is first made with potassium ferricyanide, as explained above; if ferrous salts are present, these must be oxidised to the ferric state. A portion of the solution is precipitated by ammonia, and the hydroxides obtained tested for chromium with the borax bead or microcosmic salt (§ 32, Remark).

Chromium is present.—If this be the case, the most accurate method is to treat the neutralised solution with barium carbonate and proceed under the conditions given in § 28 A. The precipitate, containing the excess of barium carbonate and Fe_2O_3, Al_2O_3, Cr_2O_3, is dissolved in hydrochloric acid, and the barium separated by precipitation from the hot solution with sulphuric acid. The solution is then filtered and tested for iron, aluminium, and chromium, as in § 35. Manganese and zinc are not precipitated by barium carbonate; they are detected in the solution according to A, the barium chloride obtained in the previous operation having been first separated with dilute sulphuric acid.[1]

Chromium is absent.—If the borax or microcosmic salt bead gives no indication of chromium, aluminium and iron may be separated as their basic acetates (§ 30). For this purpose the solution is neutralised with sodium carbonate and precipitated, while boiling, with sodium acetate (§ 30). The basic acetates obtained are dissolved in hydrochloric acid and analysed according to § 35 A. Manganese and zinc are detected in the solution according to A.

C. *Group III., Divisions* 1 *and* 2, *and Groups I. and II.*—For the separation of the two Divisions of Group III. from Groups I. and II. ammonium sulphide is employed. The precipitation must be made under the conditions mentioned in

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[1] It may not be superfluous to remark again that the oxidation of chromium to chromic acid with bromine in presence of sodium acetate cannot be employed here, as manganese peroxide would be precipitated with the basic acetates of iron and aluminium.

§§ 28 A, 36 A. The precipitate is washed as well as possible, dissolved in hydrochloric acid, and analysed according to A and B of this paragraph. (Testing for iron, oxidation, action of $BaCO_3$, etc.) The degree of oxidation in which the iron is present must be determined in separate portions of the solution. The metals of Groups I. and II. are found in the filtrate from the precipitate obtained with ammonium sulphide; the detection of these metals is explained in §§ 24 and 35 B.

GROUP III., DIVISION 3

NICKEL AND COBALT

§ **41.** In addition to the property of precipitation by ammonium sulphide, which is common to all the members of this group, the third Division is especially characterised: (1) by the insolubility of the sulphides in cold dilute hydrochloric acid; (2) negatively, by the non-formation of insoluble basic acetates, and by non-precipitation in the cold with barium carbonate.

The salts of nickel and cobaltous cobalt are, in general, easily soluble in water. Solutions of nickel salts are green, those of cobaltous salts rose-red. If the two metals are present together in solution, the colour depends upon the amount of excess of the one metal over the other, being red when cobalt is in excess, and green when nickel predominates. The solution of a mixture of one molecule of a cobaltous salt with three of a nickel salt is colourless, the two colours being exactly neutralised to white. The colour of the solution to be analysed is, therefore, of little importance, and can afford no conclusion concerning the presence of either element. Although in their chemical properties nickel and cobalt stand very closely to each other, they exhibit certain characteristic differences. These are caused chiefly by the greater tendency of cobalt to form a higher oxide (cobaltic compounds): all reactions for separating nickel from cobalt rest upon this distinctive difference.

The remarkable property which nickel (reduced by hydrogen) possesses of combining with carbon monoxide at the ordinary temperature, to form the easily volatile compound, $Ni(CO)_4$, distinguishes nickel from cobalt. This reaction, although already tried in the preparation of the pure metal for the purpose of determining the atomic weight, has not yet been turned to account in analytical experiments.

GENERAL REACTIONS

§ 42. **Sulphides.**—The sulphides are known in both the hydrated and anhydrous states. The hydrated sulphides of nickel and cobalt are obtained as black, amorphous precipitates, only slightly soluble in hydrochloric or acetic acid in the cold. They dissolve in *aqua regia*, with evolution of hydrogen sulphide and conversion to chlorides. The hydrated sulphides oxidise when exposed to the air (like the metals of the previous Division). They are formed by precipitation with hydrogen sulphide or ammonium sulphide.

Action of ammonium sulphide.—This reaction is used for separations, as in the foregoing Divisions. The experiment is made as explained in § 36. The presence of ammonium chloride is necessary to ensure complete precipitation, but if hydrochloric acid has been present and nearly neutralised by ammonia, the addition of ammonium chloride is unnecessary. The ammonium sulphide, further, must contain neither free ammonia nor polysulphide; when the latter is present a portion of the nickel remains in the solution, and can be recognised by the brown colour which it imparts to the latter (see § 46, where the removal of nickel from solution in this case is explained). In separating nickel and cobalt from the metals of the first and second Divisions, it becomes advantageous to precipitate with ammonium sulphide from the hot solution. The well-washed precipitate of the sulphides is transferred from the filter to a small beaker, and treated in the cold with dilute hydrochloric acid (1 vol. fuming acid to 10 vols. water). The sulphides of nickel and cobalt are insoluble in this medium, and after they have been filtered off, the metals of Divisions 1 and 2 are obtained in the filtrate. This method of separation is not absolutely accurate, as traces of cobalt and nickel pass into solution, and zinc sulphide may also remain behind with the nickel and cobalt sulphides, a fact which must be remembered. In the further processes of analysis, the nickel and cobalt sulphides are treated with a mixture of two parts of concentrated hydrochloric acid, and one part of concentrated nitric acid, and slightly warmed until they go into solution. This is effected chiefly by the chlorine liberated, which accounts for the formation of chlorides by the action of *aqua regia.* Sulphur usually separates out in this operation, and sometimes, especially if it has run together, is imparted a dark colour by traces of the metallic sulphides. Sulphur is not attacked by *aqua regia* when in this state, and to distinguish it from the sulphides themselves it must be ignited on a porcelain crucible cover, the sulphur burning away completely to sulphurous anhydride, while the metallic sulphides are transformed to oxides which are stable at a high heat. By the above operation a solution of the chlorides is obtained, the treatment of which is fully given below.

Action of hydrogen sulphide.—Hydrogen sulphide throws down from neutral solutions of nickel or cobaltous salts either no sulphides at all (from salts of strong mineral acids) or precipitates them only incompletely ; neutral solutions of cobalt and nickel acetates, however, are fully precipitated (when deposited from a boiling solution of the acetates, the black, amorphous precipitates of the hydrated sulphides are often accompanied by shining yellow flakes, which are probably anhydrous compounds). The precipitation does not take place in the presence of free mineral or acetic acids.

§ **43. Oxides.**—Nickel and cobalt form several compounds with oxygen; attention need here be paid only to those which are employed in analysis.

A. *Nickelous and cobaltous hydroxides.*— Nickelous hydroxide, $Ni(OH)_2$, forms a green precipitate. Cobaltous hydroxide, $Co(OH)_2$, is rose-red, easily oxidised in presence of caustic alkalies, and turns brown on exposure to the air, with formation of cobaltic hydroxide, $Co(OH)_3$. For the conditions of formation of cobaltous hydroxide through the action of caustic alkalies, see Special Reactions.

B. *Nickelic and cobaltic oxides,* Ni_2O_3 *and* Co_2O_3.—Nickelic and cobaltic hydroxides, $Ni(OH)_3$ and $Co(OH)_3$, are formed from the soluble salts of these metals by the action of chlorine, bromine, or hypochlorites, in presence of caustic alkalies ; they are characteristic black precipitates :

$$2Co(OH)_2 + 2KOH + Br_2 = 2Co(OH)_3 + 2KBr.$$

The reaction may be more correctly expressed by the following equation:

$$2Co(OH)_2 + KBrO + H_2O = 2Co(OH)_3 + KBr.$$

Nickelic oxide forms no salts, and the few which are known of cobaltic oxide cannot be prepared by the action of acids upon the hydroxide. Hydrochloric acid decomposes the higher oxides of both cobalt and nickel, with evolution of free chlorine:

$$Co_2O_3 + 6HCl = 2CoCl_2 + 3H_2O + 2Cl.$$

We shall describe in the following paragraphs the formation of the cobaltic salt, potassium cobalticyanide, and also of the double compounds of potassium nitrite with cobaltic nitrite, as these salts are employed in separating cobalt from nickel.

§ **44. Double Cyanides.**—Potassium cyanide produces in the solutions of nickel salts a green precipitate of nickel cyanide, $NiCy_2$; in cobalt salts a yellowish white precipitate of cobaltous cyanide, $CoCy_2$. The salts are dissolved by an excess of the precipitant, double salts being formed:

$$K_2NiCy_4 = 2KCy . NiCy_2,$$
$$K_4CoCy_6 = 4KCy . CoCy_2.$$

Both double salts are decomposed by hydrochloric acid, with re-formation of the simple cyanides. The distinction between these metals rests in the fact that the double cobalt salt can be converted, by the reactions described below, to the cobaltic salt, potassium cobalticyanide, $3KCy . CoCy_3$. Nickel, no salts of whose sesquioxide are known, forms no such compounds.[1]

Formation and properties of potassium cobalticyanide.—Potassium cobalticyanide, K_3CoCy_6, is formed by the oxidation of the original double salt, K_4CoCy_6. The oxidation can be accomplished by various means.

1. *By boiling in aqueous solution.*—When an aqueous solution of the lower double compound is boiled with access of air, the latter furnishes the oxygen necessary for oxidation; if the solution be boiled without exposure to the air, the water

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[1] The cobalt salts correspond to the iron salts:

K_4CoCy_6 potassium cobaltocyanide, K_4FeCy_6 potassium ferrocyanide,
K_3CoCy_6 potassium cobalticyanide, K_3FeCy_6 potassium ferricyanide.

itself is decomposed, its oxygen being used in the oxidation and free hydrogen generated:

$$2K_4CoCy_6 + O = 2K_3CoCy_6 + K_2O,$$
$$2K_4CoCy_6 + 2H_2O = 2K_3CoCy_6 + 2KOH + H_2.$$

Potassium cobalticyanide forms no precipitate when acted upon by dilute hydrochloric acid, as soluble hydrocobalticyanic acid is set free:

$$K_3CoCy_6 + 3HCl = H_3CoCy_6 + 3KCl.$$

The nickel double salt, on the contrary, is completely decomposed by the acid, a green precipitate of nickel cyanide being deposited and hydrocyanic acid formed:

$$K_2NiCy_4 + 2HCl = 2HCy + 2KCl + \underset{\text{Green precipitate.}}{NiCy_2}.$$

We now turn to the practical methods for detecting nickel in presence of cobalt, in which the foregoing reactions are employed. The solution of the salts of the two metals, which must contain only a little free acid, is precipitated by a freshly prepared solution of potassium cyanide,[1] and the precipitate dissolved in the least possible excess of the reagent. The solution is then boiled in a flask for half an hour; it is advisable to add three or four drops of hydrochloric acid as soon as the liquid begins to boil. When the boiling is finished, the solution is allowed to cool, and dilute hydrochloric acid added; the formation of a green precipitate indicates the presence of nickel. This method of separating nickel from cobalt has the objection, that no external indication concerning the completeness of the oxidation is furnished. For this reason the following method of separation is to be recommended. It should be remarked that all these operations with potassium cyanide must be performed under a hood with a good draught.

The action of acids upon the cyanogen compounds is not suitable for separating nickel and cobalt, as the composition of the precipitate depends upon the relative amounts of the metals present. If the salts exist in

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[1] Potassium cyanide is decomposed by water (slowly at the ordinary temperature, quickly on boiling) into potassium formate and ammonia:

$$KCN + 2H_2O = KCHO_2 + NH_3.$$

molecular proportions, the nickel and cobalt are both found in the precipitate as nickel cobalticyanide:

$$3K_2NiCy_4 + 2K_3CoCy_6 + 12HCl = Ni_3(CoCy_6)_2 + 12KCl + 12HCy.$$

When they are in other proportions, a part of the cobalt may remain in solution, or nickel separate out as $NiCy_2$. Nickel, however, is in all cases found in the precipitate.

2. *Oxidation with bromine.*—Potassium cobalticyanide also results from the action of bromine (bromine-water or, preferably, a 10 per cent solution of bromine in potassium bromide) upon the previously-mentioned salt, K_4CoCy_6:

$$2K_4CoCy_6 + Br_2 = 2K_3CoCy_6 + 2KBr.$$

If the nickel salt, K_2NiCy_4, be present during the treatment with bromine, it is easily decomposed on addition of caustic potash, and the black nickelic sesquioxide separates out:

$$2K_2NiCy_4 + 3KBrO + 12Br = 7KBr + 8CyBr^{*} + \underset{\text{Black precipitate.}}{Ni_2O_3}.$$

All the cobalt remains in solution, while nickel is completely precipitated as its sesquioxide. In employing this reaction, the solution of the metals (if obtained by decomposing the sulphides with *aqua regia*, after the latter has been driven off by evaporation) is precipitated by a freshly-prepared solution of potassium cyanide, and the precipitate dissolved in the least possible excess of the reagent. The solution is then made alkaline by an excess of sodium hydroxide, and bromine-water added until the colour of the bromine ceases to disappear. The black precipitate of nickelic oxide separates out on gently warming the solution, or sometimes even without the application of more heat than is evolved by the action of bromine upon the alkali. To ensure the reaction, it is absolutely necessary to use as little potassium cyanide as possible, and a large excess of sodium hydroxide and bromine-water. The precipitated nickelic hydroxide is washed, and then dissolved in hydrochloric acid for subjection to confirmatory tests; for the latter, the experiments given under the Special Reactions of nickel are employed.

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* Cyanogen bromide is a very volatile compound with extremely disagreeable odour; it is poisonous.

Although the properties of the cyanides permit the detection of nickel in presence of cobalt, through the action of bromine and a caustic alkali upon the double cyanides, these compounds are not adapted to the recognition of cobalt. The latter is obtained as potassium cobalticyanide, in which the cobalt can be found only after the decomposition of the cyanogen compound (see ferro- and ferricyanides, § 34).

§ **45. The Double Nitrites of Cobalt and Nickel with Potassium.**—Potassium nitrite forms in neutral cobalt and nickel solutions the double salts, $Co(NO_2)_2 . 2KNO_2$ and $Ni(NO_2)_2 . 4KNO_2$ respectively; both being salts of the monoxides. That of nickel is easily soluble. Nickel solutions show the same behaviour when acid; but if a cobalt salt in acid solution, especially one in acetic acid, be treated with potassium nitrite, the *cobaltic* salt, $Co(NO_2)_3 . 3KNO_2$, is thrown down as a sparingly soluble crystalline precipitate. The reaction follows the equation:

$$\begin{aligned} &CoCl_2 + 6KNO_2 + C_2H_4O_2 + HNO_2 = \\ &\quad Co(NO_2)_3 . 3KNO_2 + 2KCl + C_2H_3KO_2 + H_2O + NO. \end{aligned}$$

The conversion of a cobaltous compound to the corresponding cobaltic form is analogous to the oxidation of potassium cobaltocyanide; this is illustrated by the following equation:

$$\begin{aligned} &Co(NO_2)_2 . 2KNO_2 + 2KNO_2 + C_2H_4O_2 + HNO_2 = \\ &\quad Co(NO_2)_3 . 3KNO_2 + C_2H_3KO_2 + 2H_2O + 2NO. \end{aligned}$$

The reaction is made in analysis as follows:—The neutral solution of a cobaltous salt is strongly acidified by acetic acid, and the cobalt then precipitated by an excess of potassium nitrite. To render the precipitation complete, the liquid should be allowed to stand for some time (preferably in a warm place); its thoroughness is ascertained by retesting the solution with potassium nitrite, and observing whether, after some time, a precipitate again forms.

Although this reaction is employed in quantitative analysis as the best means of separating nickel from cobalt, the difficulty of determining the thoroughness of the precipitation may lead to inaccuracy in the detection of nickel, and it is therefore advisable to employ it only as a test for cobalt (§ 48).

Ammonia Compounds.—The salts of nickel and cobalt are characterised by their power of forming easily soluble ammonia compounds; no precipitate is produced, therefore, by the action of ammonia or ammonium carbonate on acid solutions, though the cobalt salts are turned violet, and those of nickel blue.

Especially soluble ammonia compounds are formed by the action of ammonia in *neutral* solutions (§§ 46 and 47). The composition of these ammonia compounds is very variable. The action of ammonia upon nickel sulphate gives rise to the compound $NiSO_4 . 4NH_3 . H_2O$. The cobalt compounds possess a similar composition: they are distinguished from those of nickel in becoming easily oxidised by the air in presence of ammonia (absorbing oxygen), and thus forming various compounds in which the metal is trivalent.

The compounds thus formed are called "Cobaltamine compounds," and differ greatly in their composition (roseo-cobaltamine, luteo-cobaltamine, etc.) Nickel forms no such compounds. This behaviour is turned to account in analysis as follows:—The solution of nickel and cobaltous salts is mixed with an excess of ammonia and treated with sodium hypochlorite ($NaClO$). Oxidation of the cobalt salt sets in on warming, and a dark red solution of luteo-cobaltamine results. The nickel remains unöxidised, and may be precipitated by sodium hydroxide as green nickelous hydroxide, cobalt remaining in solution (Vortmann). The separation is not exact.

SPECIAL REACTIONS

Nickel

§ **46.** Nickel is a shining gray metal, very hard, and difficultly fusible (at about 1400° C.) It has the specific gravity 8·9, and dissolves easily in nitric acid, with generation of hydrogen, but is less soluble in either sulphuric or hydrochloric acid. The salts are green in solution and when crystalline, but usually yellow in the anhydrous state.

Nickel forms many alloys. In coins it is mixed with three parts of copper, and in the so-called German silver these two metals are accompanied by zinc. Meteoric iron is an alloy of iron with varying quantities of nickel (from 5 per cent to 30 per cent). The majority of these alloys are soluble in nitric acid. For the analysis of some of them, see examples in quantitative analysis.

Reactions of Nickel Salts.—*Nickel sulphide* (§ 42).—

Ammonium sulphide, and, under certain conditions, hydrogen sulphide, precipitate the black, hydrated nickel sulphide, which is only slightly soluble in cold, dilute hydrochloric acid, but soluble in hot *aqua regia.* It dissolves to a brown solution in ammonium sulphide containing free ammonia (this reaction is a qualitative characteristic of nickel), but is reprecipitated on warming with an excess of acetic acid.

Nickelous hydroxide, $Ni(OH)_2$, and *nickel carbonate* are green precipitates, the first being thrown down from the solutions of nickel salts by caustic alkalies, the latter by sodium or potassium carbonate.

Nickelic hydroxide, $Ni(OH)_3$, is formed by the action of chlorine or bromine (not of iodine) upon nickelous hydroxide, in presence of sodium hydroxide, as a black precipitate, which dissolves in hydrochloric acid with evolution of chlorine.

Nickel cyanide.—Potassium cyanide precipitates green nickel cyanide, easily soluble in an excess of the reagent to the double salt, K_2NiCy_4. This double salt is not changed when boiled with access of air, *i.e.*, it does not oxidise. Bromine-water in presence of potassium hydroxide precipitates from its solution the black nickelic hydroxide, $Ni(OH)_3$; dilute acids, on the contrary, throw down nickel cyanide. Use in analysis § 44.

Ammonia double compounds (§ 45).—Neither ammonia nor ammonium carbonate precipitate nickel salts from acid solutions. In neutral solutions a precipitate is at first formed, but this dissolves in excess of the one or the other reagent to a sky-blue colour, and is not oxidised by sodium hypochlorite. Caustic potash precipitates nickelous hydroxide completely from ammoniacal solutions.

The above reactions are not sufficiently delicate for the detection of mere traces of nickel. For this purpose potassium thiocarbonate, K_2CS_3, is much more efficient. It produces in the solutions of nickel salts a dark red colour; the presence of other metals, including cobalt, is detrimental to the reaction.

When fused, in the dry state, with the borax bead or microcosmic salt in the oxidising flame, nickel compounds yield a brown-red glass which becomes yellow on cooling. Ignition of the microcosmic bead in the reducing flame does not affect the colour; the borax bead, owing to the reduction of the nickel, becomes gray and opaque. The presence of even traces of cobalt completely conceals the reaction.

Cobalt

§ **47.** Metallic cobalt is similar in all respects to nickel. Upon solution in acids (nitric is the best solvent), hydrogen is evolved and cobaltous salts formed. In solution the latter exhibit very characteristic colour transformations. The solutions of cobalt salts are red, but on evaporation a change often occurs, as, for instance, in cobaltous chloride and cobaltous nitrate, the red colour changing to blue. A blue solution is also obtained when the oxide or carbonate is dissolved in concentrated nitric acid. This change in the colour of cobalt solutions depends, in all probability, upon the presence of a salt containing a greater or smaller quantity of water of crystallisation. Cobaltous chloride, for example, probably exists in the red solutions as the salt, $CoCl_2 + 6H_2O$; but the composition of the dissolved salt is altered by evaporation, and the blue solution contains a salt which apparently possesses less water of crystallisation, $CoCl_2 + 2H_2O$. Cobalt salts in the dry state show exactly the same differences. The salts with water of crystallisation, *e.g.*, crystallised cobaltous chloride, cobaltous nitrate, are rose-red, but a change in colour is observed as soon as the water is driven off, anhydrous cobaltous chloride and nitrate being blue. One of the few exceptions in this regard is found in cobaltous sulphate, which is red in both the crystalline and anhydrous states.

Reactions of Cobaltous Salts.—*Cobaltous sulphide* (§ 42).—The black hydrate is completely precipitated by ammonium sulphide (and in some cases by sulphuretted hydrogen) in presence of ammonium chloride. It is only slightly soluble in dilute hydrochloric acid, but dissolves completely in *aqua regia.*

Cobaltous hydroxide and cobaltous carbonate.—Caustic alkalies at first produce a blue precipitate, consisting of a basic salt of the acid, the salt of which is employed in the experiment. This precipitate changes, when boiled with an excess of potassium hydroxide, to cobaltous hydroxide, $Co(OH)_2$, which is rose-red. The precipitate has almost invariably a brownish tinge, due to oxidation (formation of cobaltic hydroxide). In presence of alcohol in alkaline solution, complete oxidation takes place, and the brown cobalto-cobaltic hydroxide is formed. Sodium or potassium carbonate produces a violet precipitate of basic cobaltous carbonate.

Cobaltic hydroxide, $Co(OH)_3$, is obtained as a black precipitate by the action of chlorine, bromine, or iodine (distinction from nickel) in presence of caustic soda. For its properties see § 43.

Ammonia compounds (§ 45).—No precipitate is caused in acid solutions by ammonia or ammonium carbonate. Neutral solutions are precipitated, but the precipitates redissolve in an excess of the reagent; the ammoniacal solutions become oxidised by the air, turning brown. Potassium hydroxide throws down from ammoniacal solutions only a portion of the cobalt, as a blue basic salt; if the solution be completely oxidised, no precipitation ensues.

Double cyanides, K_4CoCy_6 and K_3CoCy_6 (§ 44).—Potassium cyanide produces in cobaltous solutions a yellow precipitate of cobaltous cyanide, which dissolves readily in an excess of the reagent to the double salt, K_4CoCy_6. Dilute mineral acids reprecipitate cobaltous cyanide from this solution. When acidified with acetic acid the solution of a double cyanide has imparted to it a blood-red, or if it be dilute, a rose-red colour by potassium nitrate (formation of cobalt potassium nitrocyanide). The passage into potassium cobalticyanide, K_3CoCy_6, and the use of the latter salt in analysis are explained in § 44.

Potassium cobaltic nitrite.—Potassium nitrite with acetic acid produces in the neutral solution of a cobaltous salt (the mixture must have a strong acid reaction) a yellow crystalline precipitate of $Co(NO_2)_3 . 3KNO_2 + Aq$. For its employment in analysis, see § 45.

The formula of potassium cobaltic nitrate given by Erdmann has recently been confirmed by Satler. In quantitative operations another method for obtaining the salt is employed, and it then apparently has a different composition. The solution of the cobaltous salt is made alkaline by a small excess of potassium hydroxide, and the precipitate dissolved in acetic acid. A solution of potassium nitrite, which has been previously acidified with acetic acid, is then added. A brownish precipitate is obtained which, especially on gentle warming, soon becomes yellow and crystalline. Its composition is $Co(OH)(NO_2)_2 + 4KNO_2$ (Strohmayer).

Fused on a platinum wire in the borax bead or with microcosmic salt (§ 32), cobalt compounds yield a dark blue glass; this colour is not altered by the reducing flame. The smallest quantity of a cobalt compound is sufficient to produce the coloration, and the reaction is not influenced by the presence of nickel.

SYSTEMATIC COURSE OF ANALYSIS FOR THE METALS OF GROUP III., DIVISION 3

§ **48** A. **Nickel and Cobalt.**—In the systematic course (see under B, below) nickel and cobalt are left as their hydrated sulphides, after treatment of the ammonium sulphide precipitates with cold, dilute hydrochloric acid. A portion of the washed and still wet precipitate is tested with borax or microcosmic salt; if the bead becomes blue, cobalt is present. For the detection of nickel, the sulphides are dissolved in *aqua regia* (§ 42) and the excess of acid driven off by evaporation. The resulting solution must be divided into two portions, since if the method of the double cyanides is to be employed, it is more convenient to test for nickel than for cobalt, and in using the potassium double nitrites, cobalt is, on the contrary, more easily detected than nickel. One portion is precipitated with potassium cyanide, and the precipitate dissolved in the least possible excess of the reagent (§ 44). If nickel be present the addition of bromine-water (in presence of caustic potash) produces a black precipitate. Confirmatory tests must be made with the nickelic oxide thus obtained. The other portion of the solution is saturated with sodium carbonate and precipitated, under the necessary conditions (§ 45), with potassium nitrite in presence of acetic acid. A yellow crystalline precipitate indicates the presence of cobalt.

B. *Metals of Groups III., II., and I.*—The solution is neutralised by ammonia (if acid), ammonium chloride is added, and the mixture treated at 60°-70° C. with ammonium sulphide (Conditions, §§ 36 and 42) until further addition of the reagent ceases to produce a precipitate. All the metals of Group III. are found in the precipitate, partly as sulphides, partly as hydroxides, and those of Groups II. and I. remain in solution. The precipitate is washed, removed to a small beaker with the help of the wash-bottle, and treated *in the cold* with a dilute solution (1 vol. HCl to 10 vols. H_2O) of hydrochloric acid

(§ 42). NiS and CoS remain undissolved, and are subjected to the tests mentioned in the first part of this paragraph. The solution filtered off from these sulphides is investigated according to § 40, A and B (oxidation with nitric acid or potassium chlorate, precipitation with barium carbonate, etc.)

The course of analysis as here given is applicable in all cases. The student can and should seek out for himself the other possible methods of separation. In all of them the most important point is the preliminary isolation of the three Divisions of Group III. The metals of Groups II. and I., which remain in the filtrate from the ammonium sulphide precipitates, are found according to §§ 35 A and 24.

SUPPLEMENT TO GROUP III

1

§ 49. *Analysis of native compounds of the metals of Group III.*—*Aluminium* forms one of the chief constituents of many important silicates (feldspar, mica, clay). Cyanite, topaz, chiastolite, etc., are all silicates of this metal. Cryolite has the formula $AlNaFl_4$. The analysis of these minerals will be spoken of under the corresponding metalloids, and only that of the simpler aluminium compounds considered in this paragraph. Alumina is found in nature in both the hydrated (gypsite, diaspore, bauxite) and anhydrous state (corundum, ruby, sapphire); these compounds are analysed according to the directions given in § 29. The modifications of alumina occurring in nature can be brought into solution by acid potassium sulphate; but the anhydrous oxide is preferably dissolved by fusion with caustic potash. Chromium is found principally as chrome-iron ore, $FeCr_2O_4$. The mineral is first fused with borax or acid potassium sulphate and then oxidised to chromic acid.

Iron, manganese, and zinc are found in nature as sulphides, oxides, or carbonates. The analysis of sulphides, such as iron sulphide or pyrites, FeS_2, blende, ZnS, must be described later (Section II.; Sulphur). The carbonates, chalybite, $FeCO_3$, diallogite, $MnCO_3$, calamine or smithsonite, $ZnCO_3 + ZnSiO_3$, and also all oxides; hæmatite, Fe_2O_3, limonite (hydrated Fe_2O_3), magnetic iron ore, Fe_3O_4, bromite and manganite, Mn_2O_3 (hydrated and anhydrous), are soluble in acids, and may, therefore, be analysed according to the above system. The anhydrous compounds (hæmatite, magnetic ore, bromite) are only slowly and with difficulty attacked by hot acids. Manganese dioxide dissolves in hydrochloric acid. These compounds are too complicated in their other constituents to permit an explanation of their complete analysis here; a few instances are given among the examples (Section III.), together with the alloys in which these metals are found.

The most extensive ores of *cobalt* and *nickel* are their compounds with sulphur and arsenic: smaltine (CoAs), copper nickel ($NiAs_2$), cobaltine (CoAs, CoS_2), gersdorffite (NiAs, NiS_2). The cobaltine compound, smalt (NiCoAs), similar in composition to these ores, is a blue product formed in the working of cobalt ores. Cobalt and nickel are always found together, and all of the above minerals contain both metals, the name of the ore depending upon the predominance of the one over the other. The same minerals contain also the metals, Fe, Sb, Cu, Bi, etc. The analysis of all these compounds is based upon the conversion of the sulphur and arsenic to sulphuric and arsenic acids, by fusion with sodium carbonate and potassium nitrate, or treatment with chlorine (Group V., Arsenic; Sec. II., Sulphur). If the first method be employed, the oxides are obtained, and can be dissolved in the proper acids. The second method yields the nickel and cobalt as their chlorides (which are also obtained on decomposing the minerals with *aqua regia*).

The metals of Group IV. having been removed by hydrogen sulphide, the separations of Group III. are effected by the methods previously given. The less important ores, erythrine and nickel ochre (arsenates), and black cobalt (cobalt and manganic oxides), are soluble in acids.

2

Phosphates and the salts of other acids which may be found in the ammonium sulphide precipitates with the metals of Group III.

§ **50.** Together with the metals of Group III., the ammonium sulphide precipitates obtained (from acid solutions) may also contain such phosphates, borates, silicates, and fluorides as are insoluble in water, but soluble in acids. These compounds are precipitated with the metals of Group III., because ammonium sulphide neutralises the acids by which the salts were held in solution. The presence of salts of these acids with Group III. is indicated: (1) by the necessity of an acid solution; and especially (2) by the presence of metals of Group II. (barium, etc.) in the precipitate with those of Group III. The metals of Group II. can exist in the precipitate *only* as salts of the acids under consideration. If ammonia, instead of ammonium sulphide, be cautiously added to the acid solution of Group III. until the liquid has a very slightly alkaline reaction, the formation of a precipitate under these conditions (neutralisation of the solution) indicates the presence of these acids. This method, however, is not always accurate (§ 51), and their detection can be guaranteed only by thorough familiarity with their compounds. As phosphoric acid is a very important body, and its salts show reactions closely resembling those of the metals in Division 1, we shall describe its qualitative reactions in full. The quantitative reactions (together with those of meta- and pyrophosphoric acids) are considered in Section II. The detection of the other acids in ammonium sulphide precipitates will be briefly explained: a complete description of their properties occurs in Section II.

PHOSPHORIC ACID

Phosphoric acid, PH_3O_4, forms transparent crystals, which deliquesce very quickly when exposed to the air. On being heated (in a platinum crucible) it completely volatilises, though only at a very high temperature. Phosphoric acid is tribasic. Its salts are stable at a high heat, and, with the exception of the alkali salts, are insoluble in water. The alkali salts usually employed in analysis contain two atoms of the metal, *e.g.*, Na_2HPO_4. The saturated salts, such as Na_3PO_4, are formed with difficulty, have an alkaline reaction, and are easily decomposed (for example, by carbonic acid or water), being converted to salts which contain two metallic atoms. The phosphates which are insoluble in water but soluble in acids are of the most importance.

Phosphoric acid, its acid salts, and the neutral ammonium metallic salts lose on ignition water, or water and ammonia, phosphoric acid being first converted to pyrophosphoric (at 417°) and finally to metaphosphoric acid:

$$H_3PO_4 - H_2O = HPO_3.$$

The phosphates give on ignition either pyro- or metaphosphates, according to their composition :

$$2Na_2HPO_4 - H_2O = Na_4P_2O_7,$$
$$2Mg(NH_4)PO_4 - H_2O - 2NH_3 = Mg_2P_2O_7,$$
$$Na(NH_4)HPO_4 - H_2O - NH_3 = NaPO_3.$$

The resulting metaphosphoric and pyrophosphoric acids and their salts possess properties which differ from those of the ortho-acid, and this fact must be borne in mind in the analysis, in case the phosphoric acid or its salts have been ignited. In qualitative analysis, and especially in the quantitative determination of phosphoric acid, the meta- and pyrophosphates formed must be reconverted to orthophosphates, *i.e.*, be connected with another molecule of water or of a base :

$$HPO_3 + H_2O = H_3PO_4,$$
$$Na_4P_2O_7 + Na_2CO_3 = 2Na_3PO_4 + CO_2.$$

This is accomplished by the action of alkalies or acids. The reaction sets in most easily if the metaphosphate or pyrophosphate be fused with sodium carbonate. In this case the salt of the non-alkali metal will be decomposed, sodium phosphate and the oxide or carbonate of the other metal being formed. On treatment with water, the sodium salt of normal phosphoric acid goes into solution.

Since, with the exception of the alkali salts, phosphates are soluble only in acids, their analysis must be made under conditions with which we are unfamiliar, *i.e.*, in acid solution. Before considering the reactions, let us study more closely the solubility of phosphates in acids, and the conditions under which they are deposited from acid solutions.

The solubility of phosphates in acids.—Phosphates show in regard to their solubility in acids some important and characteristic variations. (1) The salts of the metals of Group II. (barium, strontium, calcium, and magnesium) are soluble in acetic (the barium salt sparingly so) and mineral acids. (2) The salts of the metals of Group III., especially those of aluminium and ferric iron, and also of certain metals of Group IV., are insoluble in acetic acid, but soluble in mineral acids, *e.g.*, in nitric and hydrochloric acids. (3) Some salts, finally (those of tin, mercury, bismuth, molybdenum), are insoluble in nitric acid. The reactions used in separating phosphoric acid from any metal rest upon these important characteristics. If the acid of any phosphate in acid solution is to be separated from the metal to which it is bound, the acid serving as a solvent is changed, and another phosphate, insoluble in the substituted acid, prepared. The metal previously present as a phosphate goes into solution. Let it be assumed, for the purpose of illustration, that we have magnesium phosphate in a hydrochloric acid solution. To separate the magnesium from the phosphoric acid, the solution is first treated with sodium acetate, which forms with the hydrochloric acid sodium chloride, and sets acetic acid free. But though the solvent has now been changed, the solubility of the phosphate has not been disturbed, and no separation has resulted. Let ferric chloride next be added; ferric phosphate, which is insoluble in acetic acid, is precipitated, and magnesium remains in solution. The separation is thus made. To separate the metal from the phosphoric acid in salts which are soluble in hydrochloric acid, the same method is pursued; the hydrochloric acid solution is replaced by one of nitric, and the phosphoric acid precipitated as the salt of a metal which is insoluble in the latter. Phosphates which are soluble in nitric acid, finally, are decomposed by the action of bases.

Precipitation of phosphates by neutralisation of the acid solution.—Phosphates are precipitated from acid solutions upon neutralisation of the acid (the presence of ammonium salts hinders the separation of certain compounds). The precipitation is usually effected with ammonium sulphide, ammonia, the alkalies, or carbonates (also those which are insoluble, such as barium carbonate). In certain cases the precipitation of phosphates by neutralisation of the acid is attended by their decomposition.

Ammonium sulphide can not only precipitate the phosphates, but in certain cases (on warming, in great excess, when the action is prolonged, etc.) may also decompose them, with formation of metallic sulphides and ammonium phosphate. As the analysis of metals of Group III. in presence of phosphates begins with precipitation by ammonium sulphide, it becomes of the utmost importance to produce this precipitation in such a way that none of the phosphates will be decomposed. On the other hand, certain reactions are sometimes employed, in which the phosphate, *e.g.*, ferric phosphate, *must* be destroyed by the ammonium sulphide; this is accomplished on warming with a great excess of the latter. The student must be able to distinguish the various cases in which ammonium sulphide is employed, so that he can use the reagent with judgment.

The caustic alkalies, ammonia, and the alkali carbonates.—At the ordinary temperature these reagents precipitate phosphates without change, but decomposition may take place in hot solutions. Ferric phosphate, for instance, is decomposed on boiling with potassium hydroxide. The salts of calcium, strontium, and magnesium (though not of barium) are more stable in their behaviour toward alkalies, even on fusion; those of the heavy metals are mostly decomposed by this reaction. As fusion with sodium carbonate obtains the phosphoric acid in the form of the sodium salt, which is soluble, this is the most convenient method of bringing the acid of insoluble phosphates into solution.

Barium carbonate decomposes the salts of calcium and magnesium in acid solutions, barium phosphate being precipitated:

$$Mg_3(PO_4)_2 + 6HCl + 3BaCO_3 = Ba_3(PO_4)_2 + 3MgCl_2 + 3CO_2 + 3H_2O.$$

Reactions of Phosphates.—We now take up the study of the reactions. They consist in the precipitation of insoluble phosphates, the latter being grouped, according to their solubilities, into several classes. The reactions of free phosphoric acid are employed almost exclusively to distinguish it from meta- and pyrophosphoric acid, and are explained in the paragraphs on these acids (Section II., Phosphorus).

A. *Salts soluble in acetic acid* (and in mineral acids).—They are decomposed by precipitation from acid solution by barium carbonate, barium phosphate being formed. The phosphoric acid is separated from the metal by the formation of the salt of one of the other groups.

Calcium phosphate, $Ca_3(PO_4)_2$.—Calcium chloride throws down from solutions of phosphates (but not of the free acid) a white precipitate, $CaHPO_4$ or $Ca_3(PO_4)_2$, which is soluble in acetic and mineral acids and, when freshly precipitated, in ammonium chloride; from the acetic acid solution of calcium phosphate calcium oxalate (insoluble in acetic acid) is precipitated by ammonium oxalate.

Ammonium magnesium phosphate.—Magnesium sulphate slowly precipitates from a neutral solution and at the ordinary temperature the salt $MgHPO_4$; from a boiling solution it throws down $Mg_3(PO_4)_2$ immediately. Both salts are but slightly characteristic amorphous precipitates. The ammonium magnesium salt, $Mg(NH_4)PO_4$, is one of the most important salts of phosphoric acid (in both qualitative and quantitative analyses). This salt is formed as a white crystalline precipitate by the action of magnesium sulphate upon the solution of a phosphate in presence of ammonium chloride and ammonia. The properties of this salt and the conditions of its formation have already been described (§ 23). Its behaviour toward acids is analogous to that of calcium phosphate.

B. *Salts which are insoluble in acetic, but soluble in mineral acids.*—On the neutralisation of the acid solution of these salts with barium carbonate, ammonium sulphide, or ammonia, they are precipitated unaltered, but suffer decomposition when boiled with ammonium sulphide or caustic potash (the aluminium salt in presence of barium carbonate). The phosphoric acid is separated from its metal by the preparation of a phosphate of the next group.

The aluminium salt, $AlPO_4$.—Aluminium salts produce in a solution of sodium phosphate a white, gelatinous precipitate of aluminium phosphate, which is soluble in potassium hydroxide, and redeposited from this solution by ammonium chloride (like aluminium hydroxide). It is distinguished from aluminium hydroxide by its insolubility in acetic acid; the difference is made still more pronounced by the following reactions:—

If tartaric acid be added to the acid solution, to keep the aluminium salt in solution during the subsequent reactions, and then neutralised by an excess of ammonia, the addition of magnesium sulphate produces a precipitate of ammonium magnesium phosphate. The aluminium is left in solution.

Ferric phosphate, $FePO_4$.—Neutral and acetic acid solutions of phosphates deposit, upon the cautious addition (by drops) of ferric chloride, a yellowish white, gelatinous precipitate of ferric phosphate, insoluble in acetic, but soluble in mineral acids. It is decomposed on warming with caustic potash or ammonium sulphide (ferric hydroxide or ferrous sulphide being in the precipitate and the alkali phosphate in solution). The employment of ferric phosphate enables the separation of phosphoric acid from many metals. The slight solubility of ferric phosphate in a solution of ferric acetate, $Fe(C_2H_3O_2)_3$, and also in other ferric salts, necessitates the following precautions in its precipitation: (1) The ferric chloride must be added drop by drop (lest an excess of the reagent be used; ferric acetate will otherwise be formed from the acetate in solution). (2) If the solution already contains much ferric iron (this is to be determined by a preliminary test), the latter must be reduced to the ferrous state (ferrous acetate does not dissolve ferric phosphate) before the phosphoric acid is separated.

In separations which are to be employed in qualitative analysis, therefore, the experiments must be made as follows: The acid solution of the phosphate is neutralised by sodium carbonate, the latter being added drop by drop until the solution, which must be continuously stirred, assumes a permanent turbidity. After the addition of sodium acetate (a precipitate may here ensue if the solution contained the phosphates of iron, aluminium, or chromium), the yellowish white ferric phosphate is precipitated by ferric chloride, the reagent being added drop by drop. The precipitate continues to separate as long as phosphoric acid is present. As soon as the precipitation is complete, a single drop of ferric chloride in excess gives a reddish brown tint to the solution. Upon the appearance of this colour the addition of the reagent must be ceased, as it indicates that ferric acetate is formed (red-brown colour, § 34), which can result only from the action of an excess of ferric chloride upon sodium acetate. The liquid is next boiled (the soluble ferric acetate being converted on boiling to an insoluble basic salt, § 34). Ferric phosphate and basic acetate are found in the precipitate, which contains all the iron previously in solution.

The phosphates of aluminium and chromium, if present, remain unaltered in this reaction, and if they were in the solution, they will be found with the ferric phosphate in the precipitate. Barium, strontium, and calcium phosphates are decomposed, and all their phosphoric acid is obtained in the precipitate as ferric phosphate, while the metals themselves remain in solution.

When a larger quantity of ferric iron is present (see above), the reaction is made in a different manner. The acid solution is heated to boiling, and after the ferric iron has been reduced by sodium thiosulphate, a great excess of the latter being avoided, it is boiled to drive off the sulphurous acid (the operation should be performed under a hood). It is next neutralised by sodium carbonate, and an excess of sodium acetate added (aluminium and chromium phosphates may be precipitated). On the addition of bromine-water, drop by drop, a precipitate of ferric phosphate is immediately formed. The bromine-water is added until the red-brown colour of ferric acetate appears, and the solution then boiled and treated as above. All the iron except that bound to the phosphoric acid remains in solution as a ferrous compound. When manganese is present, ferric chloride forms the better precipitant, as an excess of bromine throws down manganese peroxide.

Silver phosphate, Ag_3PO_4.—Silver nitrate precipitates from neutral solutions the yellow silver phosphate, readily soluble in ammonia and nitric acid.

C. *The salts which are insoluble in nitric acid* afford the separation of phosphoric acid from all metals; with the exception of the phosphomolybdate they are not employed in qualitative reactions. These salts are decomposed by ammonia, alkalies, and alkali carbonates (method of separation of the metals from the acid in phosphates of this group).

Ammonium phosphomolybdate, $(MoO_3)_{12}(NH_4)_3PO_4$.—Bright yellow, crystalline precipitate, insoluble in nitric acid. It affords a delicate reaction for phosphoric acid.

Hundeshagen has found that this compound, when precipitated from nitric acid solution, always contains the latter acid. He ascribes to ammonium phosphomolybdate the formula:

$$12MoO_3 . (NH_4)_3PO_4 . 2NHO_3 + H_2O.$$

This compound is analogous to the dichromate, $CrO_3 . K_2CrO_4$, to the metaphosphate, $P_2O_5 . Na_3PO_4$, etc., which, for the sake of comparison, we here represent as compounds of the acid anhydrides with neutral salts. Phosphomolybdic acid is, like those enumerated, an anhydro-hydrated acid, as shown by the formula:

$$(OH)_2PO - O - [MoO_2 - O]_{11} - MoO_2(OH).$$

The reagent employed is a solution of ammonium molybdate in nitric acid. It produces in neutral or acid solutions of phosphoric acid or its salts a finely granular bright yellow precipitate of ammonium phosphomolybdate. Small quantities of phosphoric acid are precipitated only after some time has elapsed, but the reaction may be hastened if the solution be allowed to stand at a gentle heat (40° C.) Only a few drops of the concentrated solution of a phosphate are required for the reaction, and a greater quantity of the salt is detrimental (sodium phosphate dissolves ammonium phosphomolybdate). In this test the solution often becomes yellow, without depositing a precipitate, and this must not be taken as an indication of phosphates. Ammonium phosphomolybdate is somewhat soluble in water and acids, but rendered insoluble in either water or nitric acid by the presence of free ammonium molybdate. Non-volatile organic acids and, in general, all compounds which can effect reduction, such as hydriodic acid, hinder the precipitation, as they reduce the molybdic acid. Ammonia completely decomposes the salt, even in the cold, with formation of ammonium phosphate and molybdate.

SYSTEMATIC COURSE OF ANALYSIS

§ 51. The Metals of Group III. and Phosphates.—The presence of phosphates does not affect the course of analysis of Group III.

If their presence is suspected, a test is made before the precipitation with ammonium sulphide, by neutralising with ammonia. The reagent is added drop by drop until the reaction is barely alkaline, and if a precipitate appears on the solution being warmed, the presence of phosphates may be assumed. It cannot be concluded from negative results in this one experiment, however, that they are absent, since, if ammonium salts be in the solution, ammonia does not always precipitate the phosphates. It is much better to make a test with ammonium molybdate in a small portion of the liquid, first acidifying with nitric acid (§ 50). This reaction proves only the presence of phosphoric acid. The detection of the metals requires the use of a scheme of analysis based upon the methods of analysis of Group III., which is given in §§ 48 and 40. We shall treat of them briefly. The precipitation with ammonium sulphide is effected under the conditions mentioned in the respective paragraphs (see also, the precipitation of phosphates by neutralisation). To separate nickel and cobalt, the precipitate is treated with dilute hydrochloric acid in the cold. They are separated from each other according to § 48. The phosphates remain in solution with the metals of Group III., Divisions 1 and 2. The analysis of native phosphates, which never contain chromium, is described below in full. Phosphates found in nature are chiefly those of aluminium, ferric iron, calcium, and magnesium.

1. *Precipitation as basic acetates and as ferric phosphate.*—When chromium is absent, the metals of Divisions 1 and 2 are separated as their basic acetates (§ 40). In the presence of phosphates, however, the performance of the operation must be slightly modified. If ferric chloride is to be employed for the detection and separation of phosphoric acid, the presence of iron, in both the ferric and ferrous states, in the substance to be analysed, must first be determined. Special portions of the original solution are tested with ferrocyanide and ferricyanide of potassium. If these preliminary tests indicate the presence of much iron, it is necessary to protect the hydrochloric acid solution of the ammonium sulphide precipitate from oxidation (§ 50 B). After neutralisation with sodium carbonate and the

addition of sodium acetate, the solution is precipitated by ferric chloride, the reagent being added drop by drop (detection and separation of phosphates). All the conditions mentioned in § 50 B must be secured; the solution having been boiled and filtered, the precipitate contains all the phosphoric acid as $AlPO_4$ and $FePO_4$, and also the basic acetates of Fe_2O_3 and Al_2O_3, if there were salts of these metals, other than phosphates, in the solution. Not only manganese, zinc, and ferrous iron, but also any magnesium and calcium which were present as phosphates, remain in the solution. The iron having next been oxidised to the ferric state, tests are made for these metals according to §§ 40 and 24. The precipitate of mixed hydroxides and phosphates is removed from the filter and treated with caustic potash; aluminium hydroxide and phosphate go into solution, and the residue consists of ferric hydroxide and phosphate. The alkaline solution is filtered and subjected to tests for aluminium and phosphoric acid, according to § 50 B. The precipitate is treated with ammonium sulphide and gently heated, whereupon the phosphoric acid goes into solution as ammonium phosphate. After the ammonium sulphide has been decomposed by boiling with a slight excess of hydrochloric acid, and the separated sulphur has been filtered off, a test for phosphoric acid is made by precipitation with magnesium sulphate in presence of ammonia and ammonium chloride (§ 23). Under certain conditions of the experiment, it is possible that all of the phosphoric will be found with the aluminium in the caustic potash solution.

2. *Precipitation with barium carbonate.*—Let us now consider the analysis of phosphates which contain chromium. This, as has already been said, can occur only in artificially prepared mixtures. The presence of chromium is, as usually, determined by the coloration of the borax bead. When iron is present the solution is oxidised and precipitated with barium carbonate, according to the first part of § 40; before applying the reagent, the absence of barium from the original solution must be established. This question is quickly answered by the addition of sulphuric acid to a separate portion of the solution. If no precipitate forms, the solution is neutralised with sodium carbonate and treated with barium carbonate under the conditions given in § 28. After complete precipitation, all

the phosphoric acid is found in the precipitate as $AlPO_4$, $FePO_4$, $CrPO_4$, and $Ba_3(PO_4)_2$. Barium phosphate will also be obtained if the phosphates of calcium or magnesium, which are decomposed by barium carbonate, were in solution (§ 50). Al_2O_3, Fe_2O_3, Cr_2O_3, may also be in the precipitate, if their salts were in solution, and it also contains the excess of barium carbonate used. In addition to the soluble barium salts formed from the carbonate, those of manganese and zinc remain in solution, as well as calcium and magnesium salts, if phosphates of these latter metals were originally present. The further course of analysis is the same as in the previous case.

On treatment of the precipitate with potassium hydroxide a part of the chromium also goes into solution. If $AlPO_4$ be boiled with caustic potash in presence of a sufficient quantity of barium carbonate, it can be completely decomposed, with formation of aluminium hydroxide and barium phosphate. Phosphoric acid, therefore, cannot remain in solution. Chromic hydroxide, after being boiled with the alkali, remains for the most part with the iron, and its separation is therefore inaccurate.

DETECTION OF THE ACIDS IN AMMONIUM SULPHIDE PRECIPITATES

§ **52.** If the indications mentioned at the beginning of § 51 point to the presence of the acids, the latter are detected by special reactions, which are made in the hydrochloric acid solution of the precipitate obtained in the separation of Group III. Division 3, from Divisions 1 and 2 (§ 48).

Phosphoric acid.—A portion of the solution is evaporated with nitric acid, and a test made for phosphoric acid with ammonium molybdate, (§ 50 C). If found, the analysis is made according to §§ 48 and 51.

The remaining acids will be considered among the metalloids, but we shall mention the tests for them here also. (Tests to be made in the same solution.)

Silicic acid.—Evaporate the solution to dryness, heat the residue for some time at 100° C., and treat with hydrochloric acid. Test with microcosmic salt: silica skeleton (Section II.; Silicon).

Hydrofluoric acid.—The hydrochloric acid solution is precipitated with ammonia; the dry precipitate tested for fluorine (Section II.; Fluorine).

Boric acid is detected by the green colour which it imparts to the flame (Section II.; Boron).

3

BERYLLIUM, YTTRIUM, ERBIUM, YTTERBIUM, SCANDIUM, ZIRCONIUM, THORIUM, CERIUM (DIDYMIUM, SAMARIUM, LANTHANUM), TITANIUM, NIOBIUM, TANTALUM, INDIUM, GALLIUM, URANIUM, THALLIUM

These elements belong to the Third Group of metals because they are *not* precipitated from acid solutions by hydrogen sulphide, and are thrown down (as hydroxides or sulphides) by ammonium sulphide.

The chemical properties of these metals exhibit unusual variations. They include members of several families of elements. Indium, uranium, and thallium are precipitated by ammonium sulphide as sulphides, and stand, in their properties and oxides, in close relationship to aluminium and iron, and in a measure to chromium also. The remaining elements are precipitated by ammonium sulphide as hydroxides of varying composition; they resemble in part the metals of the magnesium group, and in part are, to a certain degree, analogous to silicon and tin. We group them, as much as possible, according to their chemical resemblance, but without reference to the three Divisions with which we are already familiar. A classification like that of Group III. is prevented by the widely-varying characteristics of these rare elements. They are in many respects insufficiently investigated, and their study is therefore unimportant for the beginner. This justifies, also, their isolation from the general scheme of exposition. Our unsatisfactory knowledge of these elements necessitates a departure from the methods of study which we have hitherto pursued.

Since it is impossible to include the analysis of these elements in the general systematic scheme, or to express the analysis of all their possible mixtures by a single system of formulae, we shall limit ourselves, after having learned their reactions, to the explanation of the few cases (analyses of minerals which contain the rare elements) in which such an analysis has already been accomplished.

In order to understand these elements the more perfectly we separate them into a few Divisions. I. Ammonium sulphide precipitates hydroxides (with evolution of H_2S) of varying atomic composition: beryllium, yttrium (erbium), zirconium, thorium, cerium, lanthanum, didymium, titanium, tantalum, niobium. As a basis for the division of these metals into groups, the various chemical properties of their oxides, and the analytical methods which depend upon the character of the latter, may be employed. It must be added that the similarity between the single metals is too great to permit a sharp classification. (1) Titanium, tantalum, and niobium form the oxides TiO_2, Ta_2O_5, Nb_2O_5, which are called titanic, tantalic, and niobic acids respectively. These terms indicate that these non-basic oxides possess no power, or, more correctly, possess little power of uniting with other acids, *e.g.*, sulphuric, to form salts. The oxides of the other metals are bases which do give salts with acids. This distinction in their properties is turned to account in analysis; minerals which contain these metals are treated with sulphuric acid (or acid potassium sulphate) or with hydrofluoric acid (or with acid potassium fluoride, KHF_2). In the first instance, the slightly basic oxides of Ta and Nb are not dissolved (titanium dissolves; see below), while the remainder form soluble sulphates. In the second case, the fluorides which correspond to the basic oxides do not go into solution, but titanium, tantalum, and niobium are dissolved, either as fluorides or as the double salts with potassium fluoride, TiK_2F_6, TaK_2F_7, $NbOK_2F_5$. The action of alkalies or of alkali carbonates brings Ti, Ta, and Nb into solution, and leaves the others (zirconium excepted) undissolved. The above reactions permit the classification of titanium, tantalum, and niobium as a special division. The basic oxides are especially characterised by the formation of double salts with potassium sulphate, and neutral potassium sulphate acts as a useful reagent in their analyses. (2) Soluble double sulphates are formed by beryllium, yttrium (erbium); (3) insoluble salts, by zirconium, thorium, cerium (lanthanum, didymium). II. Uranium, indium, and thallium, finally, are precipitated as sulphides by ammonium sulphide.

BERYLLIUM

§ 53. Beryllium is found in a few minerals, phenacite, beryll, euclase. The beryllium salts are similar in their properties to those of magnesium. Beryllium chloride may be sublimed, colours the flame of the gas-burner, and gives a characteristic flame-spectrum which contains a green and a red line, both brilliant.

Reactions of beryllium salts.—*The hydroxide*, $Be(OH)_2$, is deposited from the solutions of beryllium salts as a flocculent, white precipitate by the action of potassium hydroxide, ammonia, or ammonium sulphide. It is soluble in potassium hydroxide, but is reprecipitated from this solution on being boiled (when in dilute solution), and also by ammonium chloride. On continued boiling with ammonium chloride it redissolves, with formation of beryllium chloride. Tartaric acid interferes with the precipitation by caustic potash. Anhydrous beryllium oxide is brought into solution by acids with difficulty, but readily by acid potassium sulphate.

The carbonate, $BeCO_3$, is thrown down by sodium and ammonium carbonate as a white, gelatinous precipitate, which is soluble in a great excess of the reagent, but again deposited on being boiled. Barium carbonate does not precipitate beryllium salts in the cold, but throws them down completely from warm solution.

The distinctive characteristics of beryllium salts are: non-precipitation by oxalic acid, as beryllium oxalate is soluble, or by neutral potassium sulphate, the double salt, $K_2Be(SO_4)_2$, being likewise soluble.

Analysis of beryll (aluminium and beryllium silicate).—The silica is separated by fusion of the silicate with a mixture of sodium and potassium carbonates (Section II.) Aluminium is next precipitated from the solution by an excess of ammonium carbonate: this operation must be repeated several times, as the separation is not accurate. After filtration and expulsion of the ammonium salts by boiling, beryllium hydroxide is precipitated by ammonia, dried, and weighed.

YTTRIUM, YTTERBIUM, SCANDIUM, CERIUM, LANTHANUM, DIDYMIUM, SAMARIUM

These elements constitute the so-called gadolinite and cerite group. They are very numerous, and their number increases with improvement in the methods of their investigation, as it is found that compounds formerly considered pure are merely mixtures of the compounds of several metals.

The most important chemical characteristics of the gadolinite metals are as follows:—The atomic composition of the salt-forming oxides is R_2O_3; higher oxides exist for a few of the metals, for instance, of cerium: the salts which characterise these metals are the insoluble oxalates and the double salts of their sulphates with the alkali sulphates. Solutions of the salts of a few metals (erbium, didymium) give absorption-spectra (Section III.) The more perfectly investigated metals, yttrium, lanthanum, cerium, show no absorption-spectra in solution, but are characterised by their spark-spectra (Section III.) Scandium occurs with yttrium in a few minerals.

Erbium and didymium were recognised as elements by the absorption-spectra of their salts in solution, but it has been shown that the oxide, supposed to be that of erbium, also contained those of holmium, thulium, and ytterbium (Soret, Marignac). Didymium oxide was split up by Auer von Welsbach into the oxides of neodim and praseodim, and G. Krüss and Nilson have recently claimed that all these elements, and also samarium, are complicated substances. The study of the absorption-spectra has led these authors to believe that the above erbium and didymium oxides contain no less than twenty elements. Under such circumstances we may readily be excused from entering for the present into the reactions of these metals.

By the employment of new methods of investigation, the fractional precipitation of yttrium hydroxide and the phosphorescence spectrum (Section III.) of its compounds, Crookes has arrived at the conclusion that the metal now known as yttrium contains at least five, and perhaps eight elements.

Yttrium.—Yttrium exists in the minerals, gadolinite, orthite, yttrotantalite, etc. The yttrium salts do not colour the flame, yttrium chloride being non-volatile. A solution of yttrium sulphate, saturated in the cold, deposits a precipitate when heated to 40° C. Yttrium chloride gives a characteristic spark-spectrum (§ 111).

Reactions of yttrium salts.—*Yttrium hydroxide*, $Yt(OH)_3$, is thrown down by caustic potash, ammonia, or ammonium sulphide, as a white, voluminous precipitate, insoluble in excess of these reagents (a large quantity of ammonium chloride interferes with the reaction, as yttrium hydroxide decomposes ammonium chloride with formation of yttrium chloride and free ammonia). Tartaric acid does not prevent precipitation with potassium hydroxide. Both the hydroxide and anhydrous oxides dissolve readily in acids.

Yttrium carbonate, $Yt_2(CO_3)_3$.—Potassium and ammonium carbonates produce a white precipitate, soluble in a large excess of the reagent. If the solution in ammonium carbonate be boiled, it deposits yttrium hydroxide ; this reaction cannot be obtained in presence of ammonium chloride, the products being in this case free ammonia and yttrium chloride. Barium carbonate precipitates in the cold (?)

Yttrium oxalate, $Yt_2(C_2O_4)_3$.—Oxalic acid produces a white precipitate, insoluble in excess of oxalic acid or of ammonium oxalate.

Yttrium fluoride, YtF_3.—Hydrofluoric acid throws down yttrium fluoride, gelatinous, insoluble in excess : it changes to a white powder on being warmed.

Yttrium formate and *sulphate* are soluble ; the latter also dissolves in a concentrated solution of an alkali sulphate.

Analysis of gadolinite (silicate of Yt, Be, Fe, Mn, Ce, La).—The mineral is decomposed by *aqua regia* and, after the silica has been filtered off, the solution is neutralised, and the insoluble oxalates of Yt, Ce, La, precipitated by ammonium oxalate in presence of ammonium chloride. Be, Fe, Mn, remain in solution as their oxalates. The separation of the yttrium from cerium and lanthanum is effected by treatment with potassium sulphate (see Cerium). Yttrium hydroxide is precipitated from the solution of the double potassium sulphate by ammonia, and the metal determined as oxide. The analysis of gadolinite by spectroscopic methods is explained in § 111.

§ 54. **Cerium, Lanthanum.**—Cerium and its companions, lanthanum and didymium, are found chiefly in orthite and cerite (silicates of these metals).

CERIUM.—Two oxides of cerium are known, the sesquioxide, Ce_2O_3, and dioxide, CeO_2. The former is converted to the latter by ignition. Cerium salts are also of two degrees of oxidation, cerous and ceric ; the latter are, as a rule, not very stable.

Reactions of cerous salts.—These are the most stable compounds of cerium. Cerous chloride is non-volatile (distinction from zirconium, beryllium, thorium).

Cerous oxide is precipitated by caustic alkalies and ammonium sulphide as the light yellow hydroxide, $Ce(OH)_3$, which is insoluble in excess of the reagent, and assumes a yellow tint in the air (due to oxidation). On ignition it becomes orange-yellow, but returns to bright yellow on cooling. Ammonia precipitates basic salts. Tartaric acid interferes with the precipitation by ammonia or caustic alkalies (distinction from yttrium).

The *carbonate* is a white precipitate soluble in excess of sodium or potassium carbonate. Cerous solutions are thrown down slowly, but completely, on digestion with barium carbonate.

The *double sulphate*, $K_3Ce(SO_4)_3$, is obtained by precipitation with a saturated solution of neutral potassium sulphate as a white powder. This double salt is difficultly soluble in water, and practically insoluble in a concentrated solution of potassium sulphate.

The *oxalate*, $Ce_2(C_2O_4)_3$, is a white precipitate, insoluble in excess of oxalic acid, and difficultly soluble in mineral acids. A boiling solution of ammonium oxalate dissolves it, but separation again takes place on dilution with water in the cold.

The *formate* is a white precipitate which is sparingly soluble in water.

Sodium thiosulphate does not produce a precipitate.

Ceric salts.—If chlorine be led into the warm solution of a cerous salt in presence of sodium acetate, or if the solution be treated with sodium hypochlorite, all the cerium will be deposited as yellow ceric hydroxide.

The *nitrate* is formed by boiling cerous nitrate with lead dioxide and nitric acid. Its solution is deep yellow (a delicate test for cerium). Anhydrous ceric oxide, CeO_2, is obtained by the ignition of cerous oxalate in the air. It is only a weak base, and decomposes hydrochloric acid with formation of the cerous salt and generation of chlorine. The sulphate and nitrate are known only in double salts with NH_4, Mg, etc. The reactions of the ceric salts have not been investigated. In analysis they are converted to the cerous salts.

Lanthanum is to a great degree similar to cerium, but has only one oxide and one series of salts.

Reactions of lanthanum salts.—The *oxide* and hydroxide, $La(OH)_3$, are white powders.

The *potassium sulphate double salt*, $K_8La_2(SO_4)_7$, is insoluble in a saturated solution of potassium sulphate.

The *oxalate*, $La_2(C_2O_4)_3$, is a white, crystalline powder insoluble in water.

The *formate*, $La(CHO_2)_3$, is a white precipitate, difficultly soluble in water.

Solutions of lanthanum salts show no absorption-spectrum.

Analysis of cerite (silicate of Ce, La).—The mineral is heated with sulphuric acid, the excess of acid driven off, and the residue digested with water and nitric acid (separation of silica). Cerium and lanthanum (didymium) are next precipitated by a solution of potassium sulphate saturated at the ordinary temperature (or, better still, by sodium sulphate), and the precipitate washed with the same solution. There is no accurate method for their separation, but approximate results are obtained by dissolving the double salts in hydrochloric acid, reprecipitating with potassium hydroxide, and treating with chlorine (see above ; Cerium). A fair separation can also be effected by the ignition of their nitrates (at 400° C.) Bunsen recommends the indirect determination of cerium and lanthanum by means of the sulphates. The preparation of the pure compounds of these metals cannot be explained in this place.

THORIUM

Thorium is found in the very rare minerals, thorite and monazite (silicates of this metal). It possesses only one oxide, and its salts are thoroughly stable. Thorium chloride is non-volatile (it can be sublimed). The sulphate, $Th(SO_4)_2 + 2H_2O$, is precipitated, if a solution of the sulphate, $Th(SO_4)_2 + 9H_2O$, prepared in the cold, be boiled or gently warmed.

Reactions of thorium salts.—*Thorium oxide*, ThO_2 ; caustic alkalies, ammonia, and ammonium sulphide throw down the white hydroxide, insoluble in excess, but which dissolves easily in acids ; the anhydrous oxide is insoluble in acids.

The *carbonate* is precipitated by potassium or ammonium carbonate; it is soluble in excess of the reagent if the latter is concentrated (it is redeposited on heating.)

Potassium double sulphate, $K_4Th(SO_4)_4$.—Obtained by the action of a concentrated neutral solution of potassium sulphate. The precipitation is slow, but complete; the precipitate does not dissolve in mineral acids.

The *oxalate*, $Th(C_2O_4)_2$, is precipitated by oxalic acid. It is insoluble in oxalic acid or in mineral acids, but soluble in ammonium oxalate. It is soluble in ammonium acetate in presence of free acetic acid.

Thorium fluoride, ThF_4.—Hydrofluoric acid throws down a gelatinous precipitate, which later becomes crystalline. Thorium forms the insoluble potassium double salt, K_2ThF_6.

Sodium thiosulphate does not completely precipitate the solution of thorium salts.

Analysis of thorite (silicate of thorium). The silicate is decomposed with hydrochloric acid, and evaporated to dryness (separation of silica). The mass is treated with dilute sulphuric acid, strongly evaporated, and precipitated with a concentrated solution (saturated at the boiling-point) of potassium sulphate. The precipitate is washed with the same solution, dissolved in water, and the thorium hydroxide precipitated by potassium hydroxide and weighed.

ZIRCONIUM

Zirconium occurs chiefly in the mineral zircon (zirconium silicate). It has only one oxide, ZrO_2. The metal is analogous in its properties to silicon and titanium. Zirconium oxide forms salts with acids. The sulphate is difficultly soluble; zirconium chloride, $ZrCl_4$, is volatile; the fluoride is soluble in water (distinction from thorium) and forms with potassium fluoride a salt, K_2ZrF_6, which dissolves in water with difficulty. On the other hand, if zirconium oxide be fused with sodium carbonate, it drives out the carbonic acid, and forms a sodium zirconate only slightly soluble in water. This salt varies in its composition; the simplest form, Na_4ZrO_4, is obtained by the action of an excess of sodium carbonate.

Reactions of zirconium salts.—Zirconium hydroxide is precipitated by caustic alkalies, ammonia, and ammonium sulphide. It does not dissolve in excess of potassium hydroxide (distinction from aluminium and beryllium) or on being boiled with ammonium chloride. The hydroxide precipitated in the cold is easily soluble in acids; that obtained from a boiling solution, and also the ignited oxide, dissolve in acids with great difficulty (to bring them into solution, 2 parts of concentrated sulphuric acid and 1 part water is used).

The *carbonate* is characterised by its solubility in ammonium carbonate; it is redeposited from this solution by boiling.

The potassium double sulphate, $K_4Zr(SO_4)_4$, is obtained by the action of neutral potassium sulphate; it is insoluble in excess of the reagent, but dissolves in hydrochloric acid (distinction from Th, Ce; the salt precipitated from hot solution is also insoluble in hydrochloric acid).

The *oxalate* is precipitated by oxalic acid; it is insoluble in excess of oxalic acid, but soluble in hydrochloric acid, and also in ammonium oxalate (distinction from thorium).

Sodium thiosulphate produces a precipitate in zirconium salts.

Analysis of zircon.—The zircon, previously ignited, is fused with sodium carbonate, and the cake obtained digested with water, which leaves the zirconium and sodium compound (and silica) undissolved. The residue is next dissolved by hydrochloric acid (silica is insoluble and thus separated), and zirconium hydroxide precipitated from the solution and weighed. Zirconium oxide may be separated from ferric oxide by either oxalic acid or sodium thiosulphate.

TITANIUM, NIOBIUM, TANTALUM

§ **55.** Titanium, niobium, and tantalum differ in many respects from the metals just described. The higher oxides of these metals are acids. To bring their compounds into solution, they are fused with sodium or potassium carbonate, and the alkali salts of titanic, niobic, or tantalic acid formed. Another method of analysis is based upon the property which these elements possess of uniting with potassium fluoride, to form soluble double salts, when fused with acid potassium fluoride. They cannot be brought into solution by fusion with acid potassium sulphate (with the exception of titanium).

Titanium occurs in nature as titanic acid (rutile, anatase) and its salts (titanite). Titaniferous iron, $FeTiO_3$, is isomorphous with chrome-iron ore. Titanium is almost the only metal known which absorbs nitrogen on being ignited in the air. It has two oxides, Ti_2O_3 and TiO_2. Titanic chloride, $TiCl_4$, is a liquid with a boiling-point of 136° C., and dissolves in water if the latter be cautiously added, but soon decomposes to titanic acid. Rammelsberg assumes the existence of two hydrates of titanic acid, which are similar to those of stannic acid. The first is formed from titanic chloride, the second by precipitating the fusion product of titanic acid with acid sodium sulphate by ammonia.

Reactions of titanic salts.—Titanium dioxide forms compounds with both bases and acids; neither series of compounds, however, is stable. When fused with potassium carbonate a potassium titanate is formed, insoluble in water, but soluble in acids (with decomposition). The salts of titanium dioxide with other acids (such as sulphuric, etc.) are obtained in solution by this means. The same salts may be prepared by the solution of titanic acid in acids, or by the fusion of the anhydrous oxide with acid potassium sulphate. The solutions of these salts are stable only in the cold, and on being warmed (still more when boiled) the titanic acid (metatitanic acid) is completely deposited. This variety of the hydroxide is insoluble in acids. All the modifications, however, as well as anhydrous titanic dioxide, dissolve in hydrofluoric acid. On fusion with acid potassium fluoride the sparingly soluble (1 part to 96 parts H_2O) double salt, K_2TiF_6, is formed. We shall now study the reactions of the solution of titanium dioxide in acids.

Potassium hydroxide, ammonia, ammonium sulphide, barium carbonate precipitate white, gelatinous titanic acid, which is insoluble in excess of the reagent. Tartaric acid hinders the precipitation. Metatitanic hydroxide is deposited from the acid solution on boiling (and also in presence of sodium thiosulphate).

Sodium phosphate throws down from a solution of titanium chloride a white precipitate of titanium phosphate, $(TiO)HPO_4$, insoluble in hydrochloric acid.

Hydrogen peroxide colours a solution of titanium dioxide yellow or orange-red, according to the quantity of the latter present. Delicate reaction for titanium.

Zinc (or tin) causes in an acid solution of titanium dioxide, even in the presence of hydrofluoric acid (distinction from niobium), the appearance of a violet or blue colour (formation of Ti_2O_3). The blue solution gives with alkalies a blue precipitate (titanous hydroxide ?) The reduction of titanic acid by zinc and the reverse, the oxidation of titanous oxide to titanic acid by potassium permanganate, can be employed in the quantitative estimation of titanium in presence of zirconium.

Analysis of rutile, titaniferous iron, etc.—The mineral is fused with six parts by weight of acid potassium sulphate. The mixture is at first very cautiously ignited, more strongly toward the end of the operation (after it has ceased to effervesce). The residue is digested with cold water and the metatitanic acid precipitated by boiling (in presence of sodium thiosulphate or acetic acid, for the separation from iron). The titanic acid is ignited and weighed. The separation from silica (for instance in titanite) is best effected by treatment with hydrofluoric acid (estimation of the silica by difference ; Section II. Silicon).

Tantalum.—Tantalum is found (together with niobium) in the rare minerals, columbite, tantalite (tantalum and niobium silicates). It forms with oxygen only one oxide, tantalic pentoxide (not reducible by hydrogen); tantalum chloride melts at 213° C., and boils at 242° C. ; it is completely decomposed by water.

Reactions of tantalic oxide.—Tantalum pentoxide unites with both acids and bases. On fusion with caustic soda, the sodium salt, $NaTaO_3$, is formed, which is insoluble in the alkali, but dissolves as soon as the solution is freed from the latter. The hydrated tantalic acid, TaH_3O_4, does not dissolve in hydrochloric or sulphuric acid, but readily in hydrofluoric acid. This solution forms with potassium fluoride the double salt, K_2TaF_7, which is sparingly soluble in water (in 200 parts), especially when free hydrofluoric acid is present. The anhydrous tantalic oxide may be dissolved by fusion with the acid fluoride or acid sulphate of potassium ; in the latter case it is left as an insoluble sulphate, from which the pure oxide may be obtained by ignition in an atmosphere of ammonium carbonate. If sodium tantalate be decomposed by hydrochloric acid, the precipitate which forms is white and soluble in excess of the acid (sulphuric and other acids produce a hydroxide insoluble in excess). This solution shows the following reactions : ammonia and ammonium sulphide throw down either tantalic acid, TaH_3O_4, or ammonium tantalate ; tartaric acid prevents the precipitation. Zinc has no reducing action in acid solutions (a faint blue colour is obtained, but quickly disappears) ; this distinguishes tantalum from niobium and titanium.

Niobium occurs, together with tantalum, in columbite, samarskite, eschinite, etc. It forms several oxides; the highest is the pentoxide, Nb_2O_5, or niobic acid (it is reduced by hydrogen to the black niobic dioxide, NbO_2). Niobium pentachloride, $NbCl_5$, boils at 240° C. (fuses at 194° C.) The oxychloride, $NbOCl_3$, is also known.

Reactions of niobic pentoxide.—Niobic acid combines, like the foregoing metals, with either bases or acids. When fused with alkali carbonates it forms salts (the alkali salts are insoluble in a solution of potassium hydroxide). Sulphuric or hydrochloric acids produces a precipitate of niobic acid, soluble in a great excess of the reagent employed. If anhydrous niobic pentoxide or the minerals be fused with acid sodium sulphate and the mass extracted with water, the niobium is left undissolved (as sulphate ?) By fusion with acid potassium fluoride an easily soluble (in 12 parts water) double salt, K_2NbF_7, is formed. Reduction of niobic acid by zinc in acid solution causes a blue coloration, which afterwards becomes brown.

Analysis of columbite and tantalite.—The mineral is fused with acid potassium sulphate until it has completely passed into solution in the latter. The mass obtained is then subjected to prolonged boiling with water, whereupon niobic acid remains as a precipitate (usually containing small quantities of iron and, sometimes, of tin and tungstic acid). It is purified by digestion upon the filter with ammonium sulphite (stannic oxide and tungstic acid are dissolved, iron is converted to ferrous sulphide). After washing with water, the precipitate, still on the filter, is treated with very dilute hydrochloric acid (to dissolve the ferric sulphide). The niobic oxide is ignited with ammonium carbonate before weighing. No method for the quantitative separation of niobium from tantalum is known. An approximate separation is attained, according to Marignac, by solution in hydrofluoric acid, addition of potassium fluoride, and crystallisation of the double fluorides. Marignac recommends, as the best method of analysing these minerals, their fusion with acid potassium fluoride, and extraction with water and hydrofluoric acid. Another method of approximately separating niobium from titanium, which was also proposed by Marignac, consists in fusing the (impure) niobium pentoxide with a known quantity of sodium carbonate. Niobium and tantalum form easily soluble sodium salts, but titanic acid enters with difficulty into combination. After treatment of the mass with water, the greater part of the titanic oxide (with a little tantalic and niobic acids) is found in the residue. The reduction of the titanium dioxide by zinc (after conversion to the fluoride, lest niobic acid be reduced), and subsequent titration with potassium permanganate, affords a method of separation which, though only approximate, is nevertheless better than the foregoing.

URANIUM, INDIUM, GALLIUM, THALLIUM

§ **56.** Ammonium sulphide precipitates sulphides from the solutions of these metals. They show in this reaction an analogy to iron, the reagent throwing down the lower sulphides, Tl_2S, InS, UO_2S, which are easily soluble in acids. The compounds of the higher oxides, Tl_2O_3, In_2O_3, are reduced by the reaction (like the ferric compounds). The higher sulphides, Tl_2S_3 and In_2S_3, are decomposed by water. The salts of indium and uranium consist almost exclusively of those of the oxides In_2O_3 and UO_3. Thallium forms not only the thallic salts of the oxide Tl_2O_3, but also stable thallious compounds of Tl_2O.

Uranium occurs in nature chiefly in the mineral pitch blende. It unites with oxygen in several proportions, of which the principal compounds are: uranous oxide, UO_2, uranic oxide, UO_3, and the urano-uranic oxide, U_3O_8. Both uranous and uranic oxides enter into combination with acids to form salts. Those of the former are converted by the action of oxygen, chlorine, etc. to uranic compounds. The uranic compounds contain the uranium bound as part of a radical, UO_2, or "Uranyl" (see Bismuth): the hydroxide, for example, is $UO_2(OH)_2$, the sulphate, UO_2SO_4. In addition to these, many double salts are known. Uranic salts are converted to the uranous state by reduction. The hydroxide also combines with metallic hydroxides to form uranates; an example is seen in potassium uranate, $K_2U_2O_7$.

Reactions of uranous salts.—Alkalies and ammonia produce a voluminous bright green precipitate of uranous hydroxide, which is gradually changed to black by the action of the air.

Sodium bicarbonate throws down a bright green precipitate, which becomes dark when heated, and is soluble in an excess of the reagent.

Potassium ferrocyanide gives a precipitate which changes to brownish red on oxidation.

Ammonium sulphide produces a bright green precipitate, quickly turning dark brown. Tartaric acid hinders the reaction.

Barium carbonate causes complete precipitation. *Tartaric acid* prevents all the above reactions.

Reactions of uranic salts.—*Uranium oxysulphide*, $UO_2S + H_2O$, is obtained by the action of ammonium sulphide; dark brown precipitate, somewhat soluble in excess of the reagent (if the latter contain ammonium carbonate). Uranium oxide is precipitated when this solution is boiled. Hydrogen sulphide does not produce a precipitate.

Uranates.—Caustic alkalies and ammonia give yellow precipitates of $K_2U_2O_7$ and $(NH_4)_2U_2O_7$, insoluble in excess.

Carbonate.—Potassium carbonate and bicarbonate precipitate the yellow double-carbonate, $UO_2K_4(CO_3)_3$; this salt is soluble in excess of the reagent, and also in sodium and ammonium carbonates. Caustic potash, added to such a solution, throws down uranyl hydroxide $UO_2(OH)_2$.

Barium carbonate completely precipitates uranic salts in the cold.

Uranyl phosphate, $(UO_2)_3(PO_4)_2$, and the *uranium-ammonium salt*, $(UO_2)(NH_4)PO_4$.—When a uranium salt is precipitated by an acid or neutral phosphate in presence of sodium or ammonium acetate, the yellowish white salt, uranium ammonium phosphate, is obtained. (It is used in the volumetric estimation of phosphoric acid.)

Uranium ferrocyanide.—Potassium ferrocyanide produces an almost black precipitate. The reaction is very delicate.

Uranium salts show a characteristic behaviour with microcosmic salt or borax. In the oxidation flame they give a yellow bead which becomes yellowish green on cooling: in the reduction flame the bead is green.

Preparation of uranium compounds from pitch-blende (U_3O_8 mixed with several other metals).—The mineral is decomposed by sulphuric acid and digested with water (SiO_2, $PbSO_4$, $BiOSO_4$, $BiAsO_4$, remain undissolved). The metals of Groups IV. and V. are next precipitated from the solution by sulphuretted hydrogen. After filtration and oxidation with nitric acid, an excess of ammonia is added (Ni, Co, In, Mg, remain in solution); ferric hydroxide and ammonium uranate, $(NH_4)_2U_2O_7$, are precipitated (together with certain other metals). The separation of the uranium from iron is effected by warming with ammonium carbonate. The double salt, uranyl-ammonium carbonate, crystallises from the solution.

Indium is a very rare companion of zinc, its chief source being in the zinc blende of Freiburg. The metal is gray, sp. gr. 7·3, soft, and unaltered by air or water; it is easily fusible (melting-point 176°), and dissolves readily in acids with evolution of hydrogen. Only one series of indium salts is known, these corresponding to the oxide, In_2O_3. The (volatile) indium salts colour the flame blue, and the spectrum of this flame contains two brilliant blue lines (Section III.) Investigation with the spectroscope is the best method of detecting indium, as with the exception of this characteristic its salts possess great similarity to those of iron and aluminium.

Reactions of indium salts. Indium hydroxide.—Caustic alkalies precipitate the white, gelatinous hydroxide (precipitation hindered by organic acids), soluble in excess, but again deposited if the solution be warmed or allowed to stand. The hydroxide dissolves in acids easily, the anhydrous oxide with difficulty. It yields the metal on ignition in hydrogen.

The carbonate.—Alkali carbonates produce a white, gelatinous precipitate of the carbonate, soluble in excess of ammonium carbonate (redeposited on boiling). Barium carbonate precipitates indium hydroxide in the cold.

The *basic acetate* and *basic succinate* are analogous to the corresponding iron salts, and obtained in the same manner.

Indium sulphide.—Hydrogen sulphide precipitates neutral or acetic acid solutions of indium salts in the cold, yellow indium sulphide, In_2S_3, being formed. Ammonium sulphide throws down a white precipitate which is soluble in hot ammonium sulphide, but again deposited on cooling.

Zinc precipitates metallic indium.

Preparation of indium compounds.—The Freiburg zinc is dissolved in hydrochloric acid, and the solution, after being acidified with nitric acid, precipitated by hydrogen sulphide (separation of the metals of Group IV.) An impure indium hydroxide is obtained by precipitation of this solution with ammonia. This is dissolved in sulphuric acid and the metallic indium precipitated by zinc.

Gallium is extremely rare. It was discovered in the zinc blende of Pierrefitte and Bensberg. The metal is gray, and fuses at 30° C. The salts of gallium oxide, Ga_2O_3, are white; the sulphate forms an alum with the alkali sulphates. Alkalies produce in the solutions of gallium salts a white, gelatinous precipitate of the hydroxide, soluble in excess; barium carbonate throws down the hydroxide in the cold. The reaction with potassium ferrocyanide is very delicate; this reagent causes a precipitate (usually coloured by ferric ferrocyanide) which is insoluble in hydrochloric acid. The spectrum of gallium salts (spark-spectrum) consists of two violet lines, and forms the principal characteristic of the metal.

Thallium.—Thallium occurs in several pyrites. It was discovered in the sulphuric acid dust which settles in the chambers in the manufacture of sulphuric acid from pyrites. Thallium has two oxides, thallious oxide, Tl_2O, and thallic oxide, Tl_2O_3. In its thallious compounds thallium shows a great similarity to the alkali metals. Thallious oxide (hydroxide, $TlOH$) is soluble in water and alcohol, and absorbs carbonic acid from the air; the carbonate is also somewhat soluble in water. Alkalies and alkali carbonates, therefore, do not precipitate thallious salts. Nitric acid effects no change in thallious solutions, but when boiled with *aqua regia* they are converted to the thallic state. The brilliant green coloration of the flame is the most important characteristic of thallium. Its spectrum is remarkable for its simplicity, containing only one brilliant emerald-green line (Section III.)

Reactions of thallious salts. Thallious sulphide, Tl_2S.—Sulphuretted hydrogen precipitates thallium sulphide only from the acetate. (When arsenic is present, thallium is precipitated from its salts with other acids together with the arsenic.) Ammonium sulphide throws down the black monosulphide, Tl_2S, which quickly oxidises to the sulphate when exposed to the air, and is readily soluble in acids.

Thallious chloride and iodide are especially characteristic bodies. Both are insoluble in water, and are precipitated, the one by hydrochloric acid, the other by potassium iodide. Thallious chloride is white, the iodide yellow. The chloride forms a platinichloride, $PtTl_2Cl_6$. Zinc precipitates metallic thallium from its solutions.

The thallic compounds have been very slightly studied. The oxide, Tl_2O_3, is violet (its hydroxide brown), insoluble in water, and reduced to thallious oxide on ignition. It is difficultly soluble in sulphuric, but dissolves in hydrochloric acid. This solution, however, parts with its chlorine on warming, and thallious chloride is formed. Potassium iodide reduces thallic compounds with separation of free iodine. Sodium acetate completely precipitates thallic hydroxide from boiling solutions.

Preparation of thallium compounds.—The dust from the sulphuric acid chambers is repeatedly boiled with water and sulphuric acid, and thallium chloride precipitated by hydrochloric acid from the solution thus obtained. The precipitated chloride is evaporated to dryness with sulphuric acid and metallic thallium precipitated from the solution of the sulphate by zinc.

GROUP IV

SILVER, MERCURY, COPPER, CADMIUM, LEAD, BISMUTH (PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM)

This group of metals is characterised as follows:—(1) The salts of these metals are precipitated from acid solutions by hydrogen sulphide, *i.e.*, their sulphides are insoluble in dilute acids. (2) The sulphides are insoluble in ammonium sulphide.

The reactions of these metals cannot be studied according to the system hitherto followed. The different metals differ widely in their properties, and their most marked characteristics are such that an attempt to group them into divisions would be fruitless. The indistinctness of a classification of this kind can be seen by comparing the methods of separation, and therefore the chemical characteristics of the different metals, which are employed in both qualitative and quantitative work. (1) Silver, mercury in mercurous compounds, and, to certain extent, lead and copper, may be grouped together on the ground of the insolubility of their chlorides. (2) Silver, copper, mercury, and cadmium, could form a division characterised by the solubility of the cyanides in potassium cyanide. (3) Silver, copper, and cadmium are distinguished by their power of forming soluble double compounds with ammonium salts and ammonia. (4) Mercury differs from all the other metals in the insolubility of its sulphide in nitric acid. (5) Lead and mercurous mercury are characterised by the insolubility of their sulphates in water, and (6) Bismuth, by the formation of insoluble basic salts when its solutions are acted upon by water. Following these properties, we should most fittingly place silver, mercury, copper, and cadmium in one division, partly because of their behaviour toward potassium cyanide, partly because they form soluble ammonium compounds, and, finally, because their chlorides are insoluble. The second division, composed of mercury and lead, would be negatively characterised by the non-formation of soluble cyanides. A complete classification of this kind would have no value, for, as has been said, the divisions could not be sharply sustained in all the reactions. The metals of Group IV. can therefore be more conveniently considered together, without being subjected to classification. We now turn to the study of the above characteristic reactions of this group.

GENERAL REACTIONS

§ 57. **Sulphides.**—These metals do not all form sulphides corresponding to each of their degrees of oxidation; for instance, Hg_2S, the analogue of mercurous oxide, is unknown (when acted upon by hydrogen sulphide mercurous salts deposit metallic mercury and mercuric sulphide).[1] Cupric sulphide, CuS, is also unknown, but hydrogen sulphide precipitates from cupric solutions the compound, $Cu_4S_3 = 2CuS . Cu_2S$, which, on ignition, is converted to cuprous sulphide, Cu_2S. The sulphides form black, amorphous precipitates; cadmium sulphide, which

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[1] In pursuing the study of the compounds of this group of metals the student will often find that not only in the sulphides, but in many other salts as well, the compound corresponding to one of the degrees of oxidation is wanting.

is yellow, is an exception to this rule, and its formation is a good qualitative indication of cadmium salts. These compounds are almost all stable in the air (distinction from the hydrated sulphides of Group III.); lead sulphide and, still more, copper sulphide, however, absorb oxygen on exposure.

A. *The formation of the sulphides* is almost exclusively effected by precipitating the solutions with hydrogen sulphide or ammonia sulphide; more rarely with sodium thiosulphate.

Precipitation by hydrogen sulphide is a reaction which is very important in separating the metals of this group from the preceding ones. Complete precipitation requires the observance of many conditions; it is dependent not only upon the concentration of the solution, but also, in part, upon the character of the acid present. The sulphides are soluble in concentrated acids, and the precipitation with hydrogen sulphide must, therefore, be effected only in the presence of very dilute acid (*i.e.*, strongly acid solutions must be diluted with water).[1] On the other hand (in the separation from Group III.) a great excess of weak acid must be present, to prevent precipitation of the sulphides of Group III., especially that of zinc. Hydrochloric acid is the best acidifying agent, and only in cases where its use is impossible (*e.g.*, when chlorides would be precipitated) should nitric acid be employed (also in very dilute solution). A current of hydrogen sulphide is led into the acidified solution, and the flow of gas so regulated that the bubbles passing through the liquid can barely be counted. Some of the metals, when acted upon by hydrogen sulphide, form very complicated compounds. Lead and mercury solutions (in presence of hydrochloric acid) throw down at first the double compounds, $PbCl_2 . PbS$ and $Hg(NO_3)_2 . HgS$, respectively. Further action of the hydrogen sulphide completely converts these to the sulphides. The precipitation by hydrogen sulphide must be very thorough, not only on this ground, but also because the different metals are thrown down from solution one after another. The flow of hydrogen sulphide is interrupted as soon as the liquid smells strongly of the gas when shaken. As this reaction with sulphuretted hydrogen is used in

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[1] Dilution with water may precipitate insoluble basic bismuth salts, but these do not interfere with the reaction with H_2S.

separations, it must be carefully studied, so that the student may be in position to make exact separations by its means. The question as to whether the precipitation is complete is best decided by testing the filtrate from the sulphides with hydrogen sulphide water; non-precipitation might be caused either by over-acidity of the solution or an insufficient quantity of hydrogen sulphide. Operations with this gas must be performed as cautiously as possible. Its careless use may easily cause unconsciousness, which is usually preceded by the sense of smell being deadened to hydrogen sulphide.

The sulphides obtained are filtered off and washed. In washing with pure water, certain sulphides, as soon as all soluble salts are removed, may pass into solution in the colloidal state (*e.g.*, copper sulphide), and the filtrate then assumes a dark colour. The addition of hydrogen sulphide, acetic acid, or ammonia to the wash water prevents this drawback. The further treatment of the sulphides will be explained below.

The action of ammonium sulphide upon the metals of this group will be observed only in connection with its use in the separation of these metals from Group V. Ammonium sulphide precipitates the sulphides completely; copper sulphide is slightly soluble in the reagent, and thus when traces of copper are present with metals of Group V., treatment with ammonium sulphide may easily bring the copper into solution with these metals (§ 78).

Action of sodium thiosulphate.—The addition of sodium thiosulphate to hot solutions of the metals of Group IV., acidified by hydrochloric acid, precipitates the sulphides of all the metals of this group except lead and cadmium. As still better methods of separating the other metals are known, the reaction is employed only for the separation of copper from cadmium. For this purpose sodium thiosulphate is added to the solution, slightly acidified with hydrochloric acid, until the blue colour of the dissolved copper salt vanishes. This disappearance in colour is due to the reduction of the cupric salt, the cuprous salt, $KCuS_2O_3$, being formed. (The formula of the potassium salt is here given, as the sodium salt is of a much more complicated composition.) The colourless solution is then boiled until the black copper sulphide has completely separated out. (For the purpose of simplifying the equation, the formula of copper sulphide is represented as CuS.)

$$2KCuS_2O_3 = 2CuS + K_2SO_4 + SO_2.$$

All the cadmium remains in solution; its detection will be explained later.

B. *Behaviour of the sulphides toward nitric acid.*—This reaction is employed in separating mercury from the other metals of the group. All the sulphides except that of mercury dissolve in boiling nitric acid, with formation of nitrates and evolution of hydrogen sulphide:

$$Ag_2S + 2HNO_3 = 2AgNO_3 + H_2S.$$

Lead sulphide becomes partly oxidised to the sulphate. Mercuric sulphide is practically insoluble in hot concentrated nitric acid. The experiment is made in a small flask. When the reaction is finished water is added, and, after the solution has cooled, the mercuric sulphide is filtered off. It is to be remembered that as metallic mercury is deposited from mercurous solution by sulphuretted hydrogen, the separation of mercury from other metals by this method can be employed only after the precipitate has been wholly converted to the sulphide (by treatment with ammonium polysulphide, § 61); or, if the case occurs in the systematic course of analysis, after the mercurous salt has been removed by other means (§ 58). The filtered mercuric sulphide is next dissolved in *aqua regia*, and the mercuric chloride, $HgCl_2$, which is obtained, subjected to confirmatory tests. The remaining metals of Group IV. are found in the filtrate of the mercuric sulphide.

This nitric acid reaction is not actually so simple as the above indicates. The complications to which attention must be paid in qualitative analysis result from the fact that nitric acid not only causes the above reaction, but may also oxidise the reaction products. The sulphuretted hydrogen becomes oxidised, and sulphur separates out:

$$3H_2S + 2NHO_3 = 2NO + 3S + 4H_2O.$$

Under these conditions the sulphur cannot be oxidised to sulphuric acid, and upon the solution of the sulphides, therefore, a residue always remains; this may easily be mistaken for mercuric sulphide, since the sulphur (which is not deposited in the crystalline state, but as an amorphous mass) encloses, in separating, small quantities of the sulphides and is often coloured almost black by them. Lead sulphide may also be oxidised to the insoluble (white) lead sulphate, $PbSO_4$; and finally, a part of the mercury may be left as the insoluble white compound, $Hg(NO_3)_2 2HgS$. When, therefore, an insoluble residue is obtained by the action of nitric acid upon sulphides, conclusions as to its composition can be formed only from confirmatory tests, and not from the colour. The confirmatory tests to be employed will be explained in the proper paragraph. The mercuric sulphide, if the residue is composed wholly of this salt, is dissolved in *aqua regia* and recognised by the subsequent reactions of mercury (§ 62); if there is little mercury present (the residue small), by ignition of the dried precipitate with anhydrous sodium carbonate, according to § 61. If the precipitate consists entirely of sulphur, it burns when heated (in a porcelain crucible), without leaving a residue.

§ 58. **Chlorides.**—The solubility of the chlorides varies greatly in the different metals of this group. The chlorides of silver and mercurous mercury are absolutely insoluble in water, lead and cuprous chlorides only slightly soluble.[1] The other chlorides dissolve readily in water. We shall here observe only the insoluble salts, their formation being the basis of the separation of silver, mercurous mercury, and, to a certain extent, of lead, from the other metals of the group. In the course of analysis, the precipitation of these chlorides precedes (for the reason explained in § 57 B) the use of hydrogen sulphide. Silver chloride is a white, curd-like precipitate, which coagulates when shaken (and on exposure to the light becomes violet). Mercurous chloride and lead chloride are white, crystalline powders. We shall discuss their individual properties later (§§ 60 and 61), and here observe only the conditions of their formation and the reactions by which they are distinguished.

The conditions of formation.—These chlorides are formed chiefly by the precipitation of silver, mercurous, and lead salts with hydrochloric acid (more rarely with soluble chlorides). The precipitation must be made under the following conditions: —As concentrated hydrochloric acid dissolves silver and mercurous chlorides to a certain degree, only the dilute acid must be used in the reaction, but it must not be diluted with water

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[1] Lead belongs to the Fourth Group of the periodic system of elements and, like tin, should form the tetrachloride, $PbCl_4$. This compound has recently been prepared by the action of chlorine on lead chloride, $PbCl_2$. In aqueous solutions, the tetrachloride is unstable and splits up into lead dichloride and chlorine. This behaviour prevents the presence of the tetrachloride in the course of usual qualitative analysis.

to such an extent as to precipitate the bismuth basic salts. The completeness of the reaction must be ascertained by confirmatory tests. The precipitate is washed with cold water and subjected to the following tests:—

The behaviour of these chlorides to water and ammonia is employed in qualitative tests for the metals which they contain. Lead chloride, if present with the other chlorides, is detected by boiling with water. This salt is fairly soluble in boiling water (less so in the presence of free hydrochloric acid). The lead is completely dissolved after being boiled for some time with fresh water, and may readily be found in the filtered solution (by sulphuric acid or hydrogen sulphide, § 66); for this test the first part of the filtrate should be used, or, if the small amount of lead renders such a course necessary, the solution may be concentrated by evaporation.

To separate the silver chloride from that of mercury, the precipitate is digested *on the filter* with small quantities of ammonia, until the filtrate, after acidulation with nitric acid, deposits no more silver chloride. If mercurous compounds were present they remain on the filter as a black residue (see below). The separation is inexact, and the residue may contain either a part or even all of the silver chloride, according to the prevailing conditions: on protracted digestion with an excess of ammonia, the whole of the silver will be retained. If the filtrate shows no trace of silver, the black residue must be treated with concentrated nitric acid and the silver detected by precipitating its chloride from this solution.

The theory of this reaction is as follows: ammonia instantly converts mercurous chloride to the *mercuric* compound, $NHg_2Cl . NH_4Cl$, with separation of metallic mercury:

$$4HgCl + 4NH_3 = NHg_2Cl . NH_4Cl + Hg_2 + 2NH_4Cl.$$

The free mercury displaces the silver from its chloride:

$$Hg + AgCl = HgCl + Ag.$$

In the treatment of the chlorides upon the filter about 1·5 per cent of the silver is left undissolved; if the two metals are present in equivalent quantities, however, prolonged action of ammonia converts the silver chloride completely to metallic silver, and the white precipitate becomes black or grayish black:

$$2HgCl + 2AgCl + 4NH_3 = NHg_2Cl . NH_4Cl + 2Ag + 2NH_4Cl.$$

§ **59.** A. **Cyanides and Potassium Double Cyanides.**—Cyanides corresponding to all the various degrees of oxidation of the metals of this group do not exist; those derived from mercurous or cupric oxides being unknown. Of all the cyanides of the metals of Group IV. the mercuric salt is the only one soluble in water: the others form insoluble white precipitates. Only the cyanides which are the most important, analytically, can be here considered, viz., those which dissolve in potassium cyanide with formation of double salts. To this class belong the cyanides of silver, copper, cadmium, and mercury; lead and bismuth cyanides form no double compounds with potassium cyanide, and are insoluble in that reagent. The cyanides of silver, copper, and cadmium are white precipitates which are thrown down from the solutions of these metals by potassium cyanide. *The double salts* with potassium cyanide are formed by dissolving cyanides, oxides, carbonates, chlorides, and, in the case of copper (characteristic of this metal), cupric sulphide, in potassium cyanide. The soluble double salts thus formed have the composition: $3KCy.CuCy$, $2KCy.CdCy_2$, $KCy.AgCy$, $2KCy.HgCy_2$, respectively.

In qualitative analysis (and also in quantitative), the solubility of copper sulphide in potassium cyanide is employed in separating this metal from cadmium. The salts of the two metals are precipitated by potassium cyanide, and the precipitate redissolved in an excess of the reagent. If hydrogen sulphide be now passed through the solution, yellow cadmium sulphide will be deposited, while copper remains in solution; the latter can be detected by decomposition of the cyanides with concentrated sulphuric acid (§ 97). The difficulties which this method involves, however, render the separation of copper from cadmium by means of sodium thiosulphate more suitable.

B. **Ammonia Double Compounds.**—The metals of Group IV. may be divided into two classes, according to their ability of forming ammonia double compounds. Mercury, silver, copper, and cadmium form compounds of this nature; lead and bismuth do not. The compounds of mercury are insoluble; those of the other metals, silver, copper, and cadmium, are soluble. These salts are formed by the action of ammonia upon the solutions of the metals; and their composition varies between wide limits. Either true double salts of these metals with ammonium salts, such as $(NH_4)_2SO_4 . CuSO_4 + 6H_2O$, $(NH_4)_2SO_4 . CdSO_4 + 6H_2O$, may be formed, or, when the solution is neutral, the ammonia can unite directly with the metallic salts to form the so-called metallo-amines, *e.g.*, $CuSO_4 . 4NH_3 + H_2O$, $AgNO_3 . 2NH_3$. The compounds of silver and mercury are considered under the special reactions of these metals. Those of copper and cadmium may be mentioned here, as they are used in the separation of these metals (§ 68).

The formation of ammonia-compounds.—Copper differs from cadmium in the manner in which it forms these compounds. The copper compounds result from the action of either ammonia or ammonium carbonate; those of cadmium are formed through the action of ammonia alone. The copper ammonia-compounds possess a dark blue colour (a blue coloration caused by the action of ammonia is an indication of copper); the cadmium compounds are colourless. The reactions are used in analysis as follows:—The copper and cadmium solutions are mixed with ammonia, the latter being in great enough excess to dissolve the precipitate at first formed. Potassium cyanide is then added until the solution loses its colour (formation of double cyanides), and the separation of the two metals effected by the precipitation of the cadmium as cadmium sulphide with sulphuretted hydrogen (see first part of this paragraph). The difference in the behaviour of cadmium and copper salts toward ammonium carbonate is not made use of in analysis, as it is inexact.

Sulphates.—The insolubility of the sulphates is especially characteristic of lead; mercurous sulphate, which is only slightly soluble in water, is, in a measure, also important. The other metals form readily soluble sulphates. Lead can be easily separated from the remaining metals as its sulphate; the properties of this compound will be described under Lead.

The formation of insoluble basic salts by the action of water distinguishes bismuth from all the remaining metals of this group, and affords a means of separating bismuth from them; it is described under Bismuth.

SPECIAL REACTIONS

Silver

§ 60. Silver is white, of sp. gr. 10·57, fuses at 954° C., and distils at the heat of the oxyhydrogen flame (the vapour is violet). It dissolves in acids without evolution of hydrogen, the excess of acid, however, decomposing, *e.g.*, nitric oxide is generated from nitric, sulphurous anhydride from sulphuric acid:

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O,$$
$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

In coins, and also in jewelry, silver is alloyed with copper.

Reduction of silver from its salts by the wet way.—Silver salts are characterised chiefly by the ease with which metallic silver is separated from their solutions. Silver is deposited from the solutions of a majority of its salts by the action of light, and even crystallised and insoluble salts become violet from the metallic deposit when exposed to the light. The silver salts of readily oxidisable acids, such as the phosphite and sulphite, precipitate metallic silver in the experiments made for their preparation, the acids becoming oxidised to phosphoric or sulphuric acids:

$$Ag_2SO_3 + H_2O = 2Ag + H_2SO_4,$$
$$Ag_2HPO_3 + H_2O = 2Ag + H_3PO_4.$$

Potassium sulphite throws down from silver solutions a precipitate which is at first white, but quickly blackened by the silver deposited. Substances which are capable of conversion to a higher degree of oxidation, such as ferrous salts, likewise reduce silver from its compounds: ferrous sulphate readily throws down, from hot solutions, a gray precipitate of metallic silver, the iron salt being converted to ferric sulphate:

$$3AgNO_3 + 3FeSO_4 = 3Ag + Fe_2(SO_4)_3 + Fe(NO_3)_3.$$

If the reaction is effected in presence of citric acid under certain conditions, a pink solution of colloidal silver is obtained (Carey Lea).

Silver may also be reduced in alkaline solution, for instance by antimonious acid, which is itself converted in the reaction to antimonic acid (§ 76).

Ammonia-compounds.—The silver salts used in analyses, with the exception of a few, such as the iodide and sulphide, are readily soluble in ammonia. This is a marked characteristic of silver salts. The ammoniacal solution may contain, according to the conditions present, either ammonium double salts or the so-called metallo-amines. Ammonia produces no precipitate in acid solutions, since an ammonium double salt is immediately formed:

$$AgNO_3 + HNO_3 + NH_3 = AgNO_3 . NH_4(NO_3).$$

In neutral solutions a precipitate is at first caused, but this dissolves readily in an excess of ammonia, and a metallo-amine *e.g.*, $AgNO_3 . 2NH_3$, is obtained.

Reactions of Silver Salts.—*Silver chloride.*—Hydrochloric acid and soluble chlorides give with silver salts a white, amorphous precipitate of silver chloride. The precipitate becomes curdy on being shaken, and turns violet when allowed to stand under exposure to light. In very dilute solutions of silver salts hydrochloric acid causes at first only a turbidity, and the chloride is deposited gradually. In reactions in which this precipitate is to be obtained, only dilute hydrochloric acid can be employed, as the salt is somewhat soluble in an excess of hydrochloric acid; it is reprecipitated from such a solution, however, by the addition of water. The important characteristics of this salt which must be mentioned are its insolubility in dilute nitric acid and solubility in ammonia. Nitric acid reprecipitates the salt from its ammoniacal solution. The insolubility of silver chloride in water renders the separation of this metal from nearly all others possible. The application of this property in analysis is explained in § 58.

Silver chloride is the most important of all the silver compounds. As in the separation of silver all of the above characteristics can be observed in the course of the experiment, further confirmatory tests are unnecessary.

The silver compounds described below, while important, are seldom used for the detection of silver. They are expedient for that of the respective acids, however, and will be more fully considered under the latter head.

Silver bromide is thrown down by potassium bromide (or hydrobromic acid) as a pale yellow precipitate. It is insoluble in water or nitric acid, stable on exposure to the light, and difficultly soluble (less readily than silver chloride) in ammonia.

Silver iodide is thrown down by potassium iodide as a yellow precipitate; it is stable in the light and practically insoluble in nitric acid and ammonia.

Silver cyanide, AgCy, is a white precipitate obtained by the action of potassium cyanide. It is insoluble in nitric acid, but dissolves in ammonia and potassium cyanide with formation of a double salt (§ 59 A).

Silver chromate and *phosphate* are obtained by precipitation with potassium chromate or sodium phosphate. Silver chromate is red-brown, the phosphate pale yellow. Both salts are easily soluble in either ammonia or nitric acid (§§ 33 and 50).

The following compounds are less characteristic:—

Silver sulphide, Ag_2S (§ 57).—Ammonium sulphide and hydrogen sulphide precipitate black, amorphous silver sulphide, insoluble in ammonia and dilute acids (and also in ammonium sulphide, potassium sulphide, potassium cyanide), but readily soluble in nitric acid.

Silver oxide, Ag_2O (the hydroxide does not exist), is gray-brown, and obtained by the action of alkalies (in excess of which it is insoluble) and ammonia. An excess of the latter dissolves it, and produces no precipitate in acid solutions.

Silver carbonate, Ag_2CO_3, is thrown down as a white precipitate by sodium carbonate. It is insoluble in excess of the reagent, but dissolves in ammonia.

Mercury

§ 61. Mercury is distinguished from all other metals by its physical characteristics. It is a liquid at the ordinary temperature (solidifies at 39° C.), and is easily converted into vapour by heat (it has the boiling-point 360° C.) Though insoluble in hydrochloric, it is dissolved by nitric and sulphuric acids; the reaction is not accompanied by the evolution of hydrogen:

$$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO + 4H_2O,$$
$$Hg + 2SH_2O_4 = HgSO_4 + SO_2 + 2H_2O.$$

The solution in acids may result, according to the condition present, in the formation of either mercurous or mercuric salts. Mercury unites with many other metals to form the so-called amalgams. The amalgams of the alkali metals decompose water at the ordinary temperature; those of the other metals show toward acids the same behaviour as mercury itself.

The separation of mercury from its salts (both mercurous and mercuric) is a general reaction for all mercury compounds.

Although ignition decomposes the majority of the compounds, with volatilisation of the metal, reduction simply by ignition will not suffice, if the characteristic globular form of the fluid metal is to be examined as well as its volatility. Mercury may also be easily precipitated from its compounds and detected by wet methods.

1. If a mixture of a dry mercury salt and anhydrous sodium carbonate be heated in a glass tube sealed at one end, metallic mercury will separate, volatilise, and condense on the cold sides of the tube above the heated spot. When small quantities of mercury are present, a metallic mirror will be formed; greater amounts produce not only the mirror, but metallic globules. To make the experiment successfully, the substances must be thoroughly dried; the reaction is less plainly observed if performed with mercury compounds which volatilise without decomposition (mercuric chloride, etc.)

2. If a drop of the (neutral or slightly acid) solution of a mercury salt be poured upon a smooth piece of copper foil, a metallic spot is obtained (precipitation of mercury). If the foil be heated, the mercury will volatilise and the spot vanish. The following reaction is more important:—

3. Mercurous salts, when acted upon by an excess of stannous chloride, deposit a gray powder of metallic mercury:

$$2HgCl + SnCl_2 = SnCl_4 + 2Hg.$$

Mercuric solutions give, with stannous chloride in presence of hydrochloric acid (if the precipitant be in only a slight excess), a precipitate of mercurous chloride:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4.$$

The further addition of stannous chloride will then cause the separation of mercury, as above.

Mercurous salts.—Mercurous nitrate, $HgNO_3$, from which almost all mercurous compounds are obtainable, is prepared by the action of nitric acid upon an excess of metallic mercury in the cold. The methods of preparing mercurous salts which rest upon the reduction of mercuric compounds, are more rarely used. The mercurous salts, on the other hand, may be easily converted to the mercuric state. In this transition half of the mercurous salt becomes mercuric, the other half is reduced to metallic mercury; such a decomposition may be caused by the action of a high temperature, or even of boiling water. Certain compounds, such as mercurous oxide and iodide, undergo this change with extreme ease:

$$Hg_2O = HgO + Hg,$$
$$2HgI = HgI_2 + Hg.$$

When heated with nitric acid or subjected to the action of chlorine, the mercurous salts are converted to the higher compounds without the separation of metallic mercury.

$$2HgCl + Cl_2 = 2HgCl_2.$$

A few salts in the series of mercurous compounds, *e.g.*, the cyanide, HgCN, and sulphide, Hg_2S, are too unstable to exist. Efforts to prepare them result in the formation of the mercuric salts, $Hg(CN)_2$ and HgS, and separation of the metal. The existence of mercurous oxide is disputed.

Reactions of Mercurous Salts.—*Mercurous oxide* (the hydroxide is unknown).—Caustic alkalies produce a precipitate of mercurous oxide, or, perhaps, of a mixture of mercuric oxide and metallic mercury.

Metallo-amines.—Ammonia forms with mercurous salts (soluble and insoluble) insoluble amines which are remarkable for their black colour. The following equations explain the formation and constitution of these compounds:

$$2HgCl + 2NH_3 = (NH_2Hg_2)Cl + NH_4Cl,$$
$$2HgNO_3 + 2NH_3 = (NH_2Hg_2)NO_3 + (NH_4)NO_3.$$

These amines are extremely unstable. The first parts with its ammonia, even in the air, with reformation of mercurous chloride, and the second is very easily decomposed by an excess of ammonia, mercury being deposited and the mercuric salt obtained.

Mercurous chloride, HgCl.—Hydrochloric acid and soluble chlorides cause in mercurous solutions a white, crystalline precipitate of mercurous chloride. The compound is insoluble in water or dilute mineral acids. When boiled with nitric acid or *aqua regia* it is converted to mercuric chloride (goes into solution). Hydrochloric acid has the same action, but mercury separates during the operation. If mercurous chloride be digested with ammonia it turns black (see above). The use of this salt for the separation of mercurous mercury is explained in § 58. As most of the marked characteristics of the salt are employed in the separation, further confirmatory tests are superfluous.

Mercurous sulphide, Hg_2S, is unknown. Hydrogen sulphide throws down from mercurous solutions a black precipitate which contains a mixture of metallic mercury and mercuric sulphide.

As this precipitate is employed in qualitative tests for mercury, its characteristics must be more closely studied. When boiled with nitric acid it passes into a white compound which is insoluble in nitric acid, and has the composition $2HgS \cdot Hg(NO_3)_2$. The sulphide dissolves in *aqua regia*, with formation of mercuric chloride. Metallic mercury, if contained in the precipitate, is converted to the sulphide by the action of ammonium polysulphide, or the polysulphides of the alkalies (mercury unites directly with sulphur). If, during the analysis, mercurous compounds have been precipitated by hydrogen sulphide, mercurous mercury cannot be detected after treatment of the precipitate with ammonium sulphide (since the sulphide obtained is a mercuric salt). When mercurous solutions are acted upon by ammonium sulphide, the precipitate may or may not contain metallic mercury, this depending upon the excess of the reagent, and also upon its composition ; no metallic mercury is found when ammonium polysulphide is in excess, or the solution warmed during the experiment. The remaining properties of the precipitate, which are found in the characteristics of HgS, are explained under the mercuric salts. It follows from these remarks that in the systematic course of analysis mercurous compounds must be separated from solution before the precipitation with hydrogen sulphide. Otherwise the mercury will not be completely removed as mercuric sulphide (§ 57 B). Mercurous salts are separated by precipitation with hydrochloric acid.

Mercurous iodide, HgI, and *chromate*, Hg_2CrO_4, are characteristic compounds. The iodide is obtained as a greenish precipitate by the action of potassium iodide. It passes easily into the mercuric salt (mercury separates and the precipitate becomes gray). The chromate is precipitated from mercurous salts by potassium chromate. It is brick-red (§ 33).

Mercurous sulphate, Hg_2SO_4, is difficultly soluble in water. It is thrown down as a white, crystalline precipitate by either sulphuric acid or a soluble sulphate.

The characteristic reactions in which metallic mercury is deposited from mercurous salts have already been described. Its behaviour in this regard (especially with stannous chloride), together with the formation of insoluble mercurous chloride, sulphate, and the black metallo-amine, constitute the chief reactions of mercurous mercury.

§ **62.** *Mercuric salts.*—Of this class of salts mercuric chloride (corrosive sublimate) may be considered the type. Its solubility in water is especially important, as it distinguishes mercuric from mercurous compounds. The nitrate is formed by the action of an excess of hot nitric acid upon metallic mercury. The mercuric salts, moreover, are easily formed, as we have observed, from the corresponding mercurous compounds. The majority of the salts decompose at a high temperature. Mercuric chloride, bromide, and iodide, however, volatilise without decomposition on being heated (the chloride even when its solution is boiled). Reducing agents convert mercuric salts to the mercurous state. One of these reduction reactions, that of stannous chloride, has already been discussed.

Reactions of Mercuric Salts.—Mercuric salts are characterised by the solubility of the chloride and the white colour of the metallo-amines.

Mercuric oxide (no hydroxide exists).—Potassium hydroxide throws down from mercuric solutions a brown precipitate, consisting of basic salts, which on further addition of the reagent are converted into the yellow oxide (insoluble in caustic potash). Precipitation from acid solution is incomplete. In presence of ammonium salts a white precipitate of mercuric amines is obtained (see below).

Mercuric amines.—Ammonia and ammonium carbonate throw down white insoluble metallo-amines, which are distinguished from the corresponding mercurous compounds by their white colour. The composition of these compounds is shown in the following equations:

$$HgCl_2 + 2NH_3 = (NH_2Hg)Cl + NH_4Cl,$$
$$Hg(NO_3)_2 + 2NH_3 = (NH_2Hg)NO_3 + (NH_4)NO_3.$$

Mercuric sulphide, HgS.—Hydrogen sulphide throws down a precipitate which is at first white, but passes gradually through the shades of yellow, orange, and brown, and soon becomes black. The double compound, $HgCl_2 . 2HgS$ or $Hg(NO_3)_2 . 2HgS$, which is white, is at first formed, and this is converted by the further action of sulphuretted hydrogen or ammonium sulphide into black mercuric sulphide. The complete precipitation of mercuric sulphide from an acid solution can be effected only when the latter is highly diluted with water. The sulphide is insoluble in nitric acid, even at its boiling temperature (characteristic test for mercury), but dissolves in hot *aqua regia.* It is also somewhat soluble in potassium and sodium sulphides, in presence of caustic alkalies (does not dissolve in ammonium sulphide). It does not undergo oxidation on exposure to the air. The use of mercuric sulphide in analysis, and also some special points concerning the precipitation with hydrogen sulphide and the action of nitric acid, are given in §§ 57 and 61.

Mercuric iodide, HgI_2.—Potassium iodide throws down a red precipitate of mercuric iodide, which dissolves readily in an excess of the precipitant, with formation of the double salt, K_2HgI_4.

The precipitation of metallic mercury from mercuric compounds is also a characteristic reaction. It is described in § 61. The reaction with stannous chloride is to be especially noticed.

Mercuric and mercurous compounds, when occurring together, are easily distinguished by the difference between the two chlorides, $HgCl$ and $HgCl_2$. Hydrochloric acid precipitates mercurous salts, but has no action on mercuric compounds.

Copper

§ **63.** Copper possesses a peculiar red colour, has the sp. gr. 8·8, and fuses at about 1150° C. It forms alloys with various metals. It is easily soluble in nitric acid, less so in sulphuric, and is almost insoluble in hydrochloric acid. When acted upon by acids it does not liberate hydrogen (except with hydriodic acid). The salts formed are of the cupric variety. The cuprous salts are prepared by reduction of cupric compounds: the reduction may also be carried further, and the tetrantoxide obtained.

The most important alloys of copper are bronze (copper and tin), brass (copper and zinc), and German silver (§ 46). These behave toward acids like copper itself. Their analysis is explained among the examples of quantitative analysis.

Separation of copper from its compounds.—When subjected to the action of anhydrous sodium carbonate and carbon at a sufficiently high temperature (in the reduction-flame), copper compounds undergo reduction. The experiment must be made upon a charcoal stick by means of the blow-pipe.[1] If the fusion product be powdered in an agate mortar and the carbon then removed, small flakes of metallic copper will be left behind. The reduction is more easily and simply accomplished by means of the galvanic current. If a piece of zinc be introduced into a platinum dish which contains a copper solution acidified with hydrochloric acid, the current generated by the platinum and zinc speedily causes metallic copper to be deposited. Many metals, such as iron, zinc, etc., reduce copper from the acid solutions of its compounds. These reactions are rarely employed in qualitative analysis, as there are several of greater delicacy.

Copper tetrantoxide, Cu_4O, is obtained when cupric salts (in alkaline solution) are reduced by stannous oxide dissolved in potassium hydroxide (Rose):

$$4CuSO_4 + 3SnO + 14KOH = Cu_4O + 3K_2SnO_3 + 4K_2SO_4 + 7H_2O.$$

Copper tetrantoxide is a green powder which quickly oxidises to cupric oxide. Corresponding salts are unknown; when acted upon by acids, metallic copper separates and cupric salts are formed. Copper tetrantoxide is distinguished from all the other oxides in giving no double compounds with ammonia.

Cuprous salts.—Cuprous oxide, Cu_2O, and its compounds are formed by the reduction of cupric salts. The anhydrous cuprous oxide (which is found native, as red copper ore) is a red, crystalline powder, obtained by the reduction of cupric salts. In order to study the reactions of cuprous salts, the oxide may be most readily prepared by the following method:—Tartaric acid is saturated with an excess of caustic soda, and a solution of copper sulphate added in small portions until the cupric hydroxide, which is at first precipitated, redissolves to a blue colour on shaking. If a solution of grape sugar be slowly added to this mixture while boiling, cuprous oxide is deposited. Few cuprous salts are known. When the oxide is acted upon by sulphuric acid, cupric salts are formed and metallic copper separates; nitric acid yields the cupric salt directly. Hydrochloric acid dissolves cuprous oxide without decomposing it, and a solution of cuprous chloride in hydrochloric acid is thus obtained. Water produces in this solution a difficultly soluble white precipitate of CuCl. The remaining cuprous compounds are prepared from the hydrochloric acid solution of cuprous

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[1] Concerning the blow-pipe, see Section III. Supplement.

chloride. They are usually unstable, absorbing oxygen from the air and passing into the cupric state. Chlorine and nitric acid also convert them to cupric compounds. The fact is worthy of notice that certain copper compounds are known only in the cuprous state; CuI, CuCy, CuCyS, for instance, are salts which have no analogues in the cupric series. These salts are described among the compounds of cupric oxide, of which their formation is very characteristic.

Reactions of Cuprous Salts.—The reactions of cuprous oxide, or, more correctly, of the hydrochloric acid solution of its chloride, are as follows:—

Cuprous hydroxide, Cu(OH), is thrown down by caustic alkalies and their carbonates as a yellow precipitate, which quickly undergoes oxidation.

The *ammonia compound*, $CuCl . NH_3$, results from the action of ammonia or ammonium carbonate. It dissolves in water to a colourless fluid (distinction from cupric compounds). A perfectly colourless solution can be prepared only with difficulty, and when the solutions used have been previously boiled, to expel the oxygen absorbed from the air. The solution becomes blue on exposure to the air, as it takes up oxygen and passes into a cupric ammonia compound.

Cuprous sulphide, Cu_2S.—The hydrate is thrown down as a black precipitate by hydrogen sulphide.

Cuprous iodide, cyanide, and sulphocyanate must also be mentioned. These salts are obtained as white precipitates by the action of the corresponding potassium salts. They will be discussed under cupric oxide.[1]

§ **64.** *Cupric salts.*— Cupric salts are obtained when metallic copper is dissolved in acids. Their formation results according to the equations given under Mercury. Cupric chloride is prepared by the action of *aqua regia* upon metallic copper. The solutions of cupric salts are blue or green, and the salts which contain water of crystallisation have the same colours.

Reactions of Cupric Salts.—*Cupric oxide.*—Caustic soda throws down from cupric salts the voluminous blue hydroxide, $Cu(OH)_2$. If this be warmed while suspended in the mother-

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[1] As cuprous compounds are very rarely met with in analysis, we shall not consider them in the systematic course.

liquid it becomes black, being converted to the hydroxide, $3CuO . H_2O$. The latter compound is obtained directly if the reaction be made in a hot solution. The presence of ammonium salts influences the reaction (see below). When a sufficient quantity of tartaric acid is present (or in the presence of other non-volatile acids, arsenious acid, or chloroform) caustic alkalies impart a blue colour to the solutions of cupric salts.

Copper sulphide, $Cu_4S_3 = 2CuS . Cu_2S$ (§ 57).—Sulphuretted hydrogen and ammonium sulphide precipitate the black copper sulphide, which oxidises on exposure to the air. When boiled with a cupric solution slightly acidified by hydrochloric acid, sodium thiosulphate also throws down cupric sulphide (application in analysis, § 57). Cupric sulphide is soluble in potassium cyanide (slightly so in ammonium sulphide) and in concentrated acids. Acid solutions of copper salts must therefore be diluted with water before precipitation with hydrogen sulphide.

If, in the systematic course of analysis, the copper has been separated as sulphide by means of sodium thiosulphate, the precipitate must be dissolved in *aqua regia* and this solution subjected to confirmatory tests; in these the following reactions with ammonia and with potassium ferrocyanide (in slightly acid solution) are to be employed.

Cupric carbonate.—The basic salt, $CuCO_3 . Cu(OH)_2$, is thrown down as a blue precipitate by sodium carbonate, and is converted to the black hydroxide by boiling. The reaction with alkali carbonates is influenced by the presence of ammonium salts (see below).

Metallo-amines (§ 59).—Ammonia and ammonium carbonate throw down a sky-blue precipitate of a basic cupric salt; this dissolves readily in an excess of the reagent to an ammonia compound, which gives the solution a dark blue colour. Copper sulphate forms the salt, $CuSO_4 . 4NH_3 . H_2O$; copper chloride, $CuCl_2 . 4NH_3 . H_2O$. If acids are present, the addition of ammonia causes the blue colour to appear immediately. When mere traces of copper are to be detected, this reaction may be made more delicate if the solution to be examined be added drop by drop to the ammonia, in a test-tube resting on a piece of white paper. Each drop of a solution containing copper produces a blue cloud in the ammonia. This reaction, however, is not very delicate. The ammonia double compounds are easily decomposed by alkalies; when boiled with the latter, black cupric hydroxide is deposited. Potassium cyanide renders the blue solution colourless (formation of double cyanides).

Cupric ferrocyanide, $Cu_2(FeCy_6)$.—Potassium ferrocyanide, $K_4(FeCy_6)$, is a delicate and characteristic reagent for copper, producing in cupric solutions a red-brown precipitate of cupric ferrocyanide. If the solution be very dilute, only a red colour results. Dilute acids do not alter this compound, but in contact with alkalies it undergoes decomposition. Potassium ferrocyanide cannot be used to distinguish copper from the other metals of this group, for they are all precipitated by the same reagent.

Cuprous cyanide and *cuprous sulphocyanate*, $Cu(CyS)$, are white precipitates insoluble in dilute acids, and obtained by the action of potassium cyanide or sulphocyanate upon cupric solutions in presence of sulphurous acid. Cuprous cyanide dissolves in potassium cyanide, forming the double salt, K_3CuCy_4. The same compound may be prepared by dissolving cupric hydroxide, carbonate, or sulphide, in potassium cyanide. These reactions explain why copper sulphide is not precipitated from a solution of K_3CuCy_4 by hydrogen sulphide. They are employed in qualitative analysis for the separation of copper from cadmium (§ 59).

Flame coloration.—Copper salts (also metallic copper and its alloys), when brought into the non-luminous flame on a platinum wire, colour it green. The operation is most successfully performed with cupric chloride, and the delicacy of the reaction may be heightened by previously moistening the salt with hydrochloric acid. The blue coloration imparted to the borax bead in the outer flame (the bead is green while hot) is characteristic of copper. When heated with tin foil in the inner flame a colourless bead is obtained, which becomes red on cooling (reduction).

Cadmium

§ **65.** Cadmium is white, fuses at 315° C., and boils at about 815° C. When attacked by acids, hydrogen is generated (distinction from the other metals of this group). Nitric acid is the best solvent for cadmium. In its chemical properties the metal resembles zinc.

Reactions of Cadmium Salts.—*Cadmium oxide.*—Sodium hydroxide throws down from cadmium salts the white cadmium hydroxide, $Cd(OH)_2$, insoluble in excess of the precipitant.

Cadmium sulphide is yellow (distinction from the other sulphides of this group, and characteristic indication of cadmium). It is obtained by the action of hydrogen sulphide or ammonium sulphide upon the solutions of cadmium salts, and is easily soluble in acids. Before its precipitation from an acid solution, therefore, the latter must be well diluted with water. Cadmium sulphide is insoluble in potassium cyanide (distinction from copper; for application in analysis see § 59).

In analysis, the cadmium is always separated as its sulphide. In view of the marked characteristics of this compound and also of the conditions under which it is formed (usually from potassium cyanide solution, if copper be present), it need not be subjected to further confirmatory tests. Cadmium sulphide, when precipitated by ammonium sulphide, passes through the filter to a slight extent while being washed.

The ammonia compounds of cadmium are formed only by the action of ammonia. The latter produces in cadmium salts a white precipitate easily soluble in an excess (to a colourless solution). These compounds do not result from the addition of ammonium carbonate (distinction from copper, § 59 B).

Cadmium carbonate.—Ammonium and sodium carbonates precipitate the white cadmium carbonate, insoluble in excess. Ammonium salts influence the precipitation, and when free ammonia is present the reaction does not occur. The precipitate is soluble in potassium cyanide.

Cadmium cyanide.—Cadmium salts give with potassium cyanide a white precipitate, which dissolves readily in an excess of the reagent to the double salt, K_2CdCy_4. Hydrogen sulphide precipitates cadmium sulphide from the solution of this salt (see Copper, and § 59 A).

Lead

§ **66.** Metallic lead is gray. It has a specific gravity of about 11·4, melts at 335° C., and boils at a white heat, at about 1600° C. Lead is insoluble in dilute sulphuric and hydrochloric acids, but dissolves in nitric acid with evolution of nitric oxide. We meet in analysis not only the metal itself but also its alloys, *e.g.*, lead and antimony (type-metal) and lead and tin (solder).

The salts corresponding to lead monoxide, PbO, are very stable. Lead nitrate, $Pb(NO_3)_2$, is soluble in water, but insoluble in concentrated nitric acid, and therefore when lead is dissolved by the concentrated acid, a white, crystalline residue is obtained, which goes into solution upon the addition of water. Beside the monoxide, which forms salts the properties of which will be discussed below, there are several other oxides of lead known: the sesquioxide, Pb_2O_3, minium, Pb_3O_4, and the dioxide, PbO_2. These oxides have no salts. (The dioxide unites with certain bases.) They behave toward acids as peroxides, *i.e.*, they liberate chlorine from hydrochloric acid, etc. They are somewhat more stable in their behaviour toward nitric acid; this is especially true of lead dioxide (see the Manganese compounds, § 38). In analyses of acid solutions only the salts of the monoxide can be present, and they alone will be discussed. The other oxides are necessarily converted to these salts during the course of analysis.

Reactions of Lead Salts.—The most characteristic salts of lead are the sulphate, chloride, and iodide. Mention has already been made of the inability of lead to form soluble double cyanides and ammonia-compounds.

Lead oxide.—The alkalies and ammonia precipitate basic salts from lead solutions, and these are soluble in excess of the alkalies (but not of ammonia).[1] Lead hydroxide, $Pb(OH)_2$, is formed if the above reaction be reversed, *i.e.*, if the lead solution be added to the alkali.

Lead sulphate, $PbSO_4$, is marked by its very slight solubility in water. Sulphuric acid and soluble sulphates throw down a white precipitate of lead sulphate, slowly when the solution is dilute, especially if free acids be present. The delicacy of the reaction is increased if an excess of free sulphuric acid or alcohol be present (lead sulphate is less soluble in dilute sulphuric acid and in alcohol than in water). It dissolves in hot alkalies. The solubility of lead sulphate in ammonium acetate and tartrate (or in ammonia and acetic acid, or ammonia and tartaric acid) is noticeable. In these tests with ammonium salts, solution is more readily effected if ammonia be present in slight excess. Sulphuretted hydro-

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[1] The majority of lead salts are soluble in caustic potash. Lead sulphide forms an exception.

gen precipitates lead sulphide from such a solution. These tests are employed, in the course of analysis, in the investigation of the residue left when the sulphides are dissolved in nitric acid (§ 57 B). Lead sulphate is used in the separation of lead from all the other metals except mercurous mercury.

Lead chromate, $PbCrO_4$, is obtained by the action of potassium chromate. It is a yellow precipitate, soluble in potassium hydroxide (§ 33).

Lead carbonate.—The basic salt is thrown down by sodium or ammonium carbonate (completely in presence of ammonia) as a white precipitate, insoluble in potassium cyanide.

Lead sulphide, PbS (§ 57), is a black precipitate obtained by the action of sulphuretted hydrogen or ammonium sulphide. If a lead solution be precipitated by hydrogen sulphide in presence of hydrochloric acid, a brown precipitate is at first obtained. This consists of the salt, $PbCl_2 . 2PbS$, and is converted by prolonged action of the hydrogen sulphide into the normal black sulphide. Lead sulphide dissolves easily in hot nitric acid; the reaction converts a portion of it to lead sulphate, $PbSO_4$.

Lead chloride, $PbCl_2$.—Hydrochloric acid and soluble chlorides throw down a white precipitate of lead chloride. It is only slightly soluble in cold, easily soluble in boiling water (Application in analysis, *v.* § 58).

Lead iodide, PbI_2.—Potassium iodide precipitates the yellow lead iodide. This salt dissolves in boiling acetic acid, and is redeposited in gold-yellow flakes when the solution cools.

Bismuth

§ **67.** Bismuth is a white metal with a reddish lustre, brittle, easily fusible (264° C.), of sp. gr. 9·8. Nitric acid dissolves it easily (with evolution of nitric oxide), but it is only slightly soluble in hydrochloric acid, and not at all so in dilute sulphuric acid. Only one series of bismuth salts, that corresponding to the sesquioxide, is known to exist in acid solution. Bismuth resembles lead in that its cyanide does not form a soluble double salt with potassium cyanide. In addition to the oxide, Bi_2O_3, several still higher degrees of oxidation are known. Bismuthic acid (the compound $H_4Bi_2O_7$ exists in the free state) acts toward acids as a peroxide, *i.e.*, it liberates chlorine from hydrochloric acid, being itself converted to the bismuth salt (it shows the same behaviour toward sulphuric acid). The lowest oxide, bismuthous oxide, BiO, is incapable of forming salts, and gives bismuthic salts and metallic bismuth when treated with acids. In analyses, therefore, acid solutions can contain only the bismuthic salts, and the reactions of this series alone require discussion.

Reactions of Bismuth Salts.—The most important reactions of bismuth salts are those with water (both from the qualitative and quantitative standpoints).

The action of water upon bismuth salts results in the formation of insoluble basic salts. The separated acid retains a portion of the salt in solution (or so-called acid salts are formed, which are soluble). The more free acid present, the less complete is the formation of the insoluble basic salts. If these salts, therefore, are to be precipitated in an analysis, the free acid must be previously removed, either by evaporation or cautious neutralisation. It is advisable to precipitate the basic chloride (bismuth oxychloride) instead of the nitrate. The nitrate, $Bi(NO_3)_3$, dissolves in nitric acid without alteration. On the addition of water (more or less, according to the quantity of free nitric acid), a white, curdish precipitate is formed (this often becomes crystalline). One of two compounds may result, the product depending upon the amount of water used. The first product, a crystalline compound (magisterium bismuthi), $Bi(OH)_2NO_3$, is converted by the further action of water into the salt, $(BiO)_2(OH)NO_3$. The nitric acid set free during the reaction retains a portion of the salt in solution:

$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2 . NO_3 + 2HNO_3,$$
$$2Bi(OH)_2NO_3 = (BiO)_2(OH)NO_3 + HNO_3 + H_2O.$$

Bismuth chloride is completely precipitated by water, none of the salt being held back in solution:

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

The bismuth oxychloride formed is a white precipitate insoluble in water. As the precipitation is complete, this reaction is employed in both qualitative and quantitative analyses. It is in every regard the most delicate test which exists for bismuth.

The formulæ of the basic bismuth salts are derived from the hydroxide, $Bi(OH)_3$, by the partial substitution of an acid radical for one or more of the hydroxyl groups: such a salt, for example, is found in the above nitrate, $Bi(OH)_2(NO_3)$. Bismuth oxychloride, and the class of salts in general which contain the group BiO (bismuthyl), result from the abstraction of water from salts of the formula first mentioned:

$$Bi(OH)_2Cl = BiOCl + H_2O.$$

These are likewise basic salts. The more complicated nitrate, $(BiO)_2(OH)(NO_3)$, is a derivation of the anhydro-hydroxide, $(BiO)_2(OH)_2$, which stands in the following relation to the normal hydroxide:

$$Bi(OH)_3 + Bi(OH)_3 = (OH)Bi\underset{O}{\overset{O}{<\!\!>}}Bi(OH) + 2H_2O.$$

The salt under analysis is usually the nitrate; this can be converted to the oxychloride as follows: the solution is treated with hydrochloric acid or, better still, with sodium chloride (double decomposition ensues, and the nitric acid unites with the sodium); if water be now added the basic chloride separates. The reaction should be made with a concentrated (by evaporation) solution, and, if necessary, the precipitation observed upon a watch-glass.

Bismuth hydroxide.—Caustic potash and ammonia throw down a white precipitate of bismuth hydroxide, insoluble in excess of the reagents.

The (basic) *carbonate*, $(BiO)_2CO_3$, is a white precipitate thrown down by sodium and ammonium carbonates. It is insoluble in excess of the precipitant.

Bismuth sulphide, Bi_2S_3.—Hydrogen sulphide and ammonium sulphide precipitate (from as dilute a solution as possible) black bismuth sulphide; it is insoluble in ammonium sulphide, but dissolves readily in boiling nitric acid.

The chromate, $(BiO)_2Cr_2O_7$, is thrown down by potassium dichromate as an orange-yellow precipitate. It is soluble in nitric acid, but not in caustic potash.

Bismuthous oxide, BiO, is a black precipitate obtained by the action of stannous chloride in alkaline solution. The reaction is delicate and characteristic of bismuth (for the conditions of the experiment see § 74).

SYSTEMATIC COURSE OF ANALYSIS

§ **68. Metals of Group IV.**—The metals of this group show so great a variation in their properties that many reactions may be employed for their detection. The similarity between the different reactions, however, requires that they be systematically arranged, and thus one metal after the other methodically separated. We leave to the student the task of seeking out the many possible means of separation, but recommend the following as the most convenient method:—The given solution is precipitated by hydrochloric acid of medium concentration, and the precipitate washed. The conditions of the reaction, the investigation of the precipitate, and the test for silver, mercurous mercury, and lead, are explained in § 58. The solution, after being filtered and well diluted with water, is precipitated by hydrogen sulphide (the conditions given in § 57 A must be accurately observed). The thoroughness of the precipitation must be carefully ascertained by a confirmatory test. The sulphides of the different metals are deposited in succession and not simultaneously, and hence, if the precipitation be incomplete, some of the metals may remain in solution. The sulphides are well washed and then treated with boiling nitric acid (separation of, and test for, mercury). This reaction may result in the formation of several compounds, as explained in § 57 B. The nitric acid solution is evaporated, with occasional addition of water, and lead removed from the concentrated solution by means of a small quantity of sulphuric acid (separation of lead, § 66). Bismuth hydroxide is next precipitated by ammonia from the solution obtained (the separation of bismuth is followed by its solution in hydrochloric acid and subjection to the tests with water, § 67). The ammoniacal solution now contains the copper and cadmium salts. The blue solution is rendered colourless by potassium cyanide and then precipitated with hydrogen sulphide (§ 57 A). If cadmium is present a yellow precipitate of cadmium sulphide settles out (separation of Cd). As a confirmatory test for copper, sulphuric acid is added to the filtrate from the cadmium sulphide, and all the hydrocyanic acid expelled by warming; a solution of copper sulphate is thus obtained. The operations must be conducted with due circumspection. The use of potassium cyanide in the separation of copper from cadmium is avoided in the following method:—The mercury having been removed, the almost neutral solution is precipitated with sodium thiosulphate while boiling. The precipitate consists of bismuth and copper sulphides, which may be dissolved in nitric acid and separated by ammonia. Cadmium remains in the first filtrate and is precipitated as cadmium sulphide by sulphuretted hydrogen.

Confirmatory tests must be made, not only in the cases mentioned, but with the final precipitates of each of the metals.

Metals of Group IV. from Groups III., II., and I.—The separation of the fourth from the preceding groups is effected by the above scheme. The solution is first acidified with hydrochloric acid (if a precipitate appears it must be examined according to § 58), diluted with water, and the metals of Group IV. thrown down by hydrogen sulphide (we mention again the necessity of observing the conditions given in § 57 A, and also of ascertaining, by a confirmatory test, the completeness of the precipitation). The precipitate is thoroughly washed with water and investigated according to this paragraph. The metals of Groups I., II., and III. are found in the filtrate. The hydrogen sulphide must be expelled from the filtrate by boiling, if the test for acids is to be made with ammonia (comp. §§ 51 and 52, on the detection of acids). If this test is not required, the filtrate may be directly precipitated by ammonium sulphide (the necessary conditions being observed), and the analysis carried out according to the explanations in § 48 and in preceding paragraphs.

SUPPLEMENT TO GROUP IV

1

Analysis of the compounds of the metals of Group IV.—The metals of this group are important not only in their natural compounds, but also because of the numerous alloys and other artificial products in which they are found. Many of the metals occur in nature in the metallic state (bismuth and copper; more rarely, silver and mercury). The sulphides are the chief ores of lead (galena); mercury (cinnabar); silver (often in combination with antimony sulphide, mercuric, copper, and arsenic sulphides, and in gray copper); and of copper (copper pyrites). Galena usually contains small quantities of silver. Greenockite (cadmium sulphide) is of less importance. These compounds may be analysed by various methods. Galena is usually converted to lead sulphate by nitric acid ; cinnabar is dissolved in hydrochloric or nitric acid, with addition of potassium chlorate. The analysis of gray copper, a very complicated operation (Section III., Examples), is usually effected by treatment with chlorine (see quantitative separation of mercury). Lead and copper are also found in nature as carbonates (cerassite, malachite). These minerals are soluble in acids. Copper also occurs as cuprous oxide (red copper ore). The analyses of several alloys are explained among the quantitative examples (bronze, brass, German silver, etc.)

2

Application of the metals of Group IV. to analysis.—The compounds of mercury and lead are chiefly employed. The ease with which mercury compounds decompose when heated, and the volatility of mercury itself, render the use of these substances in quantitative analysis especially valuable and convenient. Mercury compounds are employed chiefly for the precipitation of magnesium (in its separation from the alkalies by mercuric oxide) ; to decompose the double cyanides (used in separation of cobalt) ; and in the formation of mercuric chromate and mercuric cobalticyanide. All of these compounds part with their mercury and other volatile constituents upon ignition, and the non-volatile residue of magnesia, nickelous oxide, chromic oxide, or cobalto-cobaltic oxide is weighed. Mercuric oxide also surrenders its oxygen readily, and can therefore be used as an oxidising agent. When antimony sulphide, for instance, is heated with mercuric oxide, it is converted to antimony tetroxide (Group V., Antimony). The readiness with which the higher lead oxides, especially the dioxide, surrender their oxygen, make these compounds valuable as oxidising agents. Lead dioxide is employed, for example, in the oxidation of chromic oxide to chromic acid (§ 32), and of manganous oxide to manganic acid (§ 38).

3

PALLADIUM, RHODIUM, RUTHENIUM, AND OSMIUM

§ **69.** These metals resemble platinum, and are found associated with that metal (and iridium). Although platinum and iridium belong to Group V., they must be mentioned here, as they are the types of the metals under discussion. The platinum metals form two groups—the first consisting of platinum, iridium, osmium ; and the second, of palladium, rhodium, and ruthenium. They are classified thus both according to the atomic weights, those of the first group being about twice as great as those of the second, and by their chemical behaviour. The oxides of the platinum metals are very weak bases, and the higher oxides of osmium, ruthenium, and, to a less degree, of rhodium are acids. The higher chlorides of the platinum metals, RCl_4 ($R = $ metal), unite with other chlorides, thus forming several series of compounds. They also lose chlorine easily, passing into the lower chlorides.

Both the chlorides, RCl_4 and RCl_2, unite with ammonia to form a series of ammoniacal compounds; examples of these are found in the platinammonium compounds. All the foregoing compounds, like the majority of double salts (*e.g.*, of the cyanides, nitrites, etc.) are employed in analysis. The formation of perosmic and perruthenic acids is less important. If we are to be guided by analytical properties, the study of the platinum metals of this group must be separated from that of their analogues which have been more thoroughly investigated. Their character can be fully understood, however, only after the study of platinum and iridium has been finished. The properties of the latter are explained in Group V. With the exception of palladium, and perhaps of osmium, the metals of this group, and especially rhodium and ruthenium, have been insufficiently investigated. Bunsen, indeed, believes that their compounds have never been obtained in a pure state, and at the same time assumes the probable existence of new platinum metals (at least one), which have not yet been isolated. Methods of separation are in many cases still imperfect. To study these more thoroughly, and also to learn the reactions of these metals in general, the closing paragraphs of this supplement will be devoted to the analysis of the so-called platinum residues.

Palladium.—Palladium usually occurs in the metallic state, sometimes with gold and silver, and also associated with platinum in the ores of the latter metal. Palladium can hardly be distinguished by its lustre or colour from platinum. When in the form of palladium-sponge it assumes, if even slightly heated, a rainbow tint extending from green to deep violet. If hydrogen be led over palladium in such a state of surface oxidation, at the ordinary temperature, the original colour of the palladium is restored; on further action, the hydrogen becomes absorbed and palladium hydride forms. The metal is difficultly soluble in nitric acid (more readily so when the latter contains nitrous acid). It dissolves in boiling sulphuric acid (with evolution of sulphur dioxide), being more easily attacked when in the finely-divided state. Hydrochloric acid has little action, but does dissolve a perceptible amount, even at the ordinary temperature (particularly in presence of other metals), if the metal is in the spongy form, and is treated with the acid under exposure to the air. Palladium is readily soluble in *aqua regia*, when it has previously been fused with acid potassium sulphate. Like platinum, it has two oxides, the monoxide, PdO, and palladic oxide, PdO_2. It also has two chlorides. Palladium tetrachloride, $PdCl_4$, is prepared by solution of the metal in *aqua regia*, and forms compounds with other chlorides, *e.g.*, K_2PdCl_6. Palladic chloride readily parts with its chlorine and passes into palladious chloride, $PdCl_2$. The palladious salts (which are usually brown) correspond to this compound. The sulphate and nitrate are soluble in water. Palladium salts are in most cases reduced to metallic palladium on ignition.

Reactions of palladious salts. Palladious oxide, PdO.—Alkalies throw down a dark brown precipitate, soluble in excess of the reagent. If this solution be boiled, brown palladious hydroxide is precipitated (the anhydrous oxide is black).

Palladium ammonia compounds.—Ammonia gives a flesh-red precipitate, $PdCl_2NH_3$, soluble in excess of ammonia. If hydrochloric acid be added to this solution, the yellow compound of palladammonium chloride, $Pd(NH_3Cl)_2$, is deposited. Salts other than the chloride show this reaction only when hydrochloric acid is present.

Palladious cyanide is obtained by precipitation with mercuric cyanide. It is a white, gelatinous precipitate, insoluble in dilute acids, but dissolving in ammonia and in potassium cyanide (to K_2PdCy_4).

Palladious iodide, PdI_2, is black, and obtained on precipitation of palladium compounds by hydriodic acid or potassium iodide.

Palladious sulphide is a black precipitate, soluble in hydrochloric acid and *aqua regia*.

The double nitrite, $K_2Pd(NO_2)_4$, is thrown down from palladium solutions by potassium nitrite as a yellow crystalline powder.

Reduction reactions.—The palladium salts, like those of platinum, readily undergo reduction. Ferrous sulphate slowly produces a black precipitate of metallic palladium (preferably from the nitrate). Stannous chloride causes a black precipitate and green solution.

Palladium in palladious salts is usually *determined quantitatively* as the metal. The salt is first precipitated as palladious cyanide (by mercuric cyanide, in absence of nitric acid), or as palladious sulphide, and the precipitate then ignited. Palladium can also be gravimetrically determined as $Pd(NH_3Cl)_2$, and, when in the palladic state, as K_2PdCl_6. The latter method is carried out just as in the case of platinum (Group V.)

Rhodium.—Rhodium, which is found only in the platinum ores, is almost white and very difficultly fusible. It is insoluble in acids. Finely-divided rhodium (obtained by reduction of its compounds in hydrogen), however, dissolves in hydrochloric acid under exposure to the air, a cherry-red solution being formed (the presence of other metals seems to increase the solubility). Rhodium dissolves in *aqua regia* only when alloyed with platinum or copper (in its alloys with gold and silver it is insoluble). It is soluble in molten phosphoric acid, and dissolves when fused with acid potassium sulphate, with formation of a rhodic salt, *e.g.*, $K_3Rh(SO_4)_3$. If the metal be treated with chlorine in presence of sodium chloride, the soluble salt, Na_3RhCl_6, is formed. Rhodium forms several oxides. The anhydrous sesquioxide, R_2O_3, is insoluble in acids; the hydroxide, $Rh(OH)_3$, difficultly soluble. Acids dissolve the hydroxide, $Rh(OH)_3 + H_2O$, on the contrary, with great readiness. The solutions of rhodium salts possess a cherry-red or brownish red colour.

Reactions of rhodium salts. Rhodium sulphide.—Hydrogen sulphide precipitates, but only from hot solutions, and even then incompletely, the brown rhodium sulphide, soluble in nitric acid.

Hydroxide.—Potassium hydroxide at first throws down a yellow precipitate of $Rh(OH)_3 + H_2O$, which is soluble in excess of the reagent at the ordinary temperature. If this solution be boiled, the gelatinous, dark brown hydroxide, $Rh(OH)_3$, separates. A solution of $RhNa_3Cl_6$ does not show this reaction immediately, but the precipitate appears in course of time: the addition of alcohol causes a black hydroxide to be precipitated at once. The hydroxide is also thrown down as the brown modification by other salts, such as sodium phosphate.

Ammonia compounds.—Ammonia produces a yellow precipitate of the hydroxide. If a rhodium salt be boiled with ammonia, an ammonia base results, which, after cooling, is precipitated by hydrochloric acid as a bright yellow crystalline salt which is difficultly soluble and has the composition $Rh(NH_3)_5Cl_3$ or $Rh_2Cl_6 . 10NH_3$ (chloropurpureorhodium chloride).

Double nitrites.—Potassium nitrite throws down from hot solutions a bright yellow precipitate of the double nitrite of potassium and rhodium.

Reduction reactions.—Rhodium compounds are reduced by hydrogen. The metal is also precipitated from its solutions by zinc.

Ruthenium.—Ruthenium is found only in platinum ores. It is barely soluble in *aqua regia*, and insoluble in acid potassium sulphate. It dissolves easily when fused with potassium hydroxide, especially on the addition of potassium nitrate. In this reaction a solution of potassium ruthenate is obtained, from which acids precipitate the hydroxide. Treatment with chlorine, in presence of potassium chloride and at a high temperature, yields the salt, K_2RuCl_5. Ruthenium unites with oxygen in several proportions. Ruthenic tetroxide, RuO_4, is solid at the ordinary temperature, but very volatile. The anhydrous oxide, R_2O_3, is insoluble in acids; its hydroxide dissolves easily in hydrochloric acid. Ruthenic sulphate, $Ru(SO_4)_2$, is the only salt with oxyacids known. The common soluble salts of ruthenium are its double chlorides, such as K_2RuCl_5 and K_2RuCl_6. The chlorides are $RuCl_2$, $RuCl_3$, and $RuCl_4$.

Reactions of ruthenium salts.—Potassium hydroxide throws down the black hydroxide. Ruthenium sulphide, RuS_2; hydrogen sulphide at first produces no precipitate, but after some time the solution becomes blue and the black sulphide is deposited (it is precipitated by ammonium sulphide at once). Potassium nitrite does not precipitate ruthenium salts (the double nitrites are soluble). If ammonium sulphide be added to the solution of these salts a characteristic crimson liquid is obtained (due to reduction). Potassium sulphocyanate causes a characteristic purple-red colour, which on application of heat becomes violet. Zinc precipitates metallic ruthenium, the solution first turning blue.

Osmium.—Osmium occurs in platinum ores and alloyed with iridium. It has two chlorides, $OsCl_2$ and $OsCl_4$, both of which combines with the alkali chlorides. Its oxides are numerous, but only the higher forms require discussion. Metallic osmium readily undergoes oxidation, and burns in the flame. In this case, and also through the action of nitric acid or *aqua regia*, or when heated in a stream of moist chlorine, osmic tetroxide, OsO_4, is formed. This compound, which is very volatile and poisonous, may also be prepared from the lower oxides. It unites with the alkalies, but does not decompose carbonates. These salts, the perosmates, are very unstable (their formulæ are undetermined). They are easily converted to osmates (*e.g.*, K_2OsO_4), especially when boiled with caustic alkalies (the reaction is accompanied by the characteristic separation of the tetroxide). A solution of perosmic acid decolorises indigo, separates iodine from potassium iodide, and oxidises alcohol to aldehyde. It is reduced by ferrous sulphate or stannous chloride. Hydrogen sulphide precipitates from its solutions the brownish black osmium sulphide, but only in presence of a strong mineral acid. Metallic osmium is easily obtained from either its solutions or solid compounds. It is precipitated from solutions by zinc or formic acid, and may be prepared by ignition of osmium compounds in a current of hydrogen.

Analysis and Metallurgy of Platinum Ores and Residues.— Without going deeply into the technicalities of the metallurgy, we shall discuss the principal points, viz., those which deal with the separation of the platinum metals. The description is based upon the works of Wöhler, Deville, Debray, and Bunsen.

a. Platinum ores. Wöhler's method.—The platinum ores usually contain small lumps and flakes of osmiridium, and sometimes of gold. The gold is extracted by boiling with very dilute *aqua regia* (and precipitated from this solution by oxalic acid). To extract the platinum the washed residue is repeatedly treated with weak *aqua regia* (5 parts fuming HCl, 1 part HNO_3), and the acid distilled off by evaporation. The distillate, which contains osmic tetroxide, is worked over for osmium (see below). The residue, insoluble in *aqua regia*, consists of osmiridium (which, in analysis, is collected upon a weighed filter) and other impurities (residue 1: its purification will be explained below). The *aqua regia* solution is next evaporated to dryness, and heated to 150° C. (to convert the iridium into $IrCl_3$). After solution in HCl, ammonium platinichloride is precipitated by ammonium chloride. The platinum is obtained by ignition with oxalic acid. To completely free it from iridium, the metal must again be treated with *aqua regia*. The mother-liquor of the ammonium platinichloride is saturated with chlorine, evaporated to dryness, and washed with alcohol of 80° Tr. This yields the palladium, rhodium, iridium (and platinum), which the liquor contained. The residue is next treated with ammonium chloride (comp. Bunsen's method): the red solution which results contains all the palladium and rhodium. To separate them, the solution is evaporated to dryness, ignited, and the metals reduced in a current of hydrogen. The greater portion of the palladium is extracted with *aqua regia*, and purified by neutralising with an alkali, precipitating palladium cyanide with mercuric cyanide, and reducing the metal in hydrogen. The rhodium requires no further purification: its solution is evaporated, ignited, and the residue reduced to metallic rhodium in hydrogen. The residue insoluble in ammonium chloride is treated with potassium chloride solution, the platinum salt forming a difficultly soluble platinichloride, while the iridium goes into solution. The solution is evaporated, ignited with potassium nitrate, and extracted with water. The iridium oxide which remains is then reduced by hydrogen.

Method of Deville and Debray.—The estimation of the sand is accomplished by fusion of 2 grams of the ore with 7 grams of pure silver and 10 grams of borax. The sand dissolves in the borax, while the platinum metals and the silver form a regulus. The weight of the latter, subtracted from that of the ore plus the silver, gives the amount of sand. The osmiridium is estimated as in Wöhler's method. The solution obtained in this operation is evaporated almost to dryness with ammonium chloride, and at a low temperature. Platinum and iridium double salts are next precipitated, the conditions given under Wöhler's method being carefully observed, and the two metals separated with *aqua regia* after reduction. The filtrate from the ammonium chloride compounds of Pt and Ir is evaporated to dryness, and, after the addition of a few drops of ammonium sulphide and 2 grams of sulphur, is heated to a red heat in a weighed crucible. Fe_3S_4, Cu_2S and Pd, Rh and Au, are thus obtained. The palladium, iron, and copper are extracted by nitric acid, the solution evaporated to dryness, ignited, and treated with hydrochloric acid, which dissolves only the iron and copper. Rhodium and gold are separated by digestion with dilute nitric acid.

b. Osmiridium.—Lixiviation yields fine grains of osmiridium (containing ruthenium). The following method of analysing *osmiridium* is recommended by Wöhler. Two grams of the substance are fused with barium dioxide (6 gr.) and barium nitrate (2 gr.) After undergoing ignition for two hours the mass is treated with water, hydrochloric acid (and nitric acid), and the osmic acid distilled into a receiver, where it is absorbed by ammonia. The residue is then dissolved in water, the barium removed by sulphuric acid, and the filtrate evaporated nearly to dryness with ammonium chloride (8 gr.) On digestion with alcohol the iridium double salt remains undissolved. The iridium itself is obtained from this salt by reduction in hydrogen; it still contains some ruthenium, however, which may be extracted by fusion with potassium hydroxide and chlorate. The fusion product, containing the ruthenium salt, is next treated with nitric acid, which separates ruthenious oxide. The rhodium, which goes into solution in the alcohol, need not be purified any further, but is treated as in *a.* Deville and Debray analyse osmiridium by fusing it without previous pulverisation, and dissolving the fused mass in hydrochloric acid. In the further processes of the analysis they follow Wöhler's method; the rhodium, however, is separated by treatment with sulphur, as described above.

c. Analysis of the residue insoluble in aqua regia (Residue 1).—This residue contains all the platinum metals, and also osmiridium. It is first lixiviated from the latter, and then mixed with sodium chloride and heated in a porcelain tube in an atmosphere of moist chlorine. The osmium is thus converted to osmic tetroxide, and is distilled into a receiver containing ammonia. (Metallic osmium is obtained from this solution by evaporation with ammonium chloride and ignition.) After the distillation, the residue in the tube consists of double compounds of the platinum metals with sodium chloride. These are dissolved in water, nitric acid added, and the remainder of the osmic tetroxide distilled off. If potassium chloride or ammonium chloride be now added, the solution, concentrated by evaporation, deposits K_2IrCl_6 on cooling. (The preparation of metallic iridium from the salt is explained above.) The remaining solution is evaporated to dryness with sodium carbonate and gently ignited. On digestion with water (water extracts the alkali chromate formed from chrome-iron ore, which occurs as an impurity in the platinum ores), the oxides of the platinum metals Ir, Ru, Rh, and iron oxide remain undissolved. These are reduced by ignition in hydrogen, and iron extracted with dilute hydrochloric acid. Platinum, rhodium, and palladium are obtained from the residue by solution in dilute *aqua regia.* Their separation is discussed in *a.* The separation of iridium from ruthenium, which usually, though not invariably, occurs in osmiridium, is explained in the analysis of osmiridium.

Method of Deville and Debray.—50 gr. of the residue are fused with 150 gr. of litharge and 50 gr. of metallic lead. The fusion is treated with dilute nitric acid at 100° C. Lead and palladium go into solution, and after the former has been removed by sulphuric acid, the solution is evaporated to dryness, the residue dissolved in water, and palladium precipitated as palladious cyanide. The portion insoluble in nitric acid is washed with hot water, evaporated to dryness, and treated with *aqua regia*. The insoluble residue consists of osmiridium. The solution is analysed according to Deville and Debray's method for analysing the platinum ores (see above).

d. The second residue is obtained in the course of the preparation of the platinum, when the mother-liquor of the ammonium platinichloride is precipitated by metallic iron. It is especially rich in rhodium and palladium, but contains all the other metals (and also sand, iron, copper, and other impurities). This residue is black. According to Wöhler, it is treated (after fusion with soda) in the same manner as the first residue. Deville and Debray also subject it to practically the same treatment as they recommend for the first residue. Bunsen, however (*Ann. d. Chem. Pharm.* 146, 265), proposes a new method. Before explaining his plan, it may be well to mention that many of the reactions involved in the separation of the platinum metals have not been published. We shall discuss *Bunsen's method* in its single steps.

Precipitation of the platinum and palladium and their separation.—Three parts of the residue are gently ignited with one part of ammonium chloride until the latter is completely volatilised. Iridium, ruthenium, and rhodium are thus rendered insoluble. If the ignited residue, therefore, be treated, first with nitric acid and subsequently with water, platinum and palladium (the latter reduced by the iron and copper of the residue) will be dissolved as $PtCl_4$ and $PdCl_2$. (Hydrochloric acid, and consequently *aqua regia*, will be formed from the decomposition of the chlorides.) Their separation is effected by potassium chloride, which precipitates K_2PtCl_6. The solution is filtered and treated with chlorine, to convert $PdCl_2$ into $PdCl_4$. Impure K_2PdCl_6 is thus obtained. This is weighed, again reduced to $PdCl_2$ with oxalic acid, and potassium platinichloride reprecipitated by potassium chloride. A portion of the palladium separates from the solution as K_2PdCl_4 on evaporation, and the remainder is precipitated as PdI_2 by potassium iodide.

Separation of ruthenium.—The insoluble residue left on treatment with nitric acid is fused with eight parts of zinc, the surface of the mixture being continually kept covered with ammonium chloride. The latter operation very much facilitates the fusion, as the platinum metals (which exist in the residue in a partly oxidised state) undergo reduction. The sand also (the stony constituents of the ore in general) remains suspended in the layer of zinc chloride and above the regulus. The latter is next granulated and treated with hydrochloric acid. It may be mentioned that lead and copper are dissolved by the acid (the platinum and zinc form a galvanic couple), and also, naturally, the iron and zinc. All the foreign metals are separated from the ores by this method, and the black residual powder consists only of the platinum metals (iridium, rhodium, and some ruthenium). This residue is mixed with anhydrous barium chloride (four parts) and heated in small portions in a retort filled with chlorine. If the mixture be now treated with water, an insoluble black powder is left, which contains all the ruthenium (together with small quantities of iridium and rhodium).

Separation of rhodium and iridium.—The barium is next separated by sulphuric acid from the solution obtained above, the acid being added cautiously and an excess avoided. The platinum metals are next separated by hydrogen (at 100° ; we shall omit the details of the operation). Platinum, palladium, rhodium, and finally iridium, are deposited in succession. They are purified by re-solution in *aqua regia*, and the impure iridium and rhodium are again treated with chlorine in presence of barium chloride. After digestion with water and removal of the barium by sulphuric acid, the solution is concentrated by evaporation with hydrochloric acid, filtered, and precipitated by an excess of acid sodium sulphite. In the course of a few days the rhodium will be deposited in the form of a very pure, citron-coloured, double sulphite, the previously brown solution becoming colourless at the same time. If, after the double salt has been filtered off, the solution be heated, more of the same precipitate will be thrown down, but mixed with the iridium salt. When evaporated on the water-bath the filtered solution yields the iridium salt (possibly containing another element as yet unknown). The final separation of iridium and rhodium is effected by treatment of the sulphites with concentrated sulphuric acid, in a platinum crucible, until all the sulphuric acid has been driven off. Water then dissolves the iridium as its sulphate, while rhodium remains as an insoluble double sodium sulphate (which has not been more accurately described). The metal itself is prepared by the well-known methods. To completely purify the products, all of these operations must be repeated several times.

Methods of Deville and Stas.—The analysis of the platinum metals has recently made considerable progress. The International Commission of Weights and Measures invited Deville and Stas to investigate and analyse the alloy of iridium and platinum to be used in the preparation of standard meters and kilograms, and these two scientists developed the following method. We give the cardinal points of the process as explained by Mylius and Förster (*Ber. d. deutschen chem. Gesellschaft*, Bd. 25, S. 665).

The alloy (5 gr.) is fused with ten parts (50 gr.) of lead in a crucible of purified retort charcoal, and the regulus boiled with very dilute nitric acid. The analysis of the solution obtained is explained below. The black residue is filtered off, washed with water, and then boiled with very dilute *aqua regia* (1 vol. HNO_3, 4 vols. HCl, 45 vols. H_2O). The resulting solution is added to the nitric acid extract obtained above. The residue consists of lustrous flakes.

1. *Analysis of the residue insoluble in* aqua regia.—This

residue contains *all* the iridium and ruthenium of the alloy. To separate these two metals it is fused with 3 gr. KNO_3 and 10 gr. K_2CO_3, and the product extracted with water. The solution and residue are then poured into a high cylinder, the insoluble powder allowed to subside, and the supernatant liquid decanted off. The residue is washed with dilute sodium carbonate and hypochlorite until the wash water is no longer yellow. The various solutions are then poured into a retort, saturated with chlorine, and distilled into a flask containing water, hydrochloric acid, and alcohol (purified by distillation over potassium oxide). Perruthenic acid passes over into the receiver and there becomes reduced to ruthenium chloride. The distillate is next evaporated to dryness, and metallic ruthenium obtained by reduction in hydrogen. The purity of the metal must be tested after it has been weighed; for this purpose it is dissolved in a concentrated solution of sodium hypochlorite.

The residue left after the product of the fusion with potassium nitrate and carbonate had been treated with water, together with that from the distillation of the perruthenic acid, contains the whole of the iridium. The two are boiled with sodium hydroxide and alcohol, and the iridium oxide obtained purified, and reduced to the metal in hydrogen for weighing.

2. *Analysis of the nitric acid and* aqua regia *solutions.*—These solutions contain all the lead and copper, and also *all* palladium, rhodium, and osmium present in the alloy. The lead is precipitated by the exact quantity of sulphuric acid requisite, and the solution evaporated to dryness and extracted with hydrochloric acid. The lead sulphate is then filtered off and the platinum metals in the filtrate converted to double salts with ammonium chloride. The compounds obtained are dried at a low temperature, and the metals reduced to the metallic state by hydrogen (by which they are obtained in the spongy form). They are next fused with acid potassium sulphate, a dark red heat being employed toward the end of the operation. Platinum remains undissolved, and rhodium and palladium, which go into solution, are extracted with cold water and the platinum filtered off. Palladium cyanide, $PdCy_2$, is precipitated from the filtrate by mercuric cyanide, and

treated according to the method usually employed in quantitative analysis. The rhodium in the filtrate from the palladium is reduced by formic acid and weighed as the metal.

In the hands of Deville and Stas this method has given excellent results. For further particulars concerning it, and also regarding the analysis of platinum ores in general, the reader is referred to the article by Mylius and Förster quoted above. Useful hints on the subject can also be found in the paper by Th. Willm (*Ber. d. deutsch. chem. Gesell.* Bd. 18, S. 2536).

GROUP V

TIN, ANTIMONY, ARSENIC, GOLD, PLATINUM (IRIDIUM, MOLYBDENUM, TUNGSTEN, GERMANIUM, VANADIUM, SELENIUM, TELLURIUM)

§ **70.** The metals of this group are characterised by the insolubility of their sulphides in dilute acids. Hydrogen sulphide precipitates their sulphides from acid solution. These salts are distinguished from the sulphides of Group IV. by their solubility in ammonium sulphide and in other soluble sulphides (*i.e.*, those of potassium, sodium, etc.), with formation of soluble thio-salts.

Classification into Divisions.—The metals of Group V. are sharply distinguished from each other. Antimony, arsenic, and tin form at a high temperature the stable oxides, arsenic acid, stannic acid, and antimonic acid. These acids are formed by fusion of compounds of the respective metals with sodium carbonate and potassium nitrate, an alkali salt of the acid, the metal of which was used, being obtained by the reaction. The oxides of gold and platinum, as well as the majority of their other compounds, are resolved into the metals and oxygen on ignition. If fused as above, the metals themselves are obtained. The ease with which gold and platinum suffer reduction affords other reactions also, which differ materially from those employed in the analysis of arsenic, antimony, and tin. A less important distinction between the metals of Group V. is found in the insolubility of gold and platinum sulphides in hot hydrochloric or nitric acid; the sulphides of arsenic, antimony, and tin are soluble in either medium. A better idea of this group is obtained, therefore, if it be divided into two divisions, according to these characteristics.

Division 1 : Tin, antimony, arsenic.
Division 2 : Gold, platinum.

GROUP V., DIVISION 1

TIN, ANTIMONY, ARSENIC.

Tin, antimony, and arsenic, form two series of compounds. The lower degrees of oxidation are: stannous oxide, SnO, antimony trioxide (antimonious acid), Sb_2O_3, arsenic trioxide (arsenious acid), As_2O_3. The higher oxides are: stannic oxide (stannic acid), SnO_2, antimony pentoxide (antimonic acid), Sb_2O_5, and arsenic pentoxide (arsenic acid), As_2O_5. Stannous oxide readily forms salts with acids, antimony trioxide does not unite with them so easily, and arsenic trioxide possesses distinct, though weak, acid properties. The higher oxides, with exception of stannic oxide, which forms salts with some acids (and at the same time yields stannates with bases), possess pronounced acid characteristics. As a result of these various properties which are shown by the oxides of the metals of Group V., the solution to be analysed may be either neutral (metallic salts of the acids), acid (salts of the oxides and acids—the more usual case), or alkaline (solution in caustic alkalies, thio-salts).

We are also acquainted with two series of sulphides of these metals, corresponding to the oxides. The lower series consists of SnS, Sb_2S_3, As_2S_3; the higher, of SnS_2, Sb_2S_5, As_2S_5. The characteristic distinction found in the oxides also exists between these series. The higher compounds are especially capable of forming thio-salts, in which they combine with the sulphides of the previous groups. Since the sulphides of this group possess the chemical character of anhydrides of thio-acids, *e.g.*,

$$2AsH_3S_4 = As_2S_5 + 3H_2S,$$

their union with the sulphides of other groups to form thio-salts is readily explained.

The series of chlorides are incomplete. Arsenic has no pentachloride. The lower compounds are $SnCl_2$, $AsCl_3$, $SbCl_3$, and in the higher series only $SnCl_4$ and $SbCl_5$ are known. The characteristic properties of these metals, which are placed in Group V. by virtue of their sulphides, and in its first division because of their oxides, are explained above. We shall now take up their general reactions: as the definition of this group indicates, the sulphides and oxides are the most important compounds for the purposes of analysis.

GENERAL REACTIONS

§ 71. **Sulphides and Thio-salts.**—Each metal has two sulphides: SnS and SnS_2, Sb_2S_3 and Sb_2S_5, As_2S_3 and As_2S_5. The colours of these compounds are characteristic. The sulphides of arsenic and stannic sulphide are yellow; the antimony compounds are orange-red; and stannous sulphide brown. The formation and properties of these compounds are as follows:—

(a) *Action of hydrogen sulphide.*—As has already been noticed, the compounds of these metals can occur in alkaline solution (*e.g.*, thio-salts), or have either a neutral (*e.g.*, arsenates) or acid reaction. Neutral and alkaline solutions are not precipitated by hydrogen sulphide, soluble thio-salts being formed instead. This is obvious from the following example:

$$K_3AsO_4 + 4H_2S = K_3AsS_4 + 4H_2O.$$

The sulphides are precipitated by sulphuretted hydrogen only from acid solutions. Before deriving the conditions necessary for this reaction, we must examine its theory. When soluble compounds of the metals of this group are precipitated from acid solution by hydrogen sulphide, not all the sulphides enumerated are obtained. Tin compounds (stannous and stannic) deposit the corresponding sulphides, SnS and SnS_2. Antimony trichloride (and the derivatives of antimony trioxide in general) precipitate Sb_2S_3; arsenic trioxide, arsenic trisulphide, As_2S_3. If an antimony compound be taken as an example, the reaction may be represented as follows:

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$$

The derivatives of antimonic and arsenic acids behave somewhat differently, as the action of hydrogen sulphide also causes their reduction. Hydrogen sulphide converts these salts into the lower compounds, having an effect similar to that which it exerts upon ferric salts (§ 34) or chromic acid (§ 33):

$$Sb_2O_5 + 2H_2S = Sb_2O_3 + 2H_2O + 2S,$$
$$As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + 2S.$$

The reaction between hydrogen sulphide and these compounds actually takes place as follows:—Antimony pentoxide is not fully reduced, and hydrogen sulphide produces in a solution of $SbCl_5$, for instance, precipitates of both antimony pentasulphide and trisulphide; the latter being thrown down from the antimony trichloride formed by reduction of the antimonic compound. If a rapid stream of hydrogen sulphide be allowed to act upon a solution of arsenic acid or its salts, which has been strongly acidified with hydrochloric acid, a precipitate is formed slowly, but consisting wholly of the pentasulphide:

$$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O.$$

If the current of hydrogen sulphide flows slowly, or if the arsenic solution is not sufficiently acid, the arsenic acid becomes partly reduced:

$$H_3AsO_4 + H_2S = H_3AsO_3 + S + H_2O.$$

From the arsenious acid thus formed, sulphuretted hydrogen precipitates the trisulphide.

Although we have represented an acid solution as absolutely necessary for the formation of the sulphides with sulphuretted hydrogen, the following exceptions to this statement must be made:—If an aqueous solution of arsenious or arsenic acid, which presents an acid reaction, be treated with hydrogen sulphide, no precipitate is deposited, but the arsenic sulphide formed remains in solution in the colloidal state. Other sulphides of this group, stannic sulphide for example, when washed until all soluble salts are removed, may pass into the same soluble condition. This may be prevented by the addition of hydrochloric acid in the first case, or, in the second, by the addition of certain salts, such as ammonium acetate, to the wash-water.

The theoretical questions having been answered, it is necessary to know, further, only the conditions involved in the practical application of the reaction.

The conditions of reaction result from the behaviour of the sulphides to the common acids (see below). In the presence of concentrated mineral acids, sulphuretted hydrogen does not precipitate the sulphides completely (this is also the case in the corresponding reactions with sulphides of Group IV.), and the reaction must therefore be made only after the solution, if strongly acid, has been well diluted with water. The best acidifying agent (if such is necessary) is hydrochloric acid; nitric acid is detrimental to thorough precipitation. If these conditions be observed, the precipitation takes place slowly but completely, especially if the liquid be heated to about 70° C. during the operation. A confirmatory test is necessary to ascertain the completeness of the precipitation, since arsenic acid may otherwise escape notice, as it is precipitated by hydrogen sulphide with difficulty. This error may be avoided by careful and not too hasty work, and observance of the necessary conditions. The confirmatory test may be made by heating the filtrate from the precipitated sulphides to about 70° C. with hydrogen sulphide water.

A certain amount of caution is necessary in washing the precipitates. Although while the mother-liquor contains a sufficient quantity of salts or acids no trouble is experienced, the sulphides of this group pass into solution in the colloidal condition as soon as these foreign substances have been removed, and the solution runs through the filter turbid. To avoid this, it is advisable, toward the end of the operation, to add to the wash water some salt, *e.g.*, ammonium acetate, which does not interfere with the detection of the metal. The washed sulphides are dissolved in ammonium sulphide.

(*b*) *Thio-salts.*—The formation of soluble thio-salts demands particular attention, as a reaction by which the metals of Group V. are separated from those of Group IV. We shall first discuss the theory of the reaction, and then consider the normal conditions under which it is brought about in practical work.

The higher sulphides, SnS_2, Sb_2S_5, As_2S_5, possess in many ways the same properties as the anhydrides of the acids. They unite with the sulphides (as the common acid anhydrides unite with metallic oxides) to form salts. These compounds are called thio-salts. Their formation and composition are obvious from the following equation, in which ammonium thio-salts are taken as examples:

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3,$$
$$As_2S_5 + 3(NH_4)_2S = 2(NH_4)_3AsS_4.$$

The composition of the antimony salt is $(NH_4)_3SbS_4$. Remembering that the stannate and arsenate have the formulæ $(NH_4)_2SnO_3$ and $(NH_4)_3AsO_4$, we see that the thio-salts are compounds in which the oxygen of the acid has been displaced by sulphur. Soluble thio-salts are formed by the metals of Groups I. and II.; in other words, soluble sulphides dissolve the higher sulphides of tin, arsenic, and antimony.

The thio-salts of the metals of other groups are insoluble. The composition of the ammonium thioarsenates is usually more complicated than the formulæ given above indicate. They correspond to a series of pyro-salts, which are formed by the following acid:

$$2H_3AsS_4 - H_2S = H_4As_2S_7.$$

Certain other alkali salts are also known which belong to this series. Their formation may be expressed by the following formula:

$$As_2S_5 + 2Na_2S = Na_4As_2S_7.$$

The thio-salts which are insoluble in water may be prepared by double-decomposition of the soluble salts, but this method has no analytical application. Of far more importance is the formation of such thio-salts, especially of the thioarsenates, with zinc or copper, when a solution containing arsenic and one of these metals is precipitated by hydrogen sulphide. It is probable that other similar salts, such as

$$PbS + SnS_2 = PbSnS_3,$$

are also formed, but the latter are decomposed by ammonium sulphide (analogy to the decomposition of the salts of heavy metals by caustic alkalies). A few, however, such as bismuth thiostannate, are not thus decomposed. It has recently been shown that ferrous, mercurous, and cadmium sulphides are soluble in the solution of a thiostannate.

The lower sulphides vary in their behaviour toward the soluble sulphides. Stannous sulphide forms no thio-salts, and is insoluble in ammonium sulphide. Antimony trisulphide is indeed dissolved, but its salts are too unstable to be well known. The arsenic salts are more familiar, although likewise unstable; the ammonium salts correspond to the formulæ $(NH_4)_3AsS_3$ and $(NH_4)_4As_2S_5$. We do not meet with these compounds in analysis, as they cannot form in aqueous solutions. Ammonium polysulphide is invariably used as the solvent of the lower sulphides, and their solution is thus effected by two consecutive reactions. The lower sulphide first unites with the extra sulphur of the ammonium polysulphide, and passes into the higher compound before being dissolved:

$$As_2S_3 + S_2 = As_2S_5.$$

The resulting thio-salt corresponds to the higher sulphide. The reactions in which thio-salts are formed require a careful examination, to which we will now turn.

Action of ammonium sulphide upon the sulphides of Group V.—As has already been mentioned, this reaction must be made with ammonium polysulphide. Ammonium sulphide becomes yellow on standing (through oxidation), and then contains the polysulphide. The latter can also be prepared by the direct solution of sulphur in ammonium sulphide. Besides this condition, the complete solution of tin sulphides, etc., in ammonium sulphide requires that the treatment with the latter be repeated three or four times, in order that the sulphides may completely unite with the sulphur. The reaction is made in practice as follows:—The precipitates of the sulphides having been collected on a filter and washed, they are transferred by means of the wash-bottle to a small beaker, and digested with warm ammonium sulphide. The supernatant liquor is then decanted, a fresh quantity of the reagent added, and the operation once more performed. If only the metals of Groups IV. and V. are present, the reaction may be made by the direct addition of ammonium sulphide, without previous precipitation by sulphuretted hydrogen, the above conditions, however, being observed. It is obvious that in a complete qualitative analysis, the latter method must not be employed if metals of Group III. are present.

Precipitation of thio-salts by acids.—In the course of analysis, the thio-salts (having been filtered from the sulphides of Group IV.) are treated with an acid. Decomposition hereupon ensues, and the sulphides of tin, antimony, and arsenic are thrown down, with separation of hydrogen sulphide (and formation of ammonium salts):

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 6NH_4Cl + 3H_2S.$$

As the thio-salts of the higher sulphides alone are formed, only these, *i.e.*, SnS_2, Sb_2S_5, and As_2S_5, are precipitated in the reaction.

The action of strong acids upon neutral salts is to displace the acid of the latter. In the present instance the thio-acids should theoretically be liberated, but as they do not exist in the free state, their thio-anhydrides are formed instead:

$$SnH_2S_3 = SnS_2 + H_2S.$$

This result is exactly analogous to that obtained by the action of strong acids upon carbonates, sulphites, chromates, etc., in which acid anhydrides are set free.

Hydrochloric acid is the reagent usually employed to precipitate the thio-salts. It must be added to their solution carefully. The precipitated sulphides are more easily filtered if they are first allowed to settle. After the sulphides have been thoroughly washed, the wash water usually begins to pass turbid through the filter (see above). The precipitate generally contains a large quantity of sulphur, formed from the decomposition of the ammonium polysulphide by hydrochloric acid. In the further processes of analysis, the sulphides are subjected to various reactions which are based upon their individual characteristics.

We may remark here, that qualitative analysis requires not only the detection of the metal, but its degree of oxidation. Such questions cannot be answered by the reactions previously given. For instance, hydrogen sulphide reduces arsenic acid (the possibility of its detection is lost); ammonium sulphide has the reverse reaction, converting lower sulphides to the higher (and thus preventing their detection). Such problems can be solved only with the original solution (see Special Reactions).

(*c*) *Properties of the sulphides of Group V. Behaviour to ammonia.*—Caustic alkalies dissolve almost all sulphides. Ammonia, and, to a still greater extent, ammonium carbonate, have a different action. Both dissolve the arsenic compounds, As_2S_3 and As_2S_5, though none of the other sulphides.

The action of caustic alkalies and ammonia is explained by the existence of a peculiar class of salts, analogous to the thio-salts. The latter are defined as compounds in which the oxygen of the acid is completely displaced by sulphur. The other class of salts is formed of those in which the oxygen is not entirely displaced by sulphur, *e.g.*, KH_2AsO_3S. This, as the formula shows, is an intermediate compound. These salts are so unstable, however, that the solution of sulphides in potassium hydroxide is usually accompanied by their partial decomposition :

$$3SnS_2 + 6KOH = K_2SnO_3 + 2K_2SnS_3 + 3H_2O.$$

In qualitative analysis we employ ammonium carbonate. The separation by its means, though not entirely accurate, is very simple. The washed precipitate of the sulphides is transferred to a beaker and digested at a slight heat with solid ammonium carbonate. The arsenic sulphide goes into solution, and is filtered from the insoluble tin and antimony compounds. Arsenic sulphide is precipitated from the solution by hydrochloric acid. The confirmatory tests are given below.

Behaviour toward acids.—Boiling hydrochloric acid dissolves the sulphides (higher and lower) of tin and antimony, with formation of chlorides and sulphuretted hydrogen. The sulphides of arsenic are insoluble in this medium.

If the reaction in which the sulphides are precipitated by hydrogen sulphide in presence of hydrochloric acid be compared with the action of hydrochloric acid upon the sulphides, an apparent contradiction is seen. According to the experiments of Berthollet this reaction depends upon the concentration of the acid. In dilute hydrochloric acid the sulphides are insoluble. The concentrated acid, on the contrary, dissolves them with liberation of hydrogen sulphide. At the point of concentration at which the acid changes from a non-solvent to a solvent, it may be expressed by the formula $HCl + 6H_2O$. An acid stronger than that represented by this formula dissolves the sulphides. More recent investigations tend to show that the manner in which hydrochloric acid acts upon antimony pentasulphide is more complicated than Berthollet assumed.

To dissolve the sulphides, they are boiled with fuming hydrochloric acid until hydrogen sulphide ceases to escape. The end of the reaction is difficultly determined, even with lead acetate paper (Section II., Hydrogen Sulphide). The higher chlorides of tin and antimony are obtained in solution (methods for their detection are given below), and arsenic sulphide remains undissolved. Confirmatory tests of this compound are necessary, as sulphur is also insoluble in hydrochloric acid. They are performed after oxidation of the sulphide.

§ 72. **Stannic Acid, Antimonic Acid, Arsenic Acid.**—To characterise the metals of this group and find confirmatory tests for their recognition, the methods of formation and the properties of the acids which the metals of Group V. yield must be studied.

Oxidation with nitric acid.—Both the metals and the majority of their compounds can be oxidised by nitric acid. To oxidise the metals themselves or their alloys, acid of sp. gr. 1·3 is used. The reaction, which sets in at the ordinary temperature, if the metal or alloy be finely divided, is finished on the water-bath. The alloys are usually analysed in this way.

To oxidise the sulphides, fuming nitric acid must be employed. The sulphides, however, must contain no free sulphur (it may be removed by carbon disulphide), as detonation may otherwise occur. This is less liable to happen if the sulphides be moistened with nitric acid of sp. gr. 1·3, before the addition of the fuming acid. In this case also the reaction sets in at the ordinary temperature, but must be finished on the water-bath. The oxidation yields a white precipitate containing all the stannic and part of the antimonic acid. Arsenic goes into solution. In presence of stannic acid, however, the arsenic may also be found in the precipitate as stannic arsenate,[1] and hence no separation is effected. As the following reaction is very convenient, it is preferable, in qualitative analysis, to avoid the oxidation of sulphides by nitric acid.

Oxidation by chlorine is employed to bring the sulphides into solution (for this it is very convenient), and to convert the lower degrees of oxidation into the higher forms. The compounds are treated with concentrated hydrochloric acid, and small pieces of potassium chlorate then added to the heated mixture. This operation is continued until the sulphides are dissolved. The residue of sulphur often withstands oxidation obstinately, and the reaction may therefore be discontinued as soon as it is ascertained that the insoluble residue is sulphur alone (by its complete combustion upon ignition). Arsenic goes into solution as arsenic acid, tin, and antimony as their higher chlorides, $SnCl_4$ and $SbCl_5$. This reaction is mostly employed to convert arsenic sulphide to arsenic acid, before its subjection to confirmatory tests.

The theory of the action of chlorine upon sulphides, *e.g.*, arsenic sulphide, As_2S_5, is as follows:—The sulphide passes into arsenic trichloride, $AsCl_3$, which is next decomposed to arsenious acid by water. The latter compound is then converted by the excess of chlorine and in presence of water into arsenic acid :

$$AsH_3O_3 + 2Cl + H_2O = AsH_3O_4 + 2HCl.$$

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[1] As $2SnO_2 . As_2O_5 + 10H_2O$. We see that this salt is analogous to stannic phosphate in its insolubility in nitric acid. Arsenic acid is apparently likewise precipitated by antimonic acid (Ljubawin).

The sulphur of the sulphide first unites with the chlorine, to sulphur dichloride, S_2Cl_2, which is decomposed by chlorine and water to sulphurous, and finally to sulphuric acid.

The separation of antimony and tin are discussed in later paragraphs. Arsenic acid, the oxidation-product of arsenic sulphide, is recognised by the precipitation of the characteristic magnesium ammonium arsenate (Special Reactions).

Oxidation with cupric oxide.—The copper oxide employed in this reaction must be prepared from cupric nitrate at the lowest possible temperature, and very finely pulverised. The washed sulphides are dissolved in a porcelain dish in as little sodium sulphide as possible, the solution made alkaline by sodium hydroxide, and cupric oxide added to this solution while boiling. After standing for five minutes the decolorised solution is filtered. The filtrate, when cool, is diluted with $\frac{1}{4}$ to $\frac{1}{3}$ of its volume of alcohol, and the mixture allowed to stand until the sodium pyroantimonate has completely subsided. The latter salt is filtered off, the alcohol removed by boiling, and ammonium chloride added to the solution, which is then treated with hydrogen sulphide. If a precipitate forms, the gas is led through the solution until this redissolves. Ammonium magnesium arsenate is precipitated from this solution, after the addition of one-third of its volume of ammonia, and the precipitate filtered off. The filtrate is precipitated by hydrochloric acid, the tin thus being deposited as sulphide. This method of separating the metals of this Division is more accurate than the foregoing, but somewhat complicated for qualitative analysis.

§ 73. Properties of the Metals and Methods for their Precipitation.—These metals possess in the free state so many characteristics, that they can be qualitatively separated by various means. The methods chosen are those which assist the further processes of analysis.

To precipitate the metals in qualitative operations, we employ reactions in which they are deposited from solutions, and their behaviour toward hydrochloric acid. All of these metals are thrown down from acid solution by zinc. As the separation of arsenic from antimony and tin can be effected by employing the properties of the sulphides (§ 71), this reaction with zinc, although not fully accurate, is used for the separation of antimony from tin. The sulphides having been dissolved according to § 72, small pieces of zinc are added to the acid solution. Care must be taken that the evolution of hydrogen does not become too strong. (Certain characteristic phenomena which may occur in this reaction and aid the detection of antimony are given in the special reactions of this metal.) Complete precipitation requires several hours. The washed metallic powder is next treated with boiling hydrochloric acid. Tin goes into solution as stannous chloride, $SnCl_2$, and is recognised by its characteristic reactions (§ 74). Antimony is insoluble in hydrochloric acid, and after collection upon a filter is subjected to confirmatory tests.

Arsenic is the only metal of this Division which is volatile; and this property, owing to the facility with which it is shown, and to other characteristic phenomena which accompany the operation, forms one of the best reactions of arsenic. Tin gives on fusion a soft, and antimony a brittle globule. For the purpose of examining their characteristics, the metals may be reduced by the "dry methods." Various reducing agents may be employed. Potassium cyanide reduces them at a high temperature, uniting (under these conditions) with their oxygen or sulphur to form potassium cyanate, KCyO, or sulphocyanate, KCyS:

$$As_2O_3 + 3KCy = 2As + 3KCyO,$$
$$As_2S_3 + 3KCy = 2As + 3KCyS.$$

These reactions are used to characterise the metals individually; the conditions of the experiments, and other reduction reactions, therefore, will be explained among the Special Reactions.

SPECIAL REACTIONS

Tin

§ **74.** Metallic tin is white, lustrous, easily fusible (228° C.), and malleable (tinfoil). It is converted to the oxide by fusion in the air. Tin dissolves in boiling concentrated hydrochloric acid to stannous chloride, $SnCl_2$; when dissolved in *aqua regia*, or subjected to the action of chlorine, it passes into stannic chloride, $SnCl_4$. Concentrated nitric acid oxidises it to metastannic acid, while the dilute solvent converts it to stannous nitrate.

Tin forms alloys with most of the metals. Bronze is composed of tin and copper, solder of tin and lead. All the easily fusible metals—*e.g.*, Wood's metal—contain tin. Still another important alloy, that of tin with iron, or tin plate, may be mentioned. The analysis of all these alloys is effected by solution in nitric acid.

Precipitation of metallic tin (§ 73).—Zinc precipitates tin from solution as metallic leaves if the solution be acid, or as a gray spongy mass if it be neutral. If the reaction be made upon a piece of platinum foil, no black spot is obtained (distinction from antimony).

Tin has two series of derivatives, the stannous and stannic salts.

Stannous salts.—Stannous chloride, from which the other stannous compounds are obtained, is prepared by the solution of tin in concentrated hydrochloric acid. If the metal be dissolved in cold dilute nitric acid, stannous nitrate is obtained (solution is not accompanied by the evolution of nitric oxide fumes). The oxygen of the air quickly oxidises stannous solution, the chloride, for instance, being converted to stannic oxychloride, $SnOCl_2$. Oxidising agents (concentrated nitric acid, *aqua regia*, chlorine) convert stannous compounds, *e.g.*, SnO, SnS, into stannic acid (§ 75). Many other substances produce the same result, suffering reduction themselves, while the stannous compounds unite with their oxygen, chlorine, etc., and pass into the stannic state:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$
$$Fe_2(SO_4)_3 + SnCl_2 + H_2O = 2FeSO_4 + H_2SO_4 + SnOCl_2.$$

The stannous compounds, as the above equations show, are powerful reducing agents. Some of the reactions involved are employed as particularly characteristic tests for tin in general, and especially for stannous salts.

Reactions of Stannous Salts.—*Stannous oxide.*—The hydroxide, $Sn_2O(OH)_2$ or $(OH)Sn - O - Sn(OH)$, is obtained as a white, amorphous precipitate when a solution of stannous chloride is acted upon by ammonia, sodium hydroxide, sodium carbonate, or ammonium carbonate. The precipitate is soluble in an excess of caustic alkali, and the solution forms a reducing agent, which is often used to effect oxidation in alkaline solutions (§§ 63 and 67, and below).

Stannous sulphide, SnS (§ 71).—The brown hydrated sulphide is obtained by precipitation of a stannous solution with hydrogen sulphide. The reaction must be made in a solution well diluted with water. The precipitate is almost insoluble in colourless ammonium sulphide, but the yellow variety dissolves it with formation of a thio-salt, first converting it to stannic sulphide. Acids precipitate the higher sulphide from this solution. Caustic alkalies dissolve stannous sulphide, but it is reprecipitated by acids. It is insoluble in ammonium carbonate. Boiling concentrated hydrochloric acid dissolves it, with generation of hydrogen sulphide. Concentrated nitric acid converts the monosulphide to metastannic acid, and by the action of hydrochloric acid and potassium chlorate, tin tetrachloride, $SnCl_4$, is obtained.

Reduction reactions.—We shall discuss those which are most valuable as qualitative reactions of tin, and especially of its stannous compounds.

It may be well to mention that, insomuch as the reactions given below are also caused by many other substances, one of two courses becomes necessary in employing them for the detection of tin. Either the absence of other reducing agents must be established, or, which is still better, the experiment be made with a solution which can contain no other metal than tin, *e.g.*, with the solution finally obtained in the course of analysis. The reduction reactions serve as confirmatory tests for separations. The above precaution must also be taken in reactions with the lower compounds of arsenic and antimony.

1. *Mercuric chloride,* $HgCl_2$.—A small quantity of stannous chloride produces a white precipitate of mercurous chloride, $HgCl$. If an excess of the reagent be added, the precipitate becomes gray and metallic mercury is deposited (§ 61).

2. *Ferric chloride.*—If ferric chloride, $FeCl_3$, be added to potassium ferricyanide, K_3FeCy_6, the solution becomes dark, but no precipitate forms. The addition of stannous chloride to such a mixture produces a blue precipitate of ferrous ferricyanide. The reaction is dependent upon the conversion of ferric chloride to ferrous chloride, $FeCl_2$ (for equation see § 34), the latter forming a blue precipitate with potassium ferricyanide (§ 37 A). The reaction is delicate, and not affected by free hydrochloric acid.

3. *Bismuth nitrate.*—If we add to a stannous chloride solution, enough potassium hydroxide to redissolve the precipitate which at first forms, and then bismuth nitrate, a black precipitate of bismuthous oxide, BiO, is obtained. This is a characteristic and delicate reaction:

$$Bi_2O_3 + SnO + 2KOH = 2BiO + K_2SnO_3 + H_2O.$$

4. *Gold chloride*, $AuCl_3$, is not fully reduced, but yields, according to the concentration of the solution, either a purple-red precipitate or a red liquid (§ 84).

§ 75. Salts of Stannic Acid (stannic oxide).—The anhydrous stannic oxide, SnO_2, possesses two hydrates: stannic acid, $SnO(OH)_2$, and metastannic acid, $Sn_5O_5(OH)_{10}$. These yield the same oxide when ignited. They form stable salts with both acids and bases. For example, corresponding to the anhydrous stannic chloride, $SnCl_4$ (a liquid boiling at 115° C.), two modifications of the hydrated chloride are known: the common chloride and metastannic chloride. We shall first discuss the properties of stannic compounds which we meet in analysis.

Stannic and metastannic acids (§ 72).—We denote by the term "metastannic," the variety of stannic acid obtained by the action of concentrated nitric acid upon metallic tin. This reaction yields a white precipitate of metastannic acid, $Sn_5O_5(OH)_{10} = 5SnO_2 + 5H_2O$, which is almost insoluble in nitric acid. Hot hydrochloric acid does not appear to dissolve it, but a reaction nevertheless takes place, the metastannic acid being converted to metastannic chloride, which is insoluble in concentrated hydrochloric acid. If the latter be poured off and water added, the hydrated chloride goes into solution. Metastannic acid dissolves in bases, with formation of salts which correspond in their composition to the above formula of the hydroxide.

Normal stannic acid forms a hydroxide, $SnH_2O_3 = SnO_2 + H_2O$, a chloride, $SnCl_4$, which for distinction's sake may be termed tin tetrachloride, and also salts such as Na_2SnO_3. All of these compounds are distinct from those of metastannic acid, and must be prepared, as we have said, in the absence of nitric acid. The compound serving as the point of departure in the preparation of derivatives of the ordinary stannic acid is stannic chloride. This salt is obtained by the action of chlorine upon tin, or upon tin compounds in general. It is soluble in water and in hydrochloric acid, and may be prepared by treating any of the tin compounds with hydrochloric acid and potassium chlorate. The addition of ammonium carbonate to its solution causes a precipitate of hydrated stannic acid, which is easily soluble in hydrochloric or nitric acid. The precipitate dissolves in alkalies with formation of stannates. (Native stannic oxide, tinstone, is insoluble in acids. When fused with caustic potash it forms a stannate.)

The conversion of the one acid into the other is easily effected. Metastannic acid is more stable in solution than the common variety, and a solution of the latter is converted quickly on being boiled, slowly by time, into metastannic acid. If the solutions furnished for study have been prepared for some time, therefore, they contain a mixture of the two varieties. In its salts, on the contrary, the normal acid is the more stable. The metastannates, when boiled with caustic soda, and still more readily when fused with it, are converted to sodium stannate.

Distinction between the two acids.—Certain differences between the stannic and metastannic chlorides have already been mentioned (the insolubility of the latter in HCl), but one more distinction may be noticed. Stannous chloride, $SnCl_2$, imparts a yellow colour to a solution of metastannic chloride. Normal stannic chloride does not show this reaction. There is also a distinction in the precipitation of the hydroxides. Sulphuric acid throws metastannic acid down readily and completely, while the normal acid is deposited only from very dilute solution (and on being boiled. An explanation is given below). Metastannic acid is also precipitated by ammonia in presence of tartaric acid, and this is not the case with the normal variety.

Reactions of Stannates (of stannic oxide).—The reactions of this oxide of tin are based upon the precipitation of stannic acid under various conditions. In this regard the two acids show in many cases the same behaviour. Any distinction between them, which occurs in the reactions given, will be pointed out.

Stannic acid is very weak, either as a base or an acid. Its solutions are precipitated, therefore, both by bases and acids, and even by many neutral salts. As we have already said, the solutions with which the student tries the reactions usually contain both varieties of the acid.

Stannic acid.—*Caustic alkalies, ammonia,* and the carbonates of sodium and ammonium produce a white precipitate of stannic or metastannic acid. The former dissolves in caustic alkalies, but is reprecipitated by a great excess of the solvent (especially of sodium hydroxide). Metastannic acid, on the contrary, is difficultly soluble in caustic alkalies (especially in caustic soda; sodium metastannate is insoluble in this medium). In presence of tartaric acid, only metastannic acid is precipitated by ammonia.

Acids.—The behaviour to dilute sulphuric acid is especially characteristic. This reagent completely precipitates metastannic acid from its cold solutions, but throws down the normal stannic acid only when the solution of the latter is very dilute; this variety, however, is also fully deposited from a hot solution. The solution with which the experiment is made must be as exactly neutral as possible. The reaction can be explained by the formation of stannic sulphate, which is immediately decomposed by water:

$$Sn(SO_4)_2 + 2H_2O = SnO_2 + 2H_2SO_4.$$

Neutral salts of the alkali metals, particularly sodium sulphate or ammonium nitrate in cold saturated solution, precipitate both stannic and metastannic acids. This is a characteristic reaction. To ensure complete precipitation, the solution must be neutralised with ammonia if acid, and treated with the reagent while hot:

$$SnCl_4 + 4Na_2SO_4 + 2H_2O = SnO_2 + 4NaCl + 4NaHSO_4.$$

The explanation given above also serves for this reaction: stannic sulphate or nitrate is formed in the first phase of the reaction, and decomposed by water in the second.

Stannic sulphide, SnS_2 (§ 71). — Hydrogen sulphide throws down a yellow precipitate of stannic sulphide (in a solution of the chloride the precipitate is at first white, but finally becomes yellow). The precipitation is complete only in the presence of very dilute hydrochloric acid. Slight heating hastens the reaction. The precipitate is readily dissolved by ammonium sulphide (and alkali sulphides). It is also soluble in caustic alkalies, though not in ammonia or ammonium carbonate, and is dissolved by boiling hydrochloric acid (and by *aqua regia*). Nitric acid converts it to metastannic acid.

The reactions of precipitation of metallic tin which can be used in qualitative analysis have been mentioned in the last paragraph.

Stannic and stannous compounds. — When these occur together they are distinguished by the reducing action of stannous compounds (action upon $HgCl_2$, $FeCl_3$, etc.) To test for stannic compounds we make use of their precipitation by sodium sulphate or dilute sulphuric acid. We have already said that, to determine the degree of oxidation of any metal, tests must be made in the original solution (§ 71): the entire analysis must be completed, however, before it is possible to tell whether the tests described are suitable or not. The compounds of the metals of this group which are used in the arts possess a relatively simple composition, and the question here presents no difficulties.

Antimony

§ **76.** Antimony is a white, lustrous, and hard (brittle) metal. It is easily fusible (425° C.), and volatilises at a very high temperature (its boiling-point is about 1200° C.) Its specific gravity is 6·7. When heated in the air the metal first fuses and then takes fire, giving off white fumes (which condense to crystals) of antimony trioxide. Antimony is almost insoluble in hydrochloric and sulphuric acids. By the action of nitric acid it is converted, according to the conditions present, into antimony trioxide, insoluble in nitric acid, or into antimonic acid. We shall discuss the individual properties of these two series of derivatives somewhat later, and shall first notice the reactions which are common to both.

Precipitation of metallic antimony.—1. If free nitric acid be absent, zinc precipitates metallic antimony in the form of a black powder. When made as follows, the reaction is especially characteristic. A few drops of the antimony solution, acidified by hydrochloric acid (nitric acid is detrimental), are poured upon platinum foil, and a piece of zinc added. The antimony deposited covers the platinum with a thin crust, and a spot, the colour of which depends upon the concentration of the antimony solution, is *immediately* formed. If the latter be dilute the spot is brown-black. The reaction is delicate and easily made, even with very dilute solutions. The spot disappears on being heated with nitric acid (antimonic acid is formed).

2. *Decomposition of antimony hydride.*—Antimony hydride is formed by the action of zinc upon an acid solution of antimony compounds. When lighted, the gas burns with a blue flame and gives off heavy fumes (due to the formation of antimony trioxide). If a porcelain dish be held in the flame for a short time a spot of metallic antimony is obtained. (It disappears again if the flame touch only one portion of the dish.) The spot has a dull, black, non-lustrous colour. It does not vanish when moistened with sodium hypochlorite (does not oxidise: compare the corresponding reactions in the Supplement to this group). The experiment is best made with a hydrochloric acid solution of an oxygen compound (thio-compounds are less suitable). Arsenic gives a similar reaction, and the method of performing the experiment is explained among the special reactions of that metal. The reaction is very delicate, but when arsenic is present it

becomes difficult to discriminate between the spots of the two metals by any simple tests, and the method will therefore not be introduced in the course of analysis.

3. *Soda and potassium cyanide.*—The conditions are described under arsenic, § 78. If the reaction be made in a glass tube the antimony is usually obtained as a black powder. When exposed to the blow-pipe flame upon a charcoal support an antimony regulus is obtained, which is brittle, and, on being heated (and indeed after removal from the flame), emits white fumes of the oxide. The carbon receives a white coating.

Salts of antimonious acid (antimony trioxide).—The representatives of this series of antimony compounds are: antimony trioxide, Sb_2O_3, antimony trichloride, $SbCl_3$, and a few salts of the oxide. The acid properties of the trioxide are slight. It dissolves in alkalies, forming with caustic soda, for example, the compound $NaSbO_2$ (the solution has a strong alkaline reaction). The oxide dissolves readily in hydrochloric and sulphuric acids, but not in nitric acid. When entering into combination with acids, the hydrogen of the acid is usually displaced by the basic radical SbO.[1] The tartrate is especially characteristic. Tartaric acid easily dissolves antimony trioxide, oxychloride, SbOCl (see below), and many other compounds, with formation of the tartrate, $(SbO)_2C_4H_4O_6$. If potassium hydroxide is present, the double salt, $K(SbO)C_4H_4O_6$, or "Tartar emetic," is formed. The antimony in these salts shows certain reactions which differ from those of the trichloride. The compounds of antimony trioxide can exist in acid, neutral, or alkaline solution: we shall observe particularly the reactions in acid solution.

Reactions of antimonious salts.—The reactions of this oxide consist in the preparation of its derivatives, and in reduction reactions caused by antimonious acid. The latter are based upon the conversion of the antimonious acid to antimonic acid (§ 70).

The action of water upon antimony trichloride is a very important qualitative reaction, as in analysis the antimony usually exists in hydrochloric acid solutions (obtained, for example, by the solution of Sb_2O_3, Sb_2S_3, in the acid). Under

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[1] Like the compounds of uranium, bismuth, etc. These are basic salts resulting from the withdrawal of water from the class of salts, $Sb(HO)_2X$ (X is the radical of a monobasic acid).

the conditions given somewhat farther on, water precipitates from such a solution a thick, white, curdy oxychloride, which becomes crystalline when a certain ratio is obtained between the weight of the water and that of the salt:

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

By the prolonged action of a large excess of water, this compound is converted to antimony trioxide:

$$2SbCl_3 + 3H_2O = Sb_2O_3 + 6HCl.$$

Large quantities of free hydrochloric acid prevent the reaction, as the acid redissolves the oxychloride deposited. The strongly acid solutions obtained in the course of an analysis must be freed from their hydrochloric acid, preferably by evaporation, in order to precipitate the oxychloride by water.

The action of water upon antimony salts is distinguished from that upon bismuth compounds (§ 67) by the fact that in the presence of tartaric acid no precipitation ensues, but a soluble antimony tartrate is formed (see above). It is obvious that antimony tartrate and antimony potassium tartrate are not precipitated by water.

Antimonious acid.—The white hydroxide, SbO(OH), is a voluminous precipitate, thrown down by caustic alkalies, ammonia, or sodium or ammonium carbonate (antimony potassium tartrate undergoes this reaction slowly and incompletely). The precipitate is soluble in an excess of potassium hydroxide.

Antimony trisulphide, Sb_2S_3 (§ 71).—Hydrogen sulphide precipitates, in solutions slightly acidified by hydrochloric acid, the orange-coloured trisulphide. Yellow ammonium sulphide redissolves the precipitate (after its transition to the pentasulphide), and the solution of the thio-salt thus obtained deposits antimony pentasulphide on the addition of acids. The trisulphide is also soluble in caustic alkalies (§ 71), but is again thrown down from the alkaline solution by acids. It is insoluble in ammonia or ammonium carbonate, but dissolves in boiling hydrochloric acid with evolution of hydrogen sulphide. If the reaction be made in the presence of potassium chlorate, antimony pentachloride is obtained in solution (§ 72).

Reduction reactions are based upon the transition of antimonious acid to antimonic acid (or of the trichloride to the pentachloride). These reduction reactions have the same importance as those of stannous tin, and must be made with the same precautions as the reactions of the latter metal require.

1. Auric chloride slowly deposits metallic gold at the ordinary temperature:

$$2AuCl_3 + 3SbCl_3 = 2Au + 3SbCl_5.$$

The reaction must be made in the presence of a large excess of hydrochloric acid (antimonic acid will otherwise separate).

2. Silver nitrate produces in an alkaline solution of antimony trioxide a brown, or almost black precipitate of silver oxide, silver, and antimony. The latter two can be distinguished only after treatment of the precipitate with ammonia, which dissolves the silver oxide:

$$AgNO_3 + 3SbKO_2 = Ag + Sb + 2KSbO_3 + KNO_3.$$

This reaction is characteristic of antimony trioxide, in distinction from the pentoxide.

Precipitation of metallic antimony.—The reactions with zinc are especially characteristic. They are described at the beginning of this paragraph, in the list of reactions in which metallic antimony is precipitated.

§ 77. **Salts of Antimonic Acid.**—The cases in which antimonic acid is formed have been mentioned in § 72 (action of concentrated nitric acid upon antimony or the derivatives of antimony trioxide). Its properties will be described below. It is tribasic, but, like phosphoric acid, forms other series of salts, *i.e.*, the meta- and pyroantimonates. Sodium pyroantimonate is an especially characteristic salt. (For its preparation in analytical operations see § 72.) It is used exclusively for the separation of antimony, but owing to the difficulty in obtaining the reaction involved, it is employed only in quantitative reactions. Potassium pyroantimonate serves as a reagent for sodium (§ 12). Antimony pentachloride (or, in general, the solution of antimonic acid in hydrochloric acid) also belongs to this series of derivatives. The solutions of the acid in hydrochloric acid are very frequently met with in practical work, and must therefore be thoroughly studied.

The reactions of antimonates will be discussed at the same time.

Reactions of antimonic salts.—*Antimonic acid* is obtained in the following reactions:—

1. Caustic alkalies, ammonia, and their carbonates, produce in acid solutions of antimony pentachloride a white precipitate of $SbO_2(OH)$.

2. A white precipitate of the same hydroxide is obtained through the action of water: this reaction is similar to that with the trichloride:

$$SbCl_5 + 3H_2O = SbO_2(OH) + 5HCl.$$

3. The solutions of antimonates are precipitated by acids. The hydrated antimonic acid dissolves both in caustic alkalies and in acids. Antimony in its higher degree of oxidation is especially characterised by the following reactions:—

Potassium iodide, when boiled with antimonic acid and hydrochloric acid, becomes decomposed, with liberation of iodine. The iodine dissolves in the hydriodic acid formed, imparting a brown colour to the liquid, and, if the solution be strongly boiled, violet fumes of iodine are given off. Antimonic acid is converted in this reaction to antimonious acid. The reaction is especially fitted to distinguish the pentoxide from the trioxide. It may be expressed by a formula in which either antimonic acid or its pentachloride (in the latter case the reaction is similar to that between potassium iodide and ferric chloride) may serve as the point of departure:

$$SbCl_5 + 2KI = SbCl_3 + 2KCl + 2I,$$
$$Sb_2O_5 + 4HCl + 4KI = Sb_2O_3 + 4KCl + 4I + 2H_2O.$$

Antimony pentasulphide.—Hydrogen sulphide throws down from acid solutions (they must be previously acidified if neutral) an orange-yellow precipitate, which consists of a mixture of the pentasulphide, trisulphide, and sulphur (§ 71 *a*). This precipitate dissolves in yellow ammonium sulphide, and on the addition of an acid the solution deposits the orange-yellow pentasulphide. The properties of this compound are in every way analogous to those of antimony trisulphide (§ 76).

Silver antimonate.—Silver nitrate produces in the solution of an antimonate a white precipitate of silver antimonate, which is soluble in ammonia. In a solution of antimony chloride the reaction is hidden by the formation of silver chloride. This reaction distinguishes antimonic from antimonious acid.

Precipitation of metallic antimony.—The reactions with zinc, etc., are discussed in § 76.

The compounds of antimonic and antimonious acids, when occurring together, are detected in separate portions of the solution; (1) antimonious acid is recognised through the reaction with silver nitrate in alkaline solution; (2) antimonic acid by that with potassium iodide in presence of hydrochloric acid (comp. also Tin, § 75).

Arsenic

§ **78.** Arsenic is an especially characteristic metal. It is gray, has a metallic lustre, and is fairly stable in the air. Its specific gravity is 5·7. It is brittle, and readily pulverised. It volatilises readily when heated, being converted into vapour without previous fusion. If heated in the air it gives out a characteristic odour resembling garlic (due to oxidation). The metal is insoluble in hydrochloric and sulphuric acids, but dissolves in nitric acid, the latter oxidising it to arsenious or arsenic acid, according to the conditions present. Arsenic not only forms these compounds and their derivatives, but often occurs, especially in nature, in arsenides, *e.g.*, $NiAs$, or still more frequently combined with sulphur, in realgar, AsS, and auripigment, As_2S_3. The chief characteristics of arsenic itself are its volatility and the accompanying odour. Its behaviour toward acids, when taken in connection with the readiness with which it is precipitated from compounds, render reactions in which the metal is deposited especially important as qualitative tests. We shall discuss these first, as they are common to all arsenic compounds.

Reactions in which metallic arsenic is precipitated.—The methods employed in making these experiments are various, and depend upon the special property of the metal to be used for its identification—the characteristic appearance of arsenic, condensed from its vapour, its smell, or, finally, its separation from arsenic hydride. These reactions will not be included in the systematic course. They are used in the preliminary tests of the substance to be analysed (comp. Sec. III.), and, more especially, when the presence of arsenic in a substance is to be quickly decided.

1. *Reduction by sodium carbonate and potassium cyanide.*—The test is made in a glass tube, one end of which is blown into the form of a bulb. The thoroughly-dried arsenic compound (the experiment is most successful with an oxide) is introduced into the bulb, and covered with six parts of a mixture of sodium carbonate and potassium cyanide. Special attention must be paid to the dryness of the substance, as the successful outcome of the experiment depends upon this point. The bulb is at first gently warmed, and the water which appears is removed by filter paper (water is due to incomplete drying). The tube is then heated more strongly, whereupon the arsenic is deposited on the sides of the tube, above the hot portion, in the form of a metallic mirror. If the test can be made in a stream of carbon dioxide (which requires an alteration in the apparatus), the delicacy of the reaction is still further increased.

2. *Reduction with carbon.*—The oxides of arsenic are reduced by a mixture of sodium carbonate and carbon, or by carbon alone. The reduction with soda is performed upon a charcoal support, before the blow-pipe: the reduced arsenic burns away completely (white fumes), and in doing so gives off its garlic-like odour. When carbon alone is used, the reduction can be effected in a tube drawn out to a point at one end (this method is less common than the foregoing one). A small piece of arsenious acid (the most suitable compound for this reaction) is placed in the end of the tube, and above it is inserted a stick of charcoal. If the tube be heated in the spot where the latter lies, the arsenic acid vapour undergoes reduction in passing over the carbon and deposits its metal as a mirror.

3. *Precipitation by zinc.*—As metallic arsenic is insoluble in hydrochloric acid, it is precipitated from a hydrochloric acid solution by zinc. The experiment almost always gives rise, however, to the formation of arsenic hydride, and the reaction with zinc is preferably obtained, therefore, by the following modification of this method:—

4. *Decomposition of arsenic hydride.*—Arsenic hydride is

formed under conditions similar to those required for the preparation of antimony hydride. In order to use its formation as a test for arsenic, the experiment is performed in a small flask, of about 50 c.c. capacity, which is closed by a double-bored cork. In one of the perforations is inserted a thick glass tube, ending just below the cork, and bent at a right angle above it; the other holds a funnel-tube which reaches to the bottom of the flask. Some zinc having been placed in the flask, hydrochloric acid and water are poured through the funnel-tube, and the flow of hydrogen allowed to proceed for some time (10-15 minutes, according to the size of the flask), until the air has been completely driven out of the apparatus. The gas issuing at the end of the tube is then lighted: if an insufficient length of time has been allowed, the ignition causes a slight explosion.[1] A small portion of the arsenic solution is now added; care must be taken not to pour in too much, as the evolution of hydrogen may become so rapid that the liquid will be forced out of the apparatus (the precipitated arsenic forms a galvanic couple with the zinc). The experiment is best made with the oxides (the arsenic acids and their compounds). On the addition of the arsenic solution, the hydrogen flame assumes a blue colour and begins to smoke (this results from the arsenic trioxide formed). If a porcelain dish be held in the flame a spot is obtained, which disappears again if the same portion of the dish be continually heated, as the arsenic quickly volatilises. The arsenic spot is brownish black and has a strong metallic lustre, which distinguishes it from antimony. It is further characterised by its immediate solution in sodium hypochlorite. This is one of the most delicate tests which we possess for arsenic: when only traces of the metal are sought for, the experiment must be made with greater caution (see Supplement, the Marsh apparatus. The reactions which distinguish arsenic from antimony are also there given). Experiments with arsenic hydride must be performed with the greatest caution, as the gas is a deadly poison.

Arsenious acid and its salts.—Arsenious anhydride, or the trioxide, As_2O_3, is difficultly soluble in water, in either its

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[1] The explosion can be prevented by a slight contrivance attached to the apparatus. The delivery tube is prepared in two sections, one wide and the other narrow, which are joined by a cork made of wire netting.

vitreous or crystalline modification. It dissolves more readily in hydrochloric acid (on evaporation of this solution the volatile arsenic trichloride is formed). Arsenious acid has weak acid properties. Its only soluble salts are those of the alkali metals.

Reactions of the Salts of Arsenious Acid.—These consist either in the preparation of characteristic arsenites, or in reductions which arsenious acid causes in passing into arsenic acid.

Arsenic trisulphide, As_2S_3.—Hydrogen sulphide throws down from slightly acid solutions a yellow precipitate of arsenic trisulphide. Neutral and alkaline solutions are not precipitated. The conditions of reaction are given in § 71. The precipitate is insoluble in colourless ammonium sulphide, but dissolves in the polysulphide with formation of a thioarsenate; acids precipitate arsenic pentasulphide from such a solution. The trisulphide also dissolves in caustic alkalies and ammonia, and its characteristic solubility in ammonium carbonate distinguishes it from both tin and antimony sulphides. Arsenic trisulphide is insoluble in boiling hydrochloric or sulphuric acid (distinction from Sn and Sb). It is converted to arsenic acid on treatment with concentrated nitric acid, or with hydrochloric acid and potassium chlorate, and also if fused with soda and potassium nitrate. The principal arsenites, analytically, are the silver and copper salts. These salts are characterised by their reduction to metallic silver and cuprous oxide respectively. The conditions under which the reactions must be performed are explained under the Stannous Salts.

Silver arsenite, $AgAsO_3$.—Silver nitrate produces in solutions of arsenites a yellowish white precipitate of silver arsenite, which dissolves in nitric acid, ammonia, or ammonium nitrate. The latter fact makes the precipitation of the silver salt from a solution in nitric acid by neutralisation with ammonia extremely difficult. Prolonged boiling of a solution of silver arsenite in ammonia causes metallic silver to be deposited, while the acid is converted to arsenic acid.

Copper arsenite is deposited as a yellowish green precipitate, when the solution of an arsenite is precipitated by copper sulphate. If a few drops of the latter be added to the solution of an arsenite which has been previously treated with a fair amount of alkali, however, no precipitate ensues, but a blue coloration of the liquid is caused. If the resulting solution be boiled, an orange-coloured precipitate of cuprous oxide separates, and the liquid becomes colourless. The arsenious acid is converted to arsenic acid:

$$AsK_3O_3 + 2CuSO_4 + 4KOH = AsK_3O_4 + Cu_2O + 2K_2SO_4 + 2H_2O.$$

Precipitation of metallic arsenic.—The reactions are given at the beginning of this paragraph. They serve as good qualitative tests for arsenic.

§ **79.** *Arsenic acid and its salts.*—Arsenic acid, H_3AsO_4, is similar in its properties to phosphoric acid (their salts are isomorphous). The salts of the alkalies alone are soluble in water, but the others dissolve in acids, with the same distinction toward the various acids as the phosphates show. Ferric and aluminium arsenates are insoluble in acetic acid, but dissolve in mineral acids. The mercury, tin, bismuth, and ammonium molybdate salts are insoluble in nitric acid. From both the qualitative and quantitative standpoints the ammonium magnesium double salt is the most characteristic (as of phosphoric acid).

Reactions of Arsenates.—The reactions of arsenic acid consist in the preparation of its characteristic salts. It is distinguished from arsenious acid by its inability to act as a reducing agent.

Arsenic pentasulphide.—Hydrogen sulphide precipitates the pentasulphide from acid solutions (conditions see § 71 *a*). Alkaline and neutral solutions are not precipitated, and must therefore be previously acidified with hydrochloric acid. The reaction takes place very slowly; no precipitate at all appears at first, unless substances are present which reduce the arsenic acid, such as a solution of sulphur dioxide, or sodium sulphite and hydrochloric acid, in which case the sulphide begins to form at once. If reducing agents cannot be used, the solution is precipitated while warm (at about 70° C.), but even then the reaction is slow (the student must bear this in mind). Arsenic pentasulphide is obtained from its solution in ammonium sulphide (from the thioarsenate, see § 71), by precipitation with an acid. The properties of the pentasulphide are completely analogous to those of the trisulphide, which are described in § 78.

Ammonium magnesium arsenate, $Mg(NH_4)AsO_4$, is the most characteristic salt of arsenic acid. In presence of ammonium chloride and ammonia, magnesium sulphate precipitates from the solutions of arsenates (under the same conditions as are required with phosphoric acid, § 23), the white, crystalline ammonium magnesium double salt. The precipitate is only slightly soluble in water, but readily so in acids. It differs from the analogous phosphate in depositing yellow arsenic pentasulphide (from its acid solution) when treated with hydrogen sulphide. The salt is also distinguished by the reaction with silver nitrate, which it shows if, after the removal of ammonium chloride by washing, it be dissolved in nitric acid. On the addition of silver nitrate this solution deposits silver arsenate. (Arsenious acid forms an ammonium magnesium double salt which at first view closely resembles this compound, but it is much more soluble in water.)

Silver arsenate, Ag_3AsO_4.—Silver nitrate throws down a brown-red precipitate of silver arsenate. This salt is soluble in nitric acid, ammonia, and ammonium nitrate; strongly nitric acid solutions are therefore not precipitated by ammonia. Metallic silver does not separate when the ammoniacal solution is boiled (distinction from arsenious acid). This silver salt affords a means of detecting arsenic acid in presence of arsenious acid. If it be dissolved in the least possible quantity of nitric acid, and ammonia cautiously added (drop by drop) until the solution is neutral, the brown-red arsenate is first precipitated, the yellow arsenite following.

The reactions in which metallic arsenic is precipitated are given in § 78. They are applicable to the compounds of arsenic acid.

The salts of arsenious and arsenic acids are distinguished from each other by the following reactions:—1. Arsenious acid is characterised by the reduction of its copper and silver salts. 2. Arsenic acid is detected through the formation of its ammonium magnesium double salt, its silver salt, and the non-reduction of the latter. (For the use of these reactions see Tin, § 75.)

COURSE OF ANALYSIS FOR THE METALS OF GROUP V., DIVISION 1

§ 80 A. **Metals of Group V., Division 1.**—The compounds of the metals of this Division may exist (1) in acid solutions—those of the acids and their compounds in hydrochloric acid, *aqua regia*, etc.; (2) in neutral solutions, which contain the soluble (alkali) salts; (3) as thio-salts in alkaline solution. Under any of the three conditions the first operation is to obtain the metals as their sulphides, but since the methods vary in the different cases, the latter must be considered separately.

1. *Acid* solutions are diluted with water, whether a precipitate forms or not, and treated with hydrogen sulphide until precipitation is complete (§ 71). It must be remembered that arsenic acid is not immediately thrown down by hydrogen sulphide. Satisfactory results are obtained only when the reaction is made according to § 78.

2. *Neutral* solutions must be acidified with hydrochloric acid before the precipitation, the reagent being added in drops until the reaction is slightly acid. Under certain conditions, such as when potassium antimony tartrate is present, this may result in the formation of a basic salt. Such a precipitate is to be disregarded, and the solution treated as in the foregoing case.

3. *Alkaline* solutions must also be acidified, the acid being added cautiously. If thio-salts are present its addition sets hydrogen sulphide free (ammonium sulphide and similar compounds are decomposed), and a precipitate of the metallic sulphides immediately forms in consequence. To determine whether the precipitation is already thorough, the filtered solution must be again treated with hydrogen sulphide. If thio-salts are present, hydrochloric acid must be added until they are completely decomposed.

The sulphides having been collected and well washed, their separation is next undertaken. Reliable methods for performing this operation are very complicated, and, as we have said in discussing the general reactions, the more or less inexact action of hydrochloric acid or ammonium carbonate upon the sulphides is usually employed.

1. *Boiling the sulphides with hydrochloric acid.*—The precipitated sulphides are introduced into a small flask and boiled with fuming hydrochloric acid until the evolution of hydrogen sulphide ceases (§ 71 *d*). The arsenic sulphide is filtered, washed, and treated with hydrochloric acid and potassium chlorate (§ 72). The ensuing solution (after concentration, if necessary; this often causes sulphur to be deposited) is subjected to the characteristic tests for arsenic acid. The solution obtained by the action of hydrochloric acid upon the mixed sulphides is tested for antimony by pouring a few drops of the liquid upon some platinum foil and adding a piece of zinc. The formation of a black spot indicates antimony. If antimony is present, it is separated from tin by the precipitation of both metals by zinc and treatment of the metallic deposit with boiling hydrochloric acid. The solution is tested for tin (by the action of $HgCl_2$, or of $FeCl_3$ and potassium ferricyanide, § 74). The black powder of metallic antimony left upon the filter is subjected to confirmatory tests according to § 76.

2. *The treatment of the sulphides with ammonium carbonate* is carried out as in § 71 *c*. The liquid is filtered, and the residual sulphides of antimony and tin washed, dissolved in hydrochloric acid, and treated as above. The solution of arsenic sulphide in ammonium carbonate is then decomposed by hydrochloric acid. Although arsenic sulphide is formed in this operation, it is still advisable to pass hydrogen sulphide through the solution. The precipitated sulphide having been dissolved in hydrochloric acid and potassium chlorate, it is tested by the reactions of arsenic acid (as in 1). The method is not accurate, and the incomplete separation may thus cause some of the reactions to fail.

In accurate analyses these metals are separated by cupric oxide in alkaline solution (§ 72).

Tests for the degree of oxidation must be made in a portion of the original solution, after the metals themselves have been detected (§§ 77 and 79). Before they are made, it must be decided whether the chosen reaction is possible in the presence of the metals which have been found.

B. *Metals of Group V., Division* 1 *from Groups I., II.,* *III., and IV.*—The course of analysis is laid as in A, but is somewhat complicated by the presence of certain foreign metals. The first operation is, as before, acidifying with hydrochloric acid. The solution may in this case also be either neutral, acid, or alkaline.

1. When an acid solution is acidified, a precipitate of silver chloride or mercurous chloride may result; lead chloride will not be fully deposited. This precipitate is filtered, washed, and analysed according to § 68. In this case hydrochloric acid must obviously be added until the chlorides are completely deposited.

2. A precipitate can also ensue when neutral or alkaline solutions are acidified. (If it redissolves when boiled it may be neglected.) If hydrogen sulphide escapes, the solution contained thio-salts, and the precipitate consists of the sulphides of Group V. This precipitate is treated as below, *e.g.*, with ammonium sulphide, etc.

After the addition of hydrochloric acid the solution is precipitated by hydrogen sulphide (or H_2S water; comp. § 79, on the precipitation of arsenic acid). The precipitated sulphides must be thoroughly washed. (This operation is controlled by evaporating a few drops of the filtrate upon platinum foil; see § 16, Remark.) The filtrate is subjected to the various tests for Groups I., II., and III. The moist precipitate, which consists of the sulphides of Groups IV. and V., is removed to a flask and twice (§ 71) digested with warm ammonium sulphide. The insoluble sulphides of Group IV. are then filtered off, thoroughly washed, and analysed according to § 68. The ammonium sulphide solution is diluted with water, and the thio-salts decomposed by the gradual addition of hydrochloric acid. The sulphides of Group V., which are precipitated, are analysed according to A. If copper is present sodium sulphide should be substituted for ammonium sulphide, but in this case mercury must be absent.

It may be remarked, in closing, that before performing all these reactions in a complete analysis, it is advisable to make the tests in separate portions of the liquid or precipitate. All the metals of the various groups are seldom found in a single analysis (for instance, the metals of Groups III. and IV. never occur in alkaline solution), and by preliminary tests, therefore much time is saved which would otherwise be consumed by the unnecessary reactions.

SUPPLEMENT

1

Analysis of tin, antimony, and arsenic compounds which occur in nature.—Tin is found in nature only as tin-stone (tin dioxide), a mineral which is insoluble in acids, and dissolved for analysis by fusion with caustic potash. The fusion-product is extracted with water, and a solution of potassium stannate thus obtained. Arsenic often occurs in the metallic state, but more frequently combined with other metals. A few of its compounds have been considered under nickel and cobalt (copper-nickel, cobaltine, etc., § 49), and still others in connection with the metals of Group IV. (gray-copper, § 68). Arsenical pyrites, FeSAs, may again be mentioned. Many of these minerals are insoluble in acids, and must be converted to soluble compounds by fusion with sodium carbonate and potassium nitrate, treatment with chlorine, or by similar methods. The two sulphides of arsenic, realgar, AsS_2, and orpiment, AsS_3, are still to be noticed. The methods for their analysis are based upon the properties of the sulphides and the conversion of the latter to arsenic acid (§ 72). The most important ore of antimony is the trisulphide, which is dissolved by hydrochloric acid with evolution of hydrogen sulphide. The compounds of antimony sulphide with the sulphides of other metals are nearly all soluble in hydrochloric acid, though in some cases potassium chlorate must be added to effect their solution.

2

Use of the compounds of the metals of this Division in analysis.—The salts of stannous oxide are principally employed in analysis as reducing agents. Stannous chloride is used to reduce chromic acid (§ 33), and cupric (§ 64) and mercury compounds (§ 61). Ferric iron may also be determined volumetrically by a solution of stannous chloride. Still more powerful reducing effects are caused by a solution of stannous oxide in caustic potash. The use of this reagent is explained under copper (§ 63), and bismuth (§ 67). Arsenious acid is also employed in volumetric analysis as a reducing agent (Section II., The Halogens).

3

§ **81.** *Marsh's apparatus.*—The properties of antimony and arsenic hydrides have already been shown to afford very delicate tests for the respective metals. The hydrides are decomposed at a high temperature, with formation of a metallic spot; as the investigation of the latter does not enable an accurate distinction to be made between the two metals, however, the experiment must be made in another manner in order to characterise them. The apparatus used for this purpose, or Marsh's apparatus, as it is called, consists of a hydrogen evolution flask. The hydrogen generated, with the attendant antimony and arsenic hydrides, is dried by passing through a calcium chloride tube, and then led into a tube made of difficultly fusible glass, which is connected with the calcium chloride tube; it is slightly contracted in two or three places, and its free end tapers out to a point. The apparatus having been filled with hydrogen, the gas is lighted at the end of the tube, and the purity of the materials used thus tested. This test is made just as the experiment itself, which will be described below. The glass of which the apparatus is composed must also contain no arsenic. If the result is satisfactory, a very small quantity of the substance to be investigated is introduced into the flask, and the change of colour in the flame noticed. A spot is not formed as in the simpler test, the hydride being decomposed by a high temperature instead. To this end the portion of the tube in the neighbourhood of a contraction is heated to redness by a gas-flame. Any arsenic or antimony hydride passing over the heated spot becomes decomposed, and the metal, which is volatile in the hydrogen current, is deposited as a mirror[1] in the contracted portion beyond. (Several mirrors are formed in the different contracted portions of the tube.) The metallic mirrors show a certain difference, that of antimony being silver-white, while a darker one is formed by arsenic or arsenic hydride. They also vary in their volatility. The arsenic mirror can easily be driven from place to place by heating in the stream of hydrogen, and the characteristic volatility of arsenic without previous fusion is seen. Antimony, on the contrary, melts without volatilising, and the small globules of the metal can readily be observed through a magnifying glass. This, however, does not suffice for the distinction between arsenic and antimony, and the mirror must be more accurately tested. For this purpose we make use of the unequal volatility of the sulphides in a stream of hydrogen sulphide, and the still more accurate conversion of antimony sulphide into the chloride by gaseous hydrochloric acid (which has no effect upon arsenic sulphide). A sulphuretted hydrogen apparatus having been substituted for the hydrogen flask, dry hydrogen sulphide is led over the heated mirror (it must first be proved that the gas is pure and contains no arsenic). The mirror vanishes, and the sulphides are obtained, the latter varying both in colour and volatility. Arsenic trisulphide is readily volatile and yellow, while the antimony compound is non-volatile and orange-red (or even black). The vapour of the arsenic trisulphide condenses beyond the heated spot, the antimony sulphide remaining unmoved, and the difference in the colours is thus easily observed. This reaction having been satisfactorily made, the next and principal test is instituted. The hydrogen sulphide apparatus is taken away, and in its stead a hydrochloric acid generator is attached to the tube and the dry gas led over the heated sulphides. Antimony sulphide is converted to the chloride, which is volatile in an atmosphere of hydrochloric acid. It may be absorbed, if necessary, in a receiver filled with water and tartaric acid. Arsenic

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[1] Retgers (*Zeits. f. anorganische Chemie*, iv. 739) has shown that the mirror is formed, not by metallic arsenic, but by the brown, solid arsenic hydride, AsH.

sulphide undergoes no change and the yellow deposit of the latter remains in the tube. Another method of analysis is based upon the variations seen in the behaviour of arsenic hydride and antimony hydride toward a solution of silver nitrate. This test requires the previous purification of the gases. They are conducted through a solution of lead acetate, which frees them from hydrochloric acid (if the hydrogen was prepared from zinc and hydrochloric acid) or from hydrogen sulphide (which is sometimes present in hydrogen prepared from zinc and sulphuric acid). The purified gases are then passed through a solution of silver nitrate. Antimony hydride precipitates black silver antimonide, while arsenic hydride throws down metallic silver and becomes oxidised to arsenious acid:

$$3AgNO_3 + SbH_3 = SbAg_3 + 3HNO_3,$$
$$6AgNO_3 + AsH_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3.$$

The precipitate is filtered, washed, and the antimony dissolved by boiling with water and tartaric acid (the resulting solution is tested according to § 76). Arsenic remains in the filtrate as silver arsenite, and upon cautious neutralisation with ammonia the yellow salt will be deposited. If the silver be precipitated from this solution by hydrochloric acid, the arsenic may also be thrown down by hydrogen sulphide as arsenic trisulphide. The confirmatory tests for arsenic must be made in either case.

4

GERMANIUM, VANADIUM, MOLYBDENUM, TUNGSTEN, SELENIUM, TELLURIUM

GERMANIUM

§ 82. Germanium was discovered by C. Winkler in argyrodite (compound of the sulphides of silver and germanium, $3Ag_2S + GeS_2$), a silver ore found in Freiberg, Saxony. The metal also occurs in very small quantities in euxenite from Bögerö, Sweden.

Germanium is a brittle, gray metal and does not oxidise in the air. It dissolves in *aqua regia*, and is oxidised by nitric acid to germanium oxide, GeO_2, which is white. Germanious oxide, GeO, is also known. The sulphides correspond to the two oxides; GeS_2 is a white precipitate which is thrown down by hydrogen sulphide from acid solutions, and soluble in ammonium sulphide. Germanium chloride, $GeCl_4$, boils at 84° C. The germanium salts show no especially characteristic reactions. In the metallurgy of the native germanium compounds, this metal is obtained in solution with the thio-salts of Group V. The liquor is diluted with water, and the fifth-group sulphides precipitated by an exactly sufficing quantity of dilute sulphuric acid. Germanium sulphide must remain in solution, which necessitates 222 parts of water. The solution is evaporated, and the sulphide thrown down by an acid, in presence of hydrogen sulphide.

VANADIUM, MOLYBDENUM, TUNGSTEN

These metals are in part analogous to phosphorus (vanadium), and in part to sulphur (molybdenum and tungsten). Their hydrated oxides, like those of arsenic, possess almost exclusively the character of acids; *e.g.*, vanadic acid, H_3VO_4, molybdic acid, H_2MoO_4, and tungstic acid, H_2WO_4. Their oxides are stable at a high temperature, and for this reason the metals are classed with Group V. Division 1. Their sulphides are also precipitated by hydrogen sulphide, and form thio-salts with soluble sulphides.

Vanadium often accompanies iron and copper in their ores, and is found in some clays, and in rare minerals; *e.g.*, in vanadinite (lead vanadate), and volborthite (copper vanadate). It has several degrees of oxidation—the monoxide, VO, sesquioxide, or vanadious oxide, V_2O_3, dioxide, VO_2, and pentoxide, or vanadic acid, V_2O_5. These oxides have their corresponding chlorides. The monoxide, VO, is gray, and was at first mistaken for the metal itself. It dissolves in acids with evolution of hydrogen, the blue solution formed being a strong reducing agent. Vanadious oxide is black, and dissolves in acids with oxidation to vanadic acid. Vanadic pentoxide, V_2O_5 (the hydrate is unknown), forms easily fusible, transparent, reddish crystals, which dissolve with difficulty in water, but readily in acids. The salts of vanadic acid are analogous to those of phosphoric acid, and are for the most part metavanadates, as $(NH_4)VO_3$; the mineral compounds are tribasic (orthovanadates) *e.g.*, $Pb_3(VO_4)_2$, $Cu_3(VO_4)_2$. The alkali vanadates are soluble, though the ammonium salt is difficultly so. Vanadyl trichloride, $VOCl_3$ (a liquid boiling at 127° C.), is similar to phosphorus oxychloride; water decomposes it to vanadic and hydrochloric acids.

Reactions of vanadic acid and its salts.—1. *The reactions of vanadic acid in acid solution* consist entirely in reductions, in which the yellow or brown solution becomes blue (reduction to the monoxide). This reaction is caused by zinc, sulphurous acid, or hydrogen sulphide. The action of ammonium sulphide is discussed below.

2. *The reactions of vanadates* consist in the formation of characteristic salts of the acid. Acids impart a yellow (reddish) colour to their solutions.

Vanadium oxysulphide, $V_2S_3O_2$.—Ammonium sulphide causes a black solution of a thiovanadate, without the formation of a precipitate. On the addition of hydrochloric acid this solution deposits a brown precipitate of $V_2S_3O_2$.

Ammonium vanadate.—Ammonium chloride produces a white precipitate of $(NH_4)VO_3$, insoluble in ammonium chloride (it is used in quantitative estimations).

The silver, lead, and copper salts are yellow precipitates which dissolve in nitric acid. Copper orthovanadate is a green precipitate (distinction from the meta-salt).

Tannic acid gives (especially in acid solutions) a black colour. The borax bead assumes a green colour in the reduction flame.

Analysis of vanadinite, $PbCl_2 + Pb_3(VO_4)_2$.—This mineral, which is rare, dissolves in nitric acid. The solution is gently heated with ammonium sulphide and ammonia, the lead filtered off, and vanadium oxysulphide precipitated by an acid. The dried precipitate is ignited, fused with a small quantity of potassium nitrate, and the potassium vanadate obtained then precipitated by ammonium chloride. The ammonium salt yields vanadium pentoxide on ignition, and this is weighed. The same method (sometimes with previous fusion with potassium nitrate) is followed in the analysis of other mineral vanadates (of iron, copper, etc.) Roscoe has recently recommended for quantitative determinations the basic lead salt (which is to be dried at 100° C.)

Molybdenum is found in molybdenite, MoS_2, wulfenite, $PbMoO_4$, and more rarely as molybdic ochre, MoO_3. It has several degrees of oxidation. The lower oxides, Mo_2O_3 and MoO_2 are converted by ignition in the air, or by the action of nitric acid, into molybdic acid; all the oxides are reduced in hydrogen to the shining white metal (soluble in nitric acid and *aqua regia*). Molybdenum unites with chlorine in various proportions, and also forms an oxychloride. The fluorides form many double salts, such as $K_2MoO_2Fl_4 + H_2O$, etc.

Reactions of molybdic acid and its salts.—Molybdic trioxide, the acid anhydride, forms white scales, and can be sublimed. When ignited, it is insoluble in acids (the non-ignited oxide is somewhat soluble). Its hydrate, molybdic acid, which is obtained by precipitation with acids, is soluble in an excess of the precipitant, and if this solution be dialysed, molybdic acid is obtained in a soluble modification. The molybdates contain a varying quantity of the metal: neutral alkali molybdates, *e.g.*, K_2MoO_4, are soluble in water. Phosphomolybdic acid, § 50. The reactions of acid solutions of molybdic acid consist mostly in reductions, and are characterised by a change in the colour of the solution. Zinc (copper) and stannous chloride produce blue solutions of very complicated molybdenum oxides (M_2O_5, M_8O_8, etc.) Hydrogen sulphide precipitates neither acid solutions of molybdic acid nor those of its salts immediately; but a brown precipitate of MoS_3 separates (from acidified solutions) on prolonged action of the gas. This precipitate dissolves in ammonium sulphide as the thiosalt, $(NH_4)_2MoS_4$; and acids throw down MoS_3 from the latter solution. If compounds of molybdenum be heated with a drop of sulphuric acid upon platinum foil, the acid turns blue.

Analysis of wulfenite, $PbMoO_4$.—The pulverised mineral is decomposed by hot nitric acid. The solution is warmed with ammonia and ammonium sulphide, and molybdenum sulphide then precipitated by nitric acid from the thiomolybdate formed. The precipitate is collected, dried at 100° C., on a weighed filter, and then weighed. A known quantity of it is then reduced by heating in a bulb-tube in a current of hydrogen, and the quantity of molybdenum calculated from the weight of the MoS_2 formed and the original weight of the precipitate.

Molybdenite is ignited in the air, extracted with ammonia, and precipitated by mercurous nitrate. The precipitate is collected upon a weighed filter (and dried at 100° C.); a weighed portion is then ignited in a current of hydrogen. The weight of the MoO_2 formed gives the weight of the entire precipitate.

Tungsten.—Tungsten occurs in nature as calcium tungstate (scheelite),

$CaWO_4$, and as $FeMn(WO_4)_2$ (wolfram). The metal is obtained by reduction of the oxides in hydrogen (or with carbon; ferro-wolfram with 80 per cent of tungsten has recently been obtained in this way). It oxidises to tungsten trioxide on ignition in the air, but is insoluble in acids. It unites with chlorine in several proportions (WCl_6, WCl_5, WCl_4): these compounds are decomposed by water. Tungsten also forms double fluorides, as $K_2WO_2Fl_4$.

Reactions of tungstic acid.—The anhydride, WO_3, is yellow, and insoluble in either water or acids. After fusion with acid potassium sulphate and digestion with water (it does not dissolve immediately) the fusion-product goes into solution as a mixture of potassium tungstate and tungstic acid (especially in presence of ammonium carbonate—distinction from silica). It forms soluble salts when fused with potassium and sodium carbonates. Hydrochloric acid throws down from the solution of a tungstate a white precipitate, which becomes yellow when boiled, and consists of the hydrated acid $WO(OH)_4$; this is insoluble in acids (distinction from Mo), but dissolves in ammonia. The insoluble tungstates of calcium, barium, lead, silver, and mercury, form white precipitates. Hydrogen sulphide throws down the brown tungsten sulphide, WS_3 (only from acid solutions), which dissolves in ammonium sulphide to the thiotungstate, $(NH_4)_2WS_4$. Stannous chloride or zinc (with hydrochloric acid) causes its solutions to assume a beautiful blue colour (reduction to W_2O_5). *Metatungstic acid*, or soluble tungstic acid, is formed by the action of sodium tungstate upon the insoluble acid, or merely by that of acetic or phosphoric acid upon solutions of tungstates. The metatungstates formed (*e.g.*, $Na_2W_4O_{13}$) are completely soluble in water. Metatungstic acid is converted by the action of alkalies to tungstic acid. The latter, like molybdic acid, forms complicated compounds with phosphoric acid (both phosphomolybdic and phosphotungstic acids form difficultly soluble salts with the alkalies, ammonia, and the organic ammonias).

Analysis of wolfram.—The lixiviated mineral is heated with a mixture of concentrated hydrochloric acid (4 parts) and nitric acid (1 part), and evaporated to dryness on the water-bath. On digestion with water the tungstic acid remains as a residue. It is filtered, washed with alcohol, and dissolved in ammonia (which often leaves a residue of niobic acid). The ammoniacal solution is evaporated, the residue ignited in the air, and the tungstic acid weighed.

SELENIUM, TELLURIUM

§ 83. These metals are analogous to sulphur, and their compounds are isomorphous with those of the latter. They are placed in Group V. because hydrogen sulphide throws down their sulphides and the precipitates are soluble in ammonium sulphide.

Selenium occurs in nature in selenides (of lead, copper, mercury), and sometimes with iron in pyrites. It is obtained as a red powder from the deposits in the sulphuric acid chambers in the manufacture of that acid. Selenium is steel-gray, fuses at 217° C., and is soluble in carbon disulphide. When quickly cooled down from the fused state, it forms a brown powder which is insoluble in carbon disulphide (see

Sulphur). When deposited from compounds it is red (see below). It boils at 700° C., and when heated in the air oxidises to selenious acid, which possesses a characteristic smell resembling that of decayed radish. Nitric acid and *aqua regia* dissolve the metal, with production of selenious acid.

Reactions of selenious acid and its salts.—Selenious anhydride, SeO_2, gives off yellow vapours at 200° C., which recondense to white needles on cooling. Selenious acid forms salts analogous to the sulphides; only the alkali selenites are soluble. The lead and mercury salts are difficultly soluble in nitric acid. Hydrogen sulphide precipitates (only from acid solution) yellow selenium sulphide, the composition of which is undetermined; it is soluble in ammonium sulphide. Barium chloride throws down white $BaSeO_3$, soluble in acids. Selenium is characterised by the ease with which it undergoes reduction (distinction from sulphur). Stannous chloride and sulphurous acid (in presence of HCl) precipitate the metal as its red modification from hot solutions, while if the latter be cold the gray variety is deposited.

Reactions of selenic acid.—Selenic acid, H_2SeO_4, is a thick liquid. The alkali salts are prepared by the fusion of metallic selenium or selenium dioxide with potassium carbonate and nitrate. Solutions of selenates are unstable; when warmed with hydrochloric acid, selenious acid is formed and chlorine escapes. Potassium selenocyanate, KCNSe, obtained by the action of potassium cyanide upon selenium or its derivatives in a current of hydrogen, does not deposit its selenium when exposed to the air (comp. Tellurium). Selenium compounds colour the non-luminous flame blue.

Analysis of Selenides (Section II., Sulphur).—This is accomplished by treatment with chlorine in a difficultly fusible glass tube. The volatile selenium chloride passes into a receiver filled with water, where it decomposes to selenious acid, and is further oxidised to selenic acid by the saturated chlorine solution. It may then be determined quantitatively as barium selenate (*v.* estimation of sulphuric acid, Part II., Sulphur). The non-volatile chlorides, $PbCl_2$, AgCl, remain in the bulb of the tube. The presence of sulphides does not render an alteration in the process necessary. The sulphate and selenate are weighed together; a portion of the precipitate is then reduced in hydrogen, whereupon barium selenite is formed, and this salt extracted with hydrochloric acid. The residual sulphate is weighed, and from the data found the proportions in the original precipitate are calculated. An accurate method of estimating selenium is based on the action of hydrochloric acid gas. The liberated chlorine is led into a potassium iodide solution, and the free iodine estimated volumetrically.

Tellurium is found pure in the metallic state and, very rarely, as tellurous acid. Tellurium is white, has a metallic lustre, fuses at above 500° C., and is volatile. When heated in the air it burns with a greenish blue flame and emits white fumes of tellurous acid. This compound is also formed when the metal is dissolved in nitric acid.

Reactions of tellurous acid.—Tellurous anhydride, TeO_2, is white, fuses at a red heat, and at a very high temperature is volatile. It is almost insoluble in water, but dissolves in alkalies and in hydrochloric acid. If this solution be diluted with water, the white TeH_2O_3, which is somewhat soluble in water and acids, is precipitated. Alkalies and carbonates throw down a white precipitate of the hydrate, which is easily soluble in an excess of the precipitant. Hydrogen sulphide throws down from acid solutions a brown precipitate which dissolves readily in ammonium sulphide. (The precipitate is apparently only a mixture of Te and S.) Sodium sulphite, stannous chloride, and zinc, precipitate black metallic tellurium.

Reactions of telluric acid.—Potassium tellurate is formed in the fusion of tellurium or its compounds with potassium carbonate and nitrate. Its solutions, and also those of other tellurates, liberate chlorine when boiled with hydrochloric acid, tellurous acid being formed. If tellurium or its compounds be fused with potassium cyanide in an atmosphere of hydrogen, potassium tellurocyanate is formed, which is easily soluble in water. Exposure to the air causes all the tellurium to separate from this solution as the metal.

The analysis of tellurium compounds is effected by the methods which are employed for selenium. On treatment with chlorine, tellurium chloride (a solid) sublimes. The solution of tellurous acid obtained is precipitated by sulphurous acid, the metallic tellurium collected upon a weighed filter, dried at 100° C., and its weight determined.

GROUP V., DIVISION 2

GOLD, PLATINUM (IRIDIUM)

Hydrogen sulphide precipitates gold and platinum from acid solution as their sulphides, AuS and PtS_2, which dissolve in ammonium sulphide (and alkali sulphides) to thio-salts (concerning the solubility of platinum sulphide in ammonium sulphide, see the Special Reactions of Platinum, § 85). They are distinguished from the metals of Division 1 principally in the character of the reactions which they afford; the insolubility of their sulphides in hydrochloric or nitric acid is also noticeable. When fused with potassium nitrate and sodium carbonate, they are reduced to the metallic state.

The instances in which these elements are met with in analysis are very simple; and as their characteristic properties are also so easily shown, we may neglect the consideration of their general reactions, and confine ourselves to a brief discussion of the manner in which the individual properties of the metals and their compounds are employed. Metallic gold and platinum are marked by their stability at a high temperature: and this property, together with their readily-effected separation from compounds, renders their analysis exceedingly simple. In separations from other metals (gold and platinum are usually found in alloys), advantage is taken of their behaviour toward acids. They dissolve neither in ordinary acids nor on fusion with acid potassium sulphate, though converted to the chlorides, $AuCl_3$ and $PtCl_4$, by the action of *aqua regia.* The reactions in which they are precipitated from solution in the metallic state are also used as qualitative tests. These reactions are caused by a variety of substances (ferrous sulphate, oxalic acid, potassium nitrite, etc.) The action of sulphurous acid is exceptional. This reagent does not immediately reduce the metals to the metallic state, but yields double salts (aurous and platinous), such as $AuNa_3(SO_3)_2$, $PtNa_2(SO_3)_2$. Gold is precipitated by sulphurous acid only from hot solutions. All these reactions are founded upon the properties of the metals themselves; few of the compounds are employed in analysis. The chlorides, $AuCl_3$ and $PtCl_4$, unite with other chlorides to form double auri- and platinichlorides, such as $(NH_4)AuCl_4$, $(NH_4)_2PtCl_6$.

In addition to these chlorides, the salts AuCl and $PtCl_2$ are also known. Each metal forms two series of oxides—the lower, Au_2O and PtO, the higher, Au_2O_3 and PtO_2. The latter possess almost no basic properties, but unite readily with bases; auric oxide forms with caustic potash the so-called potassium aurate, $KAuO_2$; and platinum yields a similar compound: it is for this reason that the alkali must not be fused in platinum dishes.

Having noticed the particular properties of gold and platinum which must be held in mind in the study of these metals, we at once proceed to the special reactions.

SPECIAL REACTIONS

Gold

§ 84. Gold is a yellow, very lustrous, soft, and malleable metal, which undergoes no change when ignited in the air, and fuses only at a very high temperature (about 1035° C.) Its specific gravity is 19·26. Its capability of uniting with other elements is slight, and all its compounds are decomposed on ignition, with separation of the metal. It is insoluble in hydrochloric, nitric, and sulphuric acids, or on fusion with acid potassium sulphate (separation from other metals). Chlorine and liquids which evolve chlorine dissolve it. Its customary solvent is *aqua regia,* which converts it to auric chloride, $AuCl_3$. This compound decomposes on gentle ignition to chlorine and aurous chloride, AuCl. Auric chloride forms double salts with many other metallic chlorides, and these are almost all soluble compounds, such as ammonium aurichloride, $(NH_4)AuCl_4$ (separation from platinum). The other gold halogenides (bromide, iodide, cyanide) also form many double salts.

Reactions of auric salts.—The typical salt of auric gold is the chloride. The reactions of this degree of oxidation consist exclusively in the separation of metallic gold and reduction to the aurous state.

Auric oxide.—Caustic potash throws down, but only from concentrated solutions, a dark brown precipitate of the hydroxide, $Au(OH)_3$, which dissolves in an excess of the reagent to form potassium aurate, $KAuO_2$. Auric oxide is most conveniently precipitated by magnesia. The hydroxide is insoluble in any dilute acid except hydrochloric; it dissolves in concentrated acids (sulphuric, nitric), but is again precipitated on dilution with water. It resolves into oxygen and aurous oxide, Au_2O, on being heated.

Reduction-reactions.—1. Ferrous sulphate precipitates from cold solutions a brown powder of metallic gold, being converted itself to the ferric salt:

$$AuCl_3 + 3FeSO_4 = Au + Fe_2(SO_4)_3 + FeCl_3.$$

2. *Oxalic acid* has an especially characteristic action. If auric chloride (free from nitric acid) be warmed with a solution of oxalic acid, the gold either separates in metallic flakes or is deposited as a mirror upon the sides of the vessel. The oxalic acid is oxidised to carbon dioxide:

$$2AuCl_3 + 3C_2H_2O_4 = 2Au + 6CO_2 + 6HCl.$$

Gold is also precipitated from its solution by potassium nitrite, sulphurous acid (on being warmed), formates, tannic acid, and many other substances.

3. *Stannous chloride.*—If a mixture of stannous and

stannic chlorides be added to a dilute auric chloride solution a brown or purple precipitate (Cassius's purple) is deposited, which is insoluble in hydrochloric acid.

Gold sulphide.—Hydrogen sulphide throws down from cold solutions a black precipitate of AuS. Boiling solutions are completely reduced to metallic gold by its action:

$$8AuCl_3 + 3H_2S + 12H_2O = 8Au + 3H_2SO_4 + 24HCl.$$

Gold sulphide is insoluble in acids, but dissolves to a thio-salt in ammonium sulphide.

Platinum

§ **85.** Platinum is gray, lustrous, soft, and malleable. It possesses the high specific gravity 21·46. It is not altered by ignition in the air, but fuses in the oxy-hydrogen flame at 1775°. Like gold, it dissolves neither in acids nor on fusion with acid potassium sulphate. With *aqua regia*, and by the action of chlorine in general, it is converted to platinic chloride, $PtCl_4$, which forms many double salts, or platinichlorides. If platinic chloride be gently heated it splits up into platinous chloride, $PtCl_2$, and chlorine. On ignition of the salts, metallic platinum is obtained.

Reactions of Platinic Salts.—The reactions of platinic chloride will be studied. They are as a rule similar to those of gold, but the reduction-reactions proceed more slowly.

Platinic oxide, PtO_2; hydroxide, $Pt(OH)_4$. — Neither potassium hydroxide nor carbonate precipitate platinic chloride solutions. On evaporation of a solution, to which one of these reagents has been added, platinic oxide and the alkali (or calcium oxide, magnesium oxide, etc.) are obtained in a state of combination. If this compound be treated with dilute acetic acid, a brown precipitate of platinic oxide separates.

Reduction-reactions.—*Ferrous sulphate* throws down metallic platinum on prolonged boiling with a platinic chloride solution; free mineral acids prevent the precipitation. *Stannous chloride* produces no precipitate, but gives a brown solution (reduction from platinic to platinous chloride). Potassium nitrite causes no precipitate immediately, but after standing for some time the solution deposits the yellow double salt, $K_2Pt(NO_2)_4$.

The *platinichlorides* are the most characteristic compounds of platinum. The ammonium and potassium platinichlorides,

$(NH_4)_2PtCl_6$ and K_2PtCl_6, are the most important salts of this class, as they are fairly insoluble compounds. They are prepared by the action of ammonium chloride or potassium chloride upon a solution of platinic chloride, and are deposited as yellow crystalline precipitates, which are only slightly soluble in water and not at all so in alcohol and ether. For the conditions under which they are formed, and their employment in analysis, compare § 8. Dilute solutions are evaporated with platinic chloride to dryness upon the water-bath, and the residue extracted with a mixture of alcohol and ether.

Platinic sulphide, PtS_2, is a black precipitate thrown down by hydrogen sulphide, but slowly and only after the solution has remained saturated by the gas for a long time. It is insoluble in all acids except *aqua regia*. Pure PtS_2 is insoluble in ammonium sulphide, but if precipitated together with the metals of Groups IV. and V. it dissolves to a certain extent. In the systematic course of analysis, therefore, tests must be made for it in both of these groups. In Group IV. it will be found with the mercuric sulphide, as platinic sulphide is insoluble in nitric acid when precipitated from hot solutions. In this case the sulphides are dried and heated in a glass tube open at one end, whereupon the mercuric sulphide sublimes. Platinic sulphide is converted into the metal by ignition in the air.

SYSTEMATIC COURSE OF ANALYSIS

§ 86 *a.* **Metals of Group V. Division 2** (Gold and platinum).—The solution is evaporated with ammonium chloride to dryness on the water-bath, and the residue extracted with alcohol, which dissolves the ammonium aurichloride. Gold is detected in this solution, after removal of the alcohol (by evaporation on the water-bath), by precipitation with ferrous sulphate, § 84. The platinum remains in the residue extracted with alcohol, as an insoluble platinichloride (together with the excess of ammonium chloride). This residue is dried, and its metallic platinum obtained by ignition.

b. Gold, platinum, and the metals of the previous Groups.—In practical work these metals are found only in the analysis of alloys, which will be discussed among the examples in quantitative analysis. They are separated by treatment with acids or fusion with acid potassium sulphate, which leaves the gold and platinum undissolved. This method is almost universally employed. The presence of either metal in the substance to be analysed, however, necessitates no change in the combination of the reactions. The solution is acidified with hydrochloric acid, as explained in § 80, and precipitated by hydrogen sulphide (see the precipitation of gold sulphide and platinic sulphide). The sulphides of Group IV. are next separated by ammonium sulphide, and those of Group V. again thrown down by hydrochloric acid. All of these operations are described in § 80. Gold and platinum are reduced by fusion with sodium carbonate and potassium nitrate, the fused mass containing them in the metallic state. They remain unchanged throughout all the operations which the alloys undergo, and, after solution in *aqua regia*, are detected as in the beginning of this paragraph.

The following method of separating the two Divisions of this Group is more complicated, but also more accurate.

The dried sulphides of Group V. are stirred together with a mixture consisting of four parts NH_4Cl and one part NH_4NO_3, and ignited in a porcelain boat inserted in a tube in a combustion furnace. The volatile chlorides of Sn, Sb, As, are drawn by means of an aspirator into a receiver containing water, while the gold and platinum remain in the boat.

SUPPLEMENT

1

Analysis of native gold and platinum compounds.—Gold occurs almost invariably in the metallic state, usually containing more or less silver (6-16 per cent). It is also found, but very seldom, combined with tellurium, and many pyrites, especially arsenical pyrites, contain this metal. It likewise occurs, though in small quantities, in a great number of the silver, copper, and lead ores. Their analysis is effected by the methods given in the foregoing paragraphs. The occurrence of platinum and the analysis of its ores are explained in § 69.

2

IRIDIUM

Iridium is found associated with platinum. Although, by the definition given of the metals of the first Division of this Group, iridium should be classed with them, it may be more properly discussed at this point, as it is very closely analogous to platinum. As regards the platinum metals in general, and also concerning their occurrence (in the platinum ores and osmiridium), we refer to the remarks found in § 69. Iridium is insoluble in all acids, including *aqua regia* (in the form obtained by reduction from solution with formic acid it is soluble). It does not go into solution when fused with acid potassium sulphate, though it becomes oxidised; on fusion with sodium oxide (and with potassium nitrate in the air), it forms peculiar and somewhat soluble compounds with the alkali. Chlorine is the best reagent by which to effect its solution. It unites with this element to form $IrCl_3$, a salt which yields double compounds with other chlorides, *e.g.*, K_3IrCl_6 (insoluble). If iridium be heated in a stream of chlorine, in presence of potassium chloride (or some other metallic chloride), another class of salts is formed (for example, K_2IrCl_6; this salt is sparingly soluble, and used in the separation of iridium). This series of compounds is unstable, and passes easily into the foregoing class.

Reactions of iridium salts (higher compounds).—Caustic alkalies produce in boiling solutions a dark-blue precipitate of $Ir(OH)_4$, which is insoluble in all acids except hydrochloric. The formation of the difficultly soluble double salts, K_2IrCl_6 and $(NH_4)_2IrCl_6$, which are deposited as black precipitates on the addition of potassium or ammonium chloride, is characteristic. On the addition of potassium nitrite to a hot solution, the latter first becomes yellow, and finally deposits a precipitate of the same colour, which is insoluble in water or acids. Hydrogen sulphide first causes reduction, and then throws down a black precipitate of Ir_2S_3. Iridium compounds are easily reduced to the metal. Sulphurous acid (sulphites), formic acid (from hot solutions), and zinc and hydrochloric acid, cause its complete reduction. Stannous chloride, ferrous sulphate, and oxalic acid convert it to lower degrees of oxidation. For the separation of iridium from other metals, and the analysis of osmiridium, see § 69.

COMPLETE COURSE OF ANALYSIS FOR THE DETECTION OF METALS

§ **87.** Now that all the metals have been studied and the systematic course has been elaborated, it may be well to describe collectively the operations required in analyses which involve the detection of any or all the metals. I hope that the student is already sufficiently acquainted with the operations, to judge for himself concerning the advice which I shall first give as regards the practical side of the work, and presuppose that intelligent study of the course of analysis has already made him familiar with the other side. The rapidity with which analyses may be carried out depends, first, upon the neatness of the work, and, secondly, upon the intelligent employment of time. The value of neatness in work is difficultly expressed in a few words, if not already made clear to the student by the experiences through which he has certainly passed. The reactions involved in an analysis must necessarily be made under the *given conditions.* If a thorough preliminary knowledge is acquired (by study of the general and special reactions), a condition, which for the moment may seem unimportant, will not escape the eye. Precipitations which effect the separation of groups or single metals must be thorough, and their thoroughness must be ascertained by confirmatory tests. Special attention must be paid to the washing of precipitates, and here, also, a confirmatory test alone can prove that the operation is finished. These measures for ensuring careful work, which, in my opinion, have the greatest influence upon the rapidity of an analysis, seem for the moment, but only for the moment, to be complicated and wearisome. A perfect reaction is obtained only in this way. Careless work brings only confusion, a result which is hardly to be wondered at, if the precipitates are not well washed, the solutions incompletely precipitated, etc. The reactions are not obtained, and the analysis must be commenced over again. Loss of time invariably results from a repetition of the analysis, while by careful and neat work this is entirely obviated. By the intelligent use of his time, I mean that the student, while engaged in one operation, *e.g.*, precipitation or washing, must take up another simultaneously, without waiting uselessly until the first is finished; in other words, he should accustom himself to performing two operations (neatly) at once; for instance, to precipitate a solution, and at the same time investigate a precipitate already obtained, etc. As it seldom happens that the substance to be analysed contains all the metals of all the groups, it is convenient to make a preliminary test (§ 80) before each separation-reaction, and thus to do away with unnecessary operations. Attention is finally called to the value of notes (sufficiently full) upon the reactions obtained in the analysis.

Before passing to the complete course of analysis, I wish to remind the student again, that the conditions to which references are made must be most carefully observed.

1. *Acidulation or precipitation with hydrochloric acid.*—

Conditions and necessity for acidulation, § 80 A. Precipitation, § 80 B. The thoroughly-washed precipitate is examined according to §§ 68 and 58. Solution is investigated according to 2.

a. Action of boiling water—test for lead.

b. Action of ammonia—mercurous mercury.

c. Action of nitric acid upon ammoniacal solution—Ag. Confirmatory tests for these metals.

2. *Separation of Groups IV. and V. from Groups I., II., III.*—Dilution with water, §§ 80 and 68; precipitation by hydrogen sulphide, §§ 80 and 68 (attention to the behaviour of arsenic acid noticed in § 79). The precipitate contains the metals of Groups IV., V., while Groups I., II., III., remain in solution. The precipitate is next to be examined. The filtrate is treated as in 6.

3. *Separation of Groups IV. and V.*—Filter, and treat the precipitate, after a thorough washing, with ammonium polysulphide, § 80. Filter and wash the residual precipitate with water and ammonium sulphide. The precipitate contains metals of Group IV.; their detection, 5. The metals of Group V. are in solution.

4. *Detection of metals in Group V.*—The solution of the thiosalts is precipitated by hydrochloric acid according to § 80, and the sulphides washed. Treat with boiling HCl, § 80.

a. As (Au, Pt) remains in the precipitate. Detection of As, § 80: confirmatory tests, § 79. (Gold and platinum are detected as in § 86.)

b. Sn and Sb are obtained in solution. Detection of Sn, by the reaction with zinc upon platinum foil, § 76. Precipitation of the solution by zinc, § 80.

c. Solution of the deposited metals in boiling HCl; separation of Sn and Sb. Detection of Sn by $HgCl_2$, etc., §§ 80 and 74. Confirmatory tests for Sb, § 76.

5. *Detection of the metals of Group IV.*:

a. The precipitate (see 3) of the sulphides is boiled with HNO_3. Detection of Hg, § 68 (*v.* also § 57; confirmatory tests for Hg, § 61. Possible presence of platinum, § 85).

b. The solution is precipitated by very dilute H_2SO_4.—Detection of Pb, § 66.

c. The filtrate from the lead sulphate is precipitated by ammonia—Bi, § 68; confirmatory tests, § 67.

d. The ammoniacal solution (when coloured blue by copper) is treated with potassium cyanide and precipitated by hydrogen sulphide, § 59—Cadmium.

e. Detection of copper in the remaining solution, §§ 59 and 63.

The following method can be substituted for that given in *c, d, e.*

c'. The filtrate from $PbSO_4$ is partially neutralised, and the still acid solution treated, while boiling, with sodium thiosulphate. Detection and separation of Cu and Bi, § 59; confirmatory tests, §§ 63 and 67.

d'. The filtrate from copper and bismuth sulphides is treated with hydrogen sulphide; detection of Cd. Confirmatory tests, § 65.

6. *Separation of Group III. from Groups I. and II.*—The filtrate from 2 (the presence of phosphates, etc., is determined by neutralisation with ammonia, after the hydrogen sulphide has been removed by boiling, §§ 51, 68) is precipitated by ammonium sulphide, careful attention being paid to the conditions in §§ 48 B and 40. The precipitate contains the metals of Group III. (and phosphates, etc.) Groups I. and II. remain in solution: the method for their investigation is given in 10.

7. *Detection of the metals of Group III., Division* 3:

a. Treatment of the washed precipitate with cold dilute HCl, § 48. NiS and CoS remain in precipitate, Divisions 1 and 2 go into solution.

b. Solution of the precipitates in *aqua regia* (preliminary tests with borax bead and microcosmic salt).

c. Separation of Ni and Co through their double salts with potassium cyanide and nitrite, § 48 A.

8. *Metals of Group III., Division* 1.—The solution is oxidised (§ 40), and precipitated:

a. With barium carbonate, § 40 B and § 28 (if chromium is present; preliminary test, § 35. Test with H_2SO_4 to ascertain the presence of barium, 8 * and 9); or (in absence of chromium) with sodium acetate, § 40 B. Al, Cr, Fe, are precipitated (together with phosphates, etc.; see below), and the solutions contain Mn, Zn, and the metals of Group II. (even if phosphates were present).

b. The metals of Division 1 are detected according to § 35. The precipitate having been dissolved in hydrochloric acid (and barium removed if necessary), the hydroxides are next thrown down by ammonia. Chromium is separated by boiling with nitric acid and potassium chlorate, or, if possible, by bromine in presence of sodium acetate, § 35.

c. In the first case, the solution must be precipitated by ammonia; in the second, the separation and detection of Al and Fe by caustic soda, § 28 B, may be directly effected (confirmatory tests, §§ 28, 31).

d. Chromium is in solution as a chromate; detection of chromium, § 33.

8*. *Phosphates, etc.*—Test for their presence, § 51. Course of Analysis, § 51.

9. *Metals of Group III., Division* 2.—The solution obtained in 8 is investigated according to § 40 (after removal of barium if its carbonate has been employed).

a. Precipitation with ammonium sulphide, § 40. Separation of Zn from Mn by action of acetic acid upon the sulphides, § 40. Detection of Zn, § 39, and of Mn, §§ 40 and 38.

b. Test for the absence of metals of Group II. (Indication of phosphates, etc.)

10. *Separation of Group II.* (with the exception of magnesium).—The solution obtained in 6 is boiled, to remove ammonium sulphide (§ 35 B), and then precipitated, according to § 24, with ammonium carbonate; the conditions mentioned must be carefully fulfilled. The precipitate contains the carbonates of Ba, Sr, Ca; Mg and the alkali metals remain in solution. Examination of the solution, 12 and 13.

11. *Tests for the metals of Group II.* are made as in § 22. The precipitated carbonates are dissolved in HCl.

a. If barium is present (determined by a preliminary test, § 22), the solution is precipitated by ammonium chromate according to § 22.

b. Ba is obtained in the precipitate, and detected as in § 22 and § 19.

c. The solution is again precipitated by ammonium carbonate and ammonia, the precipitate washed, dissolved in HCl, and treated, hot, with ammonium sulphate. The precipitate is tested for strontium, §§ 22 and 20.

d. The solution of ammonium sulphate is precipitated by ammonium oxalate. Detection of Ca, § 21.

12. *Detection of magnesium.*—A portion of the solution from 10 is tested for Mg with acid sodium phosphate, §§ 24 and 23.

13. *Separation of magnesium from the metals of Group I.*—If magnesium has been found, the solution is evaporated to dryness and the residue ignited until the ammonium salts have volatilised. The solution of the residue is treated with calcium oxide, § 24, whereupon Mg is obtained in the precipitate and the metals of Group I. in solution. The precipitate may be used for confirmatory tests for magnesium (after the removal of calcium oxide), see 14.

14. *Detection of the metals of Group I.*—The calcium is removed from solution by ammonium oxalate, and the ammonium salts driven off by ignition (§ 24). The residue is then dissolved in water, and the following tests (§ 14) made in separate portions of the solution:

a. Precipitation with tartaric acid; detection of K, § 7.

b. Precipitation with potassium pyroantimonate; detection of Na, § 12.

Confirmatory tests are made by flame colorations; § 9.

15. *Detection of ammonia.*—Ammonia must be detected in a portion of the original solution, through its liberation by caustic potash; § 13.

REMARK 1.—Reactions to determine the various degrees of oxidation of the metals must be made in the original solution.

REMARK 2.—In a complete analysis, the operations of acidifying with hydrochloric acid (1), and precipitation by hydrogen sulphide (2), must be especially noticed, since they also serve to detect certain acids, as will be explained in § 105.

SECTION II

THE METALLOIDS

THIS Section contains all the elements which have not yet been discussed. They are not precipitated by hydrogen sulphide, ammonium sulphide, ammonium carbonate (or sodium phosphate), and they form no soluble sulphides similar to those of the alkali metals. The Section includes the halogens, fluorine, sulphur, nitrogen, phosphorus, carbon, boron, and silicon. The typical compounds which it is best to study are those with hydrogen or oxygen (or both), *i.e.*, the acids and their salts.

Although the metalloids are few in number, their study is much more arduous than that of the metals, since most of them form several distinct acids. The difficult nature of the work is apparent when we attempt to classify the acids according to one system. Until now, we have been able to arrange the elements (of Section I.) strictly according to their analytical behaviour (the properties of their sulphides, and the reactions in which the latter are formed): and this arrangement has been further simplified by the fact that each element, or, more correctly, each metal, is characterised in all its degrees of oxidation by merely a few analytical reactions. Furthermore, the metals pass constantly from one degree of oxidation to another, and such conversions are easily effected. In the metalloids we encounter other characteristics. They also possess several degrees of oxidation; but the various acids of one and the same metalloid can differ widely (for instance, hydrochloric and hypochlorous acids); they are not readily converted from one to the other, and they show great variations in their reactions. Finally, the qualitative examination of the metalloids (the detection of acids) cannot be accomplished through analytical reactions (similar to those with hydrogen sulphide or ammonium sulphide) which effect general separations and can serve as a basis for classification. The course of analysis employed in investigating the acids is very distinct, as we shall see at the end of this Section, from that used for the metals. In testing for acids, previous knowledge as to which of the metals are present in the substance under analysis must be obtained. In order to study the metalloids and their compounds satisfactorily, we are compelled by these considerations to discuss each one in connection with all its derivatives, and thus to neglect the single acids as they are arranged in accordance with their analytical behaviour. By the latter course the different derivatives of one and the same element would necessarily be separated in their discussion, and thus all connection between them lost.

The analytical classification of the acids will be explained at the end of this Section, where the course of examination for the detection of acids is given. This system is based upon the various properties of the barium and silver salts of different acids. The insolubility of the barium salts in water is the general indication of one group; that of the silver salt in nitric acid (and the solubility of the barium salts in water) characterises another; the third group, finally, consists of acids, both the barium and silver salts of which are soluble in water.

THE HALOGENS

CHLORINE, BROMINE, IODINE

The halogens form with hydrogen the so-called hydrogen acids. In uniting with metals they yield the haloid salts of the metals, *i.e.*, salts of the hydrogen acids. They are found in analysis most frequently as such compounds. They also unite with oxygen, forming a series of oxy-acids. Beside these compounds, the free halogens are also employed in analytical work, as their properties are very characteristic.

Chlorine occurs in nature almost exclusively in sea water and in rock-salt. Double salts of the chlorides of the alkali metals and magnesium are also found in small quantities (the analysis of carnallite, one of these minerals, is given among the examples in Part II.) Bromine and iodine also exist in minute amounts in sea water and mineral springs.

HYDROGEN ACIDS (AND HALOGENS)

§ 88. *a.* **Hydrogen Acids and their Salts** (chlorides, iodides, and bromides).—The hydrogen compounds of all three halogens are gaseous at the ordinary temperature. When dissolved in water they form acids—hydrochloric, hydrobromic, and hydriodic acids. In combination with metals, or when saturated by bases, they give rise to the halogen compounds of the metals—salts of the hydrogen acids; these compounds are sometimes, but more rarely, formed by the direct action of the acids or halogens upon the metals. The majority of these haloid salts are soluble in water; some, however, are decomposed by it, and a few are difficultly soluble or totally insoluble (halogenides of silver, mercurous mercury, and, to some extent, of lead). The formation of insoluble compounds affords a qualitative test for the hydrogen acids. The unequal solubilities of the compounds of one metal with the various halogens furnish the methods for their quantitative separation; both palladious and cuprous iodides, for instance, are insoluble salts, while the corresponding bromides and chlorides dissolve readily in water. The insoluble haloids are converted to soluble alkali salts, by boiling (or, still better, by fusion) with sodium carbonate. This operation may be performed in various ways (§ 89).

Certain halogen compounds are decomposed when acted upon by water (*e.g.*, the compounds of bismuth, tin, arsenic, and antimony; see Section I.), the acid being liberated and the metallic oxide formed. These compounds are similar in this respect to those of the metalloids (phosphorus, sulphur, etc.), which are decomposed by water without exception:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

As such compounds yield acids, they may be regarded as the haloid anhydrides of the acids; *i.e.*, acids in which the hydroxyl groups are replaced by halogen. Many acids also, such as sulphuric and chromic, form compounds of the same nature; the chloranhydrides of these two acids have the formulae CrO_2Cl_2, SO_2Cl_2, respectively, and are both decomposed by water at the ordinary temperature. The formation of the chloranhydride of chromic acid may be used as a test for chlorine, and to distinguish the latter element from bromine and iodine, which do not yield the corresponding compounds (§ 89). All these compounds of the halogens with metalloids are distinguished, not only by the reaction with water, which is common to all, but also by their volatility. The latter characteristic is used in analysis. The majority of the haloid anhydrides are liquids, which vary in their boiling-points. As they are decomposed by water with formation of hydrogen acids, they can be analysed by the customary methods.

b. Liberation of the halogens from hydrogen acids.—As the tendency to decompose varies in the different hydrogen acids, there are various reactions by which the respective halogens are liberated more or less readily. These reactions may thus be employed in analysis. Hydriodic acid is most easily split up, and iodine most easily liberated. To detect iodine, therefore, reactions are employed which set the iodine free, but have no effect upon the bromine or chlorine compounds. Bromine is liberated with more difficulty than iodine, but with less than chlorine: chlorine forms the most stable compounds of all the halogens. The reactions in which the halogens are set free are very valuable in analysis, the characteristics of the free elements being such that their detection is very simple.

Iodine is liberated, in analysis, through the action of one of the nitrogen oxides (fuming nitric acid), potassium nitrite in acid solution, or ferric chloride, $FeCl_3$ (§ 91). None of these reagents affect the compounds of either chlorine or bromine. If no iodine is present, or after its removal, sulphuric acid, which has no effect upon chlorine, is employed to release the bromine. All these reactions are discussed among the Special Reactions. Those which liberate bromine have a like action upon iodine compounds, and those setting chlorine free decompose the compounds of both the others. The hydrogen acids are also decomposed, with liberation of their halogens, by peroxides and substances of a similar nature (manganese dioxide, lead dioxide, nickelic oxide, chromic acid, etc.) We shall become acquainted later with the extensive applications which these reactions find in analysis.

Liberation of halogens by halogens.—If chlorine be allowed to act upon soluble bromides or iodides, the bromine and iodine are set free. Bromine, however, displaces only iodine from its compounds, and iodine has no action whatever upon the other halogens:

$$KBr + Cl = KCl + Br.$$

These reactions are very often employed, both qualitatively and quantitatively. If, for example, in qualitative analysis, a mixture of bromides and iodides be subjected to the action of chlorine (or, as the reaction is more often effected, of chlorine water), the iodine is first liberated, and as soon as it is completely displaced, the soluble compound, iodine monochloride, ICl, is formed. When all the free iodine has thus united with chlorine, the excess of the latter begins to act upon the bromide (§ 91).

c. **The properties of the halogens** are very remarkable. They will be discussed under the special description of each halogen, and in this paragraph attention will simply be called to the principal characteristics, which are more fully explained later. Chlorine is a gas, bromine a volatile fluid (its vapour is reddish-brown), iodine a solid body (steel-gray—its vapour is violet). The solution of iodine in carbon disulphide or chloroform, CH_3Cl, is violet, that of bromine, yellowish-red. We make use of these characteristics in detecting iodine and bromine by their liberation (see the Liberation-reactions). Their chemical properties are also important. Chlorine and, to a less extent, bromine, act, in presence of water, as powerful oxidising agents, *e.g.*, they decolorise indigo or litmus, oxidise ferrous salts, etc. In presence of alkalies, chlorine has a still more energetic action, and converts many metals into their peroxides. This reaction, which we have already frequently employed (see lead, nickel, manganese, etc.), is also used as a test for free chlorine or bromine. Iodine does not show this reaction, but possesses characteristics of a similar nature. Its property of forming with starch a blue compound soluble in water is important, and distinguishes this halogen from bromine and chlorine (§ 91). If to these clearly-defined characteristics we add that the halogens are set free from their compounds in extremely distinctive reactions, it will be seen that there is hardly another series of compounds (or elements) which possesses so marked a character.

Free bromine and chlorine are often used in analysis as oxidising agents. As a rule, chlorine-water is employed, but the solubility of chlorine is so slight (the solution contains only ½ per cent Cl) that bromine-water (containing 2·3 per cent Br) is preferable. When possible, a solution of bromine in concentrated hydrochloric acid (13 per cent Br) or in potassium bromide is employed.

d. Conversion of the halogens to hydrogen acids.—The reactions which are employed in analysis for this purpose occur only in the presence of water (those taking place between hydrogen and the halogens may be neglected). The hydrogen of the water unites with the halogen, the oxygen attaching itself to the third substance (a reducing agent) which causes the reaction. A reducing agent is a substance which readily combines with oxygen (becomes oxidised). For analytical purposes we usually employ sulphurous acid (and sulphites) or thiosulphates. The former is oxidised by iodine to sulphuric acid, the latter are converted to tetrathionates (chlorine and bromine change them to sulphates):

$$2I + Na_2SO_3 + H_2O = 2HI + Na_2SO_4,$$
$$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

In passing to the Special Reactions, we shall divide their study, in accordance with the above, as follows: (1) the insoluble salts of the acids; (2) the conditions under which the halogens are set free; (3) the properties of the halogens. In this way the halogens themselves and their hydrogen acids are studied side by side. The reactions of the one class supplement those of the others.

Hydrochloric Acid (Chlorides) and Chlorine

§ 89. **Chlorine** is a yellowish-green gas (sp. gr. = 2·45), which possesses a characteristic and unpleasant odour, and sharply attacks the mucous membrane. It is soluble in water, its solution showing the same reactions as the gas. Chlorine unites at the ordinary temperature with many metals, such as antimony, tin, and mercury (chlorine can be removed from solution, for example, in chlorine-water, by shaking with metallic mercury). The chemical properties used in analysis are discussed below.

Hydrochloric acid gas (sp. gr. 1·259) fumes in the air, and dissolves readily in water (500 vols. at + 3° C.) This solution is the customary hydrochloric acid. Fuming hydrochloric acid contains about 40 per cent of the gas. The properties of the chlorides are given in § 88 *a*.

The reactions of hydrochloric acid and soluble chlorides consist in the formation of insoluble chlorides, in the liberation of chlorine, and in illustration of the characteristics of the latter. These reactions supplement each other. Insoluble chlorides are obtained in solution by fusion with sodium carbonate (§ 88 *a*).

Silver chloride.—Silver nitrate throws down from hydrochloric acid or soluble chlorides a white precipitate of silver chloride, which is insoluble in nitric acid, but dissolves in ammonia. Conditions necessary for its formation and its characteristics are explained in § 60. This reaction is very delicate. The chlorine in this insoluble compound is most easily detected by treatment with zinc and dilute sulphuric acid, by which means it is obtained in solution as zinc chloride.

Mercurous chloride, $HgCl$, and lead chloride, $PbCl_2$, are less characteristic. They are precipitated by mercurous or lead salts (§§ 61 and 66).

Although the above chlorides afford the most delicate tests for hydrochloric acid, they furnish no means for its detection in presence of bromides or hydrobromic acid, as the latter show the same reactions. For this purpose the following reaction is to be recommended.

The chloranhydride of chromic acid, CrO_2Cl_2, or chromyl chloride (incorrectly called chlorchromic acid), is a compound by means of which chlorine may be qualitatively distinguished from bromine or iodine, as the latter halogens form no corresponding compounds. As the chloranhydrides of acids are decomposed by water, the latter must be avoided in the analytical operations. Any dry chloride (sodium chloride, for example) is rubbed together with potassium dichromate, the mixture introduced into a flask connected with a delivery tube, and treated with concentrated sulphuric acid. On the application of gentle heat the red-brown vapour (similar to that of bromine) of the chromyl chloride appears within the flask. This chloranhydride is a liquid boiling at 118° C.

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = 2CrO_2Cl_2 + K_2SO_4 + 2Na_2SO_4 + 3H_2O.$$

If the gas be led into a test-tube containing some ammonia, the latter will become yellow, and after the action is complete the solution contains ammonium chloride and ammonium chromate. The chloranhydride of chromic acid is decomposed directly by water:

$$CrO_2Cl_2 + 4NH_3 + 2H_2O = (NH_4)_2CrO_4 + 2NH_4Cl.$$

Neither bromine nor iodine form volatile chromium compounds, but are set free by the sulphuric acid, and when absorbed by ammonia yield colourless solutions. It is to be noticed that if too little potassium dichromate has been taken, in proportion to the chloride, the latter may give off chlorine instead of chromyl chloride, according to the equation:

$$K_2Cr_2O_7 + 6KCl + 7H_2SO_4 = Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 6Cl.$$

Liberation of chlorine, and reactions of free chlorine.—The above-described reactions, though suitable for the detection of chlorides, is insufficient for the recognition of free chlorine. The various methods of liberating chlorine, in comparison with bromine and iodine, are discussed in § 88 *b*. Manganese dioxide, by its action upon hydrochloric acid or upon a chloride in presence of sulphuric acid, sets the chlorine free. The test is made in a flask fitted with a delivery tube. The mixture is gently heated, and the free chlorine evolved led into water, chlorine-water being the result. The chlorine can be detected in this solution by the following reactions. A few drops of the chlorine-water are added to a mixed solution of ammonium ferrous sulphate and potassium sulphocyanate, which must not be coloured (through the presence of ferric salts). Upon the addition of the chlorine-water, the ferrous salt becomes oxidised by the halogen, and a blood-red solution of ferric sulphocyanate is obtained (§ 34). The following reaction is also delicate. A few drops of chlorine-water are added to a solution of potassium iodide in starch paste. The liquid is turned blue (see Iodine) by the iodine which the chlorine sets free. Chlorine-water also decolorises an indigo solution.

Chlorine is detected in a mixture of gases by its yellow-green colour and penetrating odour. Paper coloured by indigo solution or litmus loses its colour in presence of chlorine. Mercury extracts the halogen from a mixture of gases at the ordinary temperature, with formation of mercurous chloride.

Hydrobromic Acid (Bromides), and Bromine

§ **90. Bromine** is a red-brown, almost black, liquid, which boils at 58·5° C. Its vapour is dark-brown. Bromine dissolves only slightly in water (bromine-water), but readily in carbon disulphide or chloroform (see below). These solutions are dark-brown. The chemical properties of bromine have already been described (§ 88); they will be further considered below.

Hydrobromic acid is a gas which fumes in the air and dissolves very readily in water. It is even more soluble than hydrochloric acid gas, and its concentrated solution contains 88 per cent of the acid. The bromides, which bear a great similarity to the chlorides, are described in § 88.

The reactions of hydrobromic acid and bromides also consist in the production of insoluble compounds, in the liberation of bromine, and in tests of the latter.

Silver bromide.—Silver nitrate causes a yellow precipitate of silver bromide, insoluble in nitric acid (§ 60). It is brought into solution in the same manner as silver chloride, and the detection of its bromine is likewise effected after the decomposition of the silver salt by zinc and sulphuric acid.

Palladious bromide is thrown down by palladious nitrate, though not by palladious chloride. It is a brown precipitate which forms immediately only in concentrated solutions (distinction from chlorine).

Auric bromide.—Auric chloride colours the solution of a bromide yellow or orange-red (presence of iodine interferes with the reaction).

Liberation of bromine and reactions of free bromine.—The insoluble bromides cannot be used to detect bromine in presence of chlorine, as they are very similar to the corresponding chlorides. In such cases reactions are employed in which bromine is set free from bromides, but not the chlorine from chlorides. At present only the characteristic reactions will be described. The choice as to which reaction should be used depends upon the particular property of bromine by which the latter is to be characterised.

1. *With chlorine, chlorine-water* (§ 88 *b*).—The property which chlorine possesses of forming the soluble chlorine bromide must be remembered, and an excess of chlorine be avoided. A few drops of carbon disulphide and some chlorine-water are successively added to the solution in a test-tube, and the mixture shaken. The carbon disulphide takes up the liberated bromine, becoming brown, and, as it is heavier than water, sinks to the bottom of the tube. If only traces of bromine are present, the carbon disulphide becomes yellow. The colour is destroyed by an excess of chlorine, the two halogens, as we have said, then entering into combination. Potassium hydroxide also causes its disappearance (chiefly owing to the formation of potassium bromide). Further reactions for bromine can be made after the alkaline solution has been evaporated.

2. *Sulphuric acid* liberates bromine from hydrobromic acid and all bromides except AgBr and HgBr (distinction from chlorine):

$$2HBr + H_2SO_4 = 2Br + SO_2 + 2H_2O.$$

The detection of the bromine can be effected either by the foregoing method or according to 3. The reaction occurs only in concentrated solutions and when concentrated sulphuric acid is used. In weak solutions, the opposite reaction also takes place, the bromine being converted to hydrobromic acid by the sulphurous acid. Dilute solutions must therefore be evaporated.

3. *The liberation of bromine by manganese dioxide* is less characteristic, as this reaction is common to all the halogens. The experiment is made either according to § 89, or as follows. The reaction is brought about in a small beaker, which is covered by a watch-glass having a piece of paper fastened to its under side: this paper is moistened with starch-paste, and has starch sprinkled over it. On the vessel becoming warm, the released bromine colours the starch yellow.

Hydriodic Acid, Iodides, and Iodine

§ **91.** Iodine is dark-gray (rhombic crystals), melts at 107° C., and boils at 180° C., with evolution of violet fumes which condense directly to crystals.[1] Iodine is difficultly soluble in water, but readily so in potassium iodide. Its solution in carbon disulphide or chloroform is violet; when concentrated, almost black.

Hydriodic acid is a gas which forms thick white fumes in the air, and is completely decomposed by sulphuric acid. It is usually prepared by the action of water upon phosphorus iodide (or by that of hydrogen sulphide upon iodine). When dissolved in water, it yields the familiar hydriodic acid. The most important properties of the iodides, and their formation, have already been given (§ 88 *a*).

Reactions of Hydriodic Acid and Iodides. *Insoluble*

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[1] According to Stas, absolutely pure iodine, obtained by precipitation of a solution of iodine in potassium iodide with water, or by decomposition of nitrogen iodide by water at 60°, gives off blue fumes, fuses at 115° C., and boils at 200° C.

iodides. Silver iodide.—Silver nitrate produces a yellow precipitate of silver iodide, insoluble in either nitric acid or ammonia (§ 60). No method of separation of iodine from chlorine and bromine, however, can be based upon the insolubility of silver iodide in ammonia. If the salt be fused with sodium carbonate, sodium iodide is obtained and metallic silver separates.

Cuprous iodide, CuI.—If a solution of potassium iodide be precipitated by cupric sulphate, cuprous iodide and free iodine are obtained, half of the iodine uniting with the copper:

$$CuSO_4 + 2KI = CuI + K_2SO_4 + I.$$

If the reaction take place in presence of some substance which converts iodine into hydriodic acid (sulphurous acid or sodium thiosulphate is usually employed; ferrous sulphate is less convenient), and a sufficient amount of cupric sulphate be added, all the iodine is obtained in the precipitate as its cuprous salt. Cuprous iodide is a white, crystalline precipitate, which is insoluble in water or dilute acids but dissolves in sodium thiosulphate to a colourless solution.

As bromides or chlorides are not precipitated as their corresponding cuprous compounds, this reaction may be used, qualitatively, to separate iodine from chlorine and bromine. The solution of the mixed salts is precipitated by an excess of cupric sulphate, and sodium thiosulphate then added, drop by drop, until the colour of the iodine vanishes from the solution. An excess of sodium thiosulphate, however, must be carefully avoided. After the disappearance of the colour caused by iodine, the solution must have a blue tint, given by the excess of copper sulphate. All the iodine is then in the precipitate as its cuprous salt, bromine and chlorine remaining in the solution, together with the excess of cupric sulphate. The copper is next removed by hydrogen sulphide, and after evaporation of the solution to dryness, the chlorides and bromides are obtained (§ 92). The method is not quantitative, and the directions must therefore be followed with the greatest possible accuracy. In *very dilute* solutions potassium iodide has a different action upon cupric sulphate (see Hydrogen peroxide, § 104).

Palladious iodide, PdI_2, is thrown down as a dark-brown precipitate by palladious chloride or nitrate. The compound is almost insoluble in cold dilute hydrochloric acid or nitric acid. Iodine can be separated from chlorine and bromine by precipitation with palladious chloride (the reaction is used for the quantitative separation and estimation of iodine), but as the student rarely has access to palladium salts, the reaction will not be included in the systematic course of analysis.

Characteristic tests for iodine are also found in the formation of certain other iodides, such as the mercurous (§ 62) and lead (§ 66) salts.

Liberation and reactions of iodine.—A direct test for the presence of iodine must be made, before the reactions for its separation from chlorine and bromine are instituted. For this purpose, one of the following reactions is used. The first two are the most characteristic, and are caused by iodine but not by chlorine or bromine. It may be remarked again that the reaction to be chosen depends upon the special property of iodine to be used for its detection. The reaction with starch-paste is the most delicate.

1. *By nitrous acid.*—Dilute nitric acid has no action upon soluble iodides; the fuming acid (which contains the lower oxides of nitrogen), or, better still, potassium nitrite (in presence of sulphuric or hydrochloric acid) releases iodine. The solution becomes of a brown colour, and if a large quantity of the iodine was present, it is deposited as a black precipitate:

$$2HI + 2KNO_2 + H_2SO_4 = 2I + 2NO + 2H_2O + K_2SO_4.$$

It is convenient to detect the iodine by means of its action upon starch-paste (carbon disulphide may also be employed—its use will be described below). Iodine unites with starch in the cold, forming a compound, of undetermined composition, which dissolves in water to a dark-blue colour. The test is made with very dilute starch-paste.[1] The liquid to be investigated is acidified by hydrochloric or sulphuric acid, and starch-paste and a few drops of a concentrated solution of potassium nitrite (fuming nitric acid is less suitable) are then added. A dark-blue coloration is obtained, or, if only traces of iodine are present, a reddish-violet solution. If too little starch be present, in proportion to the iodine, the solution assumes a green tint, but on the addition of more starch-paste it becomes

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[1] The starch-paste is made very thin; 1 part of starch is agitated with 100 parts of water, and the mixture gently warmed and allowed to settle. The almost clear solution is used for the reaction, about 10-20 c.c. being taken. Starch-paste is not permanent in dilute solution, part of it passing into dextrine, upon which iodine has no colouring action. It is therefore well to prepare a fresh paste for each experiment.

blue. The reaction must take place in the cold. It is still more delicate if the solution be cooled, and the colour disappears on warming. Iodine may easily be detected in presence of both chlorine and bromine by this test.

2. *Ferric chloride*, and ferric salts in general, liberate iodine from potassium iodide in presence of hydrochloric acid, as the ferric salt, FeI_3, is incapable of existence. The free iodine is recognised by the brown colour imparted to the solution and the violet fumes of iodine which escape when the liquid is boiled. The iodine vapour can also be detected by the introduction of a bit of paper moistened with starch-paste, the latter turning blue. This reaction is not as delicate as the foregoing, but still serves to distinguish iodine from chlorine and bromine:

$$FeCl_3 + HI = I + FeCl_2 + HCl.$$

3. *Liberation by chlorine* (chlorine-water).—The reaction is less characteristic. Chloroform or carbon disulphide may be used to detect the iodine released (starch-paste may also be employed). The test is made as for bromine (§ 90): the colour of the carbon disulphide becomes violet or almost black, according to the amount of iodine set free. An excess of chlorine destroys the colour, and also that of starch-paste, the colourless compound ICl being formed.

This reaction is not as characteristic as the others, since, if bromides are present, chlorine releases the bromine as well. With some practice, however, the reaction can be used to detect both halogens. If chlorine-water be added very cautiously to the solution under examination, in presence of carbon disulphide, a violet colour appears, since the chlorine liberates iodine first (iodine expels the bromine from a solution of the latter in carbon disulphide or chloroform under water). Upon further careful addition of the chlorine-water, the colour begins to vanish, and when it has entirely disappeared, *i.e.*, when all the iodine has combined with chlorine, the separation of bromine commences, and the carbon disulphide becomes brown. The chlorine-water must be added very cautiously, and drop by drop. The colour of the bromine also vanishes in presence of an excess of chlorine.

Iodine is also released from its compounds by the methods given for chlorine (action of manganese dioxide), and for bromine (sulphuric acid). They are not characteristic, therefore, of iodine.

COURSE OF ANALYSIS FOR THE DETECTION OF CHLORINE, BROMINE, AND IODINE

§ **92.** The presence of iodine interferes with the detection of bromine and chlorine. When present, therefore, it must be removed from the solution under examination. The first operation is the detection of iodine, in a special portion of the liquid, by means of sulphuric acid and potassium nitrite in presence of starch-paste (§ 91). If iodine be found, the solution is next treated with cupric sulphate and sodium thiosulphate (§ 91). The cuprous iodide having been filtered off (it may be used, if necessary, for further tests for iodine), the excess of cupric sulphate is removed by hydrogen sulphide, and the filtrate evaporated to dryness. The residue is divided into two portions, in one of which chlorine is detected by the formation of chromyl chloride (Conditions, see § 89), and the other being examined for bromine. The portion of the residue taken for the latter purpose is dissolved in as little water as possible, and chlorine-water or sulphuric acid added in presence of carbon disulphide (§ 90). If the solution contain the haloid salts of the heavy metals, it is precipitated by sodium carbonate, filtered, and the above tests made with the solution of sodium salts obtained. Insoluble haloids (§ 88) are fused with sodium carbonate, the fusion product extracted with water, and the solution thus prepared tested for the halogens. The insoluble silver compounds are brought into solution according to § 89, and the halogens detected in the resulting zinc salts.

The above method for detecting the halogens is not accurate, better results being obtained by the following process. A concentrated solution of the haloid salts, in a special portion of which iodine has already been recognised, is introduced into a flask connected with a delivery tube, and treated with ferric sulphate until all the iodine is precipitated. The latter is completely removed by steam, for which purpose the solution must be boiled for a sufficiently prolonged period. A portion of the cooled solution is then mixed with chloroform, and a test made for bromine, with solid potassium permanganate. If it is present, the entire solution is subjected to the same operation, and the liberated halogen removed by boiling the solution (finally under the addition of water). The solution (to which the potassium permanganate has given a red colour) is then decolorised with alcohol, filtered, the filtrate acidified with nitric acid, and the chloride which it contains detected by silver nitrate.

THE OXYACIDS OF THE HALOGENS

§ **93.** The halogens, especially chlorine, form several different oxygen acids. Those of chlorine are prepared by the action of the free halogen upon metallic oxides (of the alkalies or of Group II.) Either hypochlorites (bleaching powder, $CaClO$) or chlorates (*e.g.*, $KClO_3$ Berthollet's salt) are formed, according to the conditions present. The remaining chlorine acids are formed from the chlorates by reduction (chlorous acid, $HClO_2$) or oxidation (perchloric acid, $HClO_4$). In many respects the acids possess similar properties. Their salts are resolved by heat into chlorides and oxygen, which explains their employment as oxidising agents in the dry methods. When treated with hydrochloric acid they evolve chlorine; this characteristic is used in oxidation reactions in the wet way. This class of reactions is also employed for the detection of the oxyacids; they are similar to those of chlorine itself. Reducing-agents completely convert the oxyacids into hydrochloric acid or chlorides.

Hypochlorous Acid, $HClO$

The anhydride of the acid, Cl_2O, is a yellowish-green gas. Hypochlorous acid is known only in very dilute solution, and is prepared by conducting chlorine into cold water which holds mercuric oxide in suspension:

$$2Cl_2 + HgO + H_2O = 2HClO + HgCl_2.$$

The hypochlorites are called bleaching salts (the latter usually contain chlorides), and occur principally as "Chloride of lime" and "Javelle's lye" (sodium hypochlorite). Their formation has already been given (action of chlorine upon metallic oxides). They are easily decomposed, especially if their solutions be boiled; on treatment with acids they yield chlorine, or, more rarely, hypochlorous anhydride.

The reactions of hypochlorites consist in the oxidation reactions which they cause (Chlorine, § 89). Both litmus and indigo solutions are decolorised by hypochlorites in presence of free sulphuric or some other acid. The oxidation of ferrous salts or the liberation of iodine can be employed for their detection, as for that of chlorine (§ 89). The formation of peroxides, *e.g.*, nickelic oxide or lead dioxide, in alkaline solution may also denote hypochlorites as well as chlorine. Silver nitrate causes a precipitate of silver chloride, the silver hypochlorite which is at first formed being decomposed:

$$3AgClO = AgClO_3 + 2AgCl.$$

When the free acid is treated with metallic mercury the reddish-yellow or dark-brown mercuric oxychloride results (distinction from chlorine, which forms mercurous chloride, HgCl). The salts of hypochlorous acid convert mercury to mercuric oxide:

$$2HClO + 2Hg = HgCl_2 . HgO + H_2O,$$
$$NaClO + Hg = HgO + NaCl.$$

Chloric Acid, $HClO_3$

This acid is known only in solution. Its solution is a powerful oxidising agent, bleaches organic matter, and is decomposed by heat:

$$(1)\quad 3HClO_3 = HClO_4 + 2Cl + 4O + H_2O.$$

When acted upon by hydrochloric acid it evolves chlorine (also hypochlorous anhydride and other products, according to the conditions present):

$$(2)\quad HClO_3 + 5HCl = 6Cl + 3H_2O.$$

It is converted by reducing agents, in acid solution, into hydrochloric acid. The chlorates, *e.g.*, potassium chlorate, show the same reactions as the free acid. Their decomposition proceeds according to equation (1) on being warmed, according to (2) when treated with hydrochloric acid. Their value as oxidising agents is obvious (see Metals, Group III. §§ 37 and 32; Group V. § 72). A mixture of potassium chlorate and nitric acid forms an especially powerful oxidising agent. The preparation of chloric acid is described at the beginning of this paragraph.

Reactions of Chlorates. — These consist in oxidation reactions which are caused by the released chlorine (or more rarely, by the chloric acid itself). Chlorates are not precipitated by barium chloride or silver nitrate. The solution of a chlorate, acidified with hydrochloric acid, decolorises indigo, the reaction being caused by the chlorine which is set free.

If a dry chlorate be introduced into a drawn-out glass tube, a few small pieces of charcoal placed above the salt, and the latter then heated until it melts, the carbon takes fire in the oxygen evolved and burns with an intense light.

If a small quantity of a chlorate be heated upon platinum foil with potassium cyanide, a violent explosion ensues. (The experiment must be made with but very small quantities.)

Certain oxidation reactions (such as that with chromic oxide) can also serve as tests for chlorates.

If the dry salts be acted upon by *sulphuric acid*, a yellow coloration is caused; the experiment is accompanied by the evolution of a yellowish-green gas, ClO_2, which has a characteristic smell resembling chlorine. (Very small quantities of the substances must be used, as an explosion may otherwise ensue):

$$3KClO_3 + H_2SO_4 = 2ClO_2 + KClO_4 + K_2SO_4 + H_2O.$$

Silver nitrate produces no precipitate; if a few drops of a solution of sulphurous acid be added, however, silver chloride is deposited. This reaction is used for the detection of chlorates in presence of chlorides.

A solution of *diphenylamine* in concentrated sulphuric acid is coloured dark-blue by chlorates (*v.* Nitric acid).

Iodic Acid, HIO_3

Iodic acid is prepared by the oxidation of iodine with nitric acid, or by gently heating iodine with potassium chlorate. It is soluble in water, and easily split up into iodine and oxygen. When acted upon by hydrochloric acid chlorine is evolved (and ClI formed).

The reactions consist in the preparation of insoluble salts and the separation of free iodine. *Insoluble salts.—Barium iodate* is a white precipitate which dissolves in nitric acid. Silver iodate is thrown down as a white crystalline precipitate, soluble in ammonia but difficultly so in nitric acid. *Reactions in which iodine is released.* Hydrogen sulphide decomposes iodic acid, iodine and sulphur separating (the liquid becomes brown) and water being formed:

$$2HIO_3+5H_2S=I_2+S_5+6H_2O.$$

The free iodine is converted by further action of the hydrogen sulphide into hydriodic acid, and the solution loses its colour. As a result of these characteristics iodic acid may be detected in the course of the systematic examination for the metals (when the metals are precipitated by hydrogen sulphide). Many other substances, such as sulphurous acid, hydriodic acid, hydrochloric acid, etc., also release iodine from iodic acid. The reactions of the free halogen are given in § 91.

FLUORINE

Hydrofluoric Acid and Fluorides

§ **94.** Fluorine is prepared by the electrolysis (in a platinum vessel) of anhydrous hydrofluoric acid, in which potassium fluoride is dissolved to render the liquid conducting. The fluorine collects at the positive electrode as a faintly yellow gas, which possesses a powerful odour similar to that of the chlorine oxides and acts violently upon the mucous membrane of the mouth and eyes. Fluorine unites directly with hydrogen; its combination with sulphur, phosphorus, and antimony is accompanied by a flash of light. It has no effect upon gold or platinum in the cold, but decomposes water instantly, with formation of hydrofluoric acid and ozone. Glass is also attacked by it, yielding silicon fluoride. The properties of fluorine render it impossible for this element to be found in the free state in analysis. The fluorides are more often seen, but hydrofluoric acid itself need seldom be looked for.

Fluorine occurs in nature chiefly as fluor spar, or calcium fluoride; it is found less frequently as cryolite, $NaAlF_4$.

Anhydrous hydrofluoric acid is a colourless, fuming liquid which boils at 20° C., and mixes readily with water. Its solution, the common hydrofluoric acid,[1] colours paper soaked with Brazil-wood tincture yellow. Hydrofluoric dissolves all the metals except gold and platinum, with evolution of hydrogen. It is also a solvent for many oxygen acids, which

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[1] Hydrofluoric acid is poisonous, and its solution causes obstinate sores.

form compounds with the fluorine (silicic acid, titanic acid, etc.) The action of hydrofluoric acid upon silica is especially characteristic (see below). The fluorides of the alkali metals are soluble, the others, with the exception of FeF_3, SnF_4, HgF_2, AgF, are insoluble. They are not decomposed by ignition (some of them volatilise when heated; the compounds with metalloids are all volatile). So-called acid salts of the alkali metals, *e.g.*, KHF_2, are also known, and there are numerous double fluorides analogous to them. Sulphuric acid releases hydrofluoric acid from fluorides.

The reactions of fluorides consist in the formation of insoluble salts, and in the peculiar action of hydrofluoric acid upon silica; the latter is principally employed.

Insoluble fluorides.—Only a few of the many available compounds will be discussed. Their conversion to soluble fluorides is effected by fusion with sodium carbonate (fluorides of Group II. are not decomposed by this operation).

Calcium fluoride, CaF_2.—Calcium chloride produces in a solution of potassium fluoride, a gelatinous, almost transparent precipitate, which is not immediately visible. It subsides more quickly in an ammoniacal solution. Calcium fluoride is insoluble in water, but dissolves, though with difficulty, in nitric and hydrochloric acids. Its acid solution is incompletely or not at all precipitated on neutralisation with ammonia.

Barium fluoride, BaF_2.—Barium chloride throws down a voluminous white precipitate, which is almost insoluble in water, and difficultly soluble in hydrochloric or nitric acid. It is incompletely or not at all deposited from this solution by ammonia.

Action upon silica.—Hydrofluoric acid acts upon silica to form silicon fluoride:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

The reaction is also shown by aqueous hydrofluoric acid, or when fluorides are warmed with sulphuric acid and silica. In qualitative analysis, the experiment may be performed in various ways. The hydrofluoric acid is detected by its power of etching glass, or by the properties of the silicon fluoride formed.

1. The pulverised fluoride is covered with sulphuric acid

in a platinum crucible, and the latter covered by a watch-glass and very gently warmed. As the fumes of sulphuric acid alone etch many kinds of glass, it is preferable to use for the experiment the difficultly fusible Bohemian variety. If hydrofluoric acid is present it escapes, and the glass becomes etched, the silica of the latter being converted to silicon fluoride. The reaction is still more delicate if the glass be covered by a film of wax (solution of wax in turpentine) and some small design scratched in the wax with a needle. This involves no modification in the method of procedure. When the reaction has subsided, and the wax been removed by heat and rubbing, the engraved design becomes visible.

2. The above test is insufficient when the fluorides contain silica (or when the substance is a mixture of the two), as the action of sulphuric acid in this case is to form silicon fluoride, and not hydrofluoric acid. The properties of the silicon fluoride itself must therefore be used to detect the fluorine. The fluoride is warmed with sulphuric acid and glass (or without glass, if silica is already present), in a test-tube closed by a cork which supports a delivery-tube. The escaping silicon fluoride fumes in the air, and if led under water deposits an amorphous, white precipitate of silica, hydrofluosilicic acid remaining in the solution:

$$3SiF_4 + 2H_2O = 2SiH_2F_6 + SiO_2.$$

If the formation of this precipitate is not sufficient, a confirmatory test may be made by evaporating the solution to dryness (after filtering off the silica and neutralising with sodium carbonate), and testing the residue according to 1. Silicates which are not decomposable by sulphuric acid are fused with a mixture of sodium and potassium carbonates, the fusion product extracted with water, and, after saturation with hydrochloric acid, precipitated by calcium chloride. The precipitate of calcium fluoride is subjected to the above tests.

Both experiments may be modified as follows. The substance to be tested is mixed with powdered microcosmic salt and carbon (prepared by fusing carbon and microcosmic salt together and pulverising the product), and placed in a small tray made of platinum foil. The tray is then set in a glass tube open at each end, heated before the blow-pipe, and the products formed by the intense heat allowed to flow through the tube. Any hydrofluoric acid evolved may be detected by its peculiar smell, its action upon logwood paper, and by the glass becoming etched. In presence of silica the silicon fluoride is recognised by its action upon logwood paper (which turns yellow), and by the deposit of silica on the sides of the tube.

Hydrofluosilicic acid, H_2SiF_6.—The formation of this acid from silicon fluoride has already been described. It exists only in solution, and on evaporation splits up into silicon fluoride and hydrofluoric acid. It is very easily decomposed, either as the free acid or in its salts, by concentrated sulphuric acid. These two reactions serve for the detection of hydrofluosilicic acid. Its salts are for the most part insoluble in water, and are converted to the fluorides and silicon fluoride on ignition. The formation of the salt, K_2SiF_6, is characteristic as a reaction of potassium. Ammonia precipitates hydrated silicic acid from a solution of hydrofluosilicic acid. Barium silicofluoride is also characteristic, being insoluble in either water or dilute acids.

SULPHUR

§ **95.** Sulphur is known in both amorphous and crystalline modifications. The crystalline variety is dimorphous. It occurs in the native state in rhombic octahedra, and takes this form, also, in crystallising from solution in carbon disulphide. Molten sulphur solidifies to monoclinic prisms on cooling, and then passes under various conditions into the rhombic form. Sulphur fuses at 114·5° C., and boils at 440° C. The amorphous sulphur also exists in many varieties; some of them result when the element is melted, or heated to 260° C., and then suddenly cooled off. It is also obtained in the amorphous state when precipitated from certain of its compounds. The crystalline modifications dissolve in carbon disulphide, but with the exception of a few of its varieties amorphous sulphur is insoluble in this medium. Sulphur is also dissolved by many other substances, such as caustic potash, thiosulphates, etc.; in this case, however, it unites with the solvent to form a chemical compound.

Free sulphur may be detected by its following properties:

(1) it volatilises in yellowish-brown vapours, which condense to brown drops, the latter turning yellow on cooling. (2) When lighted in the air sulphur burns with a blue flame, and emits the stifling odour of sulphurous anhydride. If the test is to be made with a mixture of sulphur with other substances, it should be performed in a glass tube open at both ends. The tube is held obliquely by a support, and heat applied to the portion which contains the substance, the properties of the sulphur dioxide being shown at the upper end of the tube. (3) Oxidising agents convert sulphur to sulphuric acid; this reaction will be described below.

The principal compounds of sulphur are hydrogen sulphide, the metallic sulphides, and sulphuric acid. There are also many other acids, with their salts and derivatives.

The mineral kingdom contains sulphur both in the native and combined states (in pyrites, blendes, etc.) Of its oxygen compounds, calcium sulphate (gypsum, anhydrite) is the most common. The analyses of these minerals will be discussed later.

Hydrogen Sulphide and Metallic Sulphides

Hydrogen sulphide is a poisonous gas which has a disagreeable odour (that of rotten eggs). When lighted, it burns to sulphur dioxide and water. It is obtained by the action of acids upon metallic sulphides (usually ferrous sulphide). Hydrogen sulphide is soluble in water, but neither the gas nor its solution is stable. When exposed to the air the latter deposits sulphur.

The precipitation of sulphur by the action of hydrogen sulphide is used as a qualitative test for ferric salts and chromic acid. In this reaction the hydrogen of the hydrogen sulphide becomes oxidised to water, or unites with chlorine, etc. Nitric and sulphurous acids have the same action upon hydrogen sulphide, and it is also decomposed by the halogens, with formation of free sulphur and the respective hydrogen acids.

The *sulphides* are formed directly by ignition of metals, oxides, or carbonates with sulphur. They may also be prepared by the action of carbon, at a high temperature, upon the alkali sulphates or salts of other sulphur acids. The sulphides of the heavy metals yield sodium sulphide when fused with sodium carbonate and carbon. (The application of this reaction as a test for sulphur is given below.) Finally, they are formed, as we already know, in the important reaction between hydrogen sulphide and the salts of certain metals.

Properties of the sulphides.—We assume that the solubilities of the sulphides have already been learned, as they have formed the basis for the classification of the metals. Native sulphides, however, often show a more obstinate behaviour toward acids than those which are artificially prepared. Galena, iron pyrites, etc., are thus insoluble in acids, while artificial lead and ferrous sulphides, on the contrary, are readily dissolved by these agents. The sulphides of Groups I. and II., which are soluble in water, are unstable in solution, absorbing oxygen from the air and passing into polysulphides (and thiosulphates). Their solutions are also decomposed by carbonic acid. Insoluble sulphides are brought into solution by the general method—fusion with sodium carbonate. (The operation results, as will be remembered, in the formation of either a carbonate or the metal itself, the product depending upon the metal fused.)

So much importance, analytically, is attached to the sulphides, that it may be well to mention a few of their properties again. The conditions necessary for their conversion to sulphuric acid are especially important. The oxidising agents used for effecting this reaction are very diverse (action of HNO_3, § 72, fusion with sodium carbonate and potassium nitrate or chlorate, etc. § 32). Chlorine may also be employed in various ways: oxidation with potassium chlorate and hydrochloric acid (§§ 40, 72) or nitric acid (§ 32), which is still better, has already been discussed. The final method to be mentioned is the treatment of the heated sulphide with gaseous chlorine. In this reaction the metallic chloride and sulphur chloride, S_2Cl_2 (a liquid boiling at 138°), are formed. The experiment is made in a bulb-tube which connects with a receiver containing sodium hydroxide; the sulphur chloride is first decomposed to sulphurous acid, and this product becomes finally oxidised to sulphuric acid by the excess of chlorine. Bromine is a still better reagent, and is employed either in the free state or in hydrochloric acid solution. These reactions will be more exactly described in the discussion of quantitative determinations. All these methods may also be employed in the analysis of mineral sulphides, *i.e.*, of the pyrites, blendes, etc.

Reactions of Hydrogen Sulphide and the Metallic Sulphides.—Free hydrogen sulphide is detected by its unpleasant odour, or, more accurately, by means of paper moistened with lead acetate or silver nitrate. The metallic sulphides which form colour the paper black. A piece of paper moistened with sodium nitroprusside[1] and previously exposed to the action of gaseous ammonia, becomes of a beautiful purple-red colour in contact with hydrogen sulphide.

These methods also serve for the detection of sulphur in sulphides which are decomposed by acids with evolution of hydrogen sulphide. The experiment is made in a test-tube, and the liberation of hydrogen sulphide determined by holding in the mouth of the tube a piece of paper soaked in the respective reagent.

Traces of hydrogen sulphide gas may be detected as follows: The substance is placed in a hydrogen generator and the hydrogen lighted at the end of the exit tube. If a porcelain disk be held in the flame, the presence of hydrogen sulphides causes the portion of the latter which touches the disk to assume a characteristic blue tint.

Sulphides: 1. *Soluble sulphides.*—(*a*) When treated with acids the salts of this class evolve hydrogen sulphide, which is detected according to the foregoing methods. The polysulphides deposit sulphur on the addition of acids. (*b*) The solution of the sulphides is tested with lead acetate or silver nitrate, these reagents causing a black precipitate. If alkalies or soluble carbonates are present, this reaction is made with a solution of lead oxide in potassium hydroxide. (*c*) Sodium nitroprusside, after the addition of caustic soda, causes a purple-red colour. It has no action upon free sulphuretted hydrogen. (*d*) The solution is treated with $\frac{1}{50}$ of its volume of fuming hydrochloric acid and a few crystals of the sulphate of para-amidodimethylaniline,  $C_6H_4\left\langle\begin{matrix}NH_2\\N(CH_3)_2\end{matrix}\right.$. As soon as the latter are dissolved, two drops of a dilute solution of ferric chloride are added; if hydrogen sulphide is present, methylene blue, $C_{16}H_{18}N_3SCl$, forms, and the solution becomes dark-blue. This is the most delicate test for hydrogen sulphide known, and follows the equation:

$$2C_8H_{12}N_2 + H_2S + 3O + 2HCl = C_{16}H_{18}N_3SCl + NH_4Cl + 3H_2O.$$

2. *Sulphides which are decomposed by acids with difficulty,* are treated with hydrochloric acid in presence of finely-divided

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[1] Sodium nitroprusside, $Na_2Fe(NO)Cy_5$, is prepared by the action of nitric acid upon potassium ferrocyanide. The action of soluble sulphides upon the compound has not been sufficiently studied to allow an explanation of this reaction.

iron (*ferrum alcoholisatum*), whereupon hydrogen and hydrogen sulphide are evolved. The reaction is made in a test-tube which is loosely closed by a cork wrapped in lead acetate paper.

3. *Sulphides which are insoluble in acids*, are fused with sodium oxide in a silver crucible. If the fused mass be placed upon a bright piece of silver (a coin) and moistened with warm water, a black spot of silver sulphide forms. The solution of the fusion products can also be examined, after this test is made.

As a general method of detecting sulphur, the formation of sulphuric acid as an oxidation-product of the sulphides may be used. The substance is mixed with anhydrous sodium carbonate, and potassium nitrate, in small enough quantity to prevent an explosion on its being fused, is then added (the amount of KNO_3 to be taken is determined by a previous test). The mixture is placed in a platinum crucible and ignited. When the oxidation is complete and the resultant mass has been treated with water, the aqueous solution is neutralised by an acid and tested for sulphuric acid.

When heated in a glass tube, which is open at each end and held somewhat obliquely, sulphides give off sulphurous acid; the latter is recognised by its odour or other characteristics (see below).

Sulphuric Acid and Sulphates

§ **96.** Sulphuric acid, H_2SO_4, is an oily liquid which boils at 338° C., undergoing partial dissociation into sulphuric anhydride and water. It becomes heated when mixed with water, and absorbs the latter from moist gases (it is therefore used for drying purposes). Many organic substances become carbonised when in contact with sulphuric acid, the reaction often being accompanied by the evolution of sulphur dioxide. As sulphuric acid has a high boiling-point, it displaces a great many acids (those which are more volatile) in their salts, *e.g.*, chlorides, nitrates, acetates, etc. The hot concentrated acid dissolves a majority of the metals. Its character as a powerful salt-forming acid is used in analysis, for the purpose of obtaining insoluble oxides in solution (Metals, Group III.) Many of the sulphates dissolve in water, but all, with the exception of the ferric salt, are insoluble in alcohol. The characteristic reactions of sulphuric acid consist in the formation of insoluble sulphates. The latter are brought into solution by the general method—fusion with sodium carbonate (gypsum, heavy spar, and other mineral sulphates are analysed by these means).

Reactions of Sulphates. *Insoluble salts. Barium sulphate.*—This salt is precipitated by barium chloride. Its most important property, which has already been discussed (§ 19), may be mentioned again, *i.e.*, its insolubility in water or dilute acids. The reaction must be made in sufficiently dilute solutions, as in concentrated solutions barium chloride may cause a precipitate of other barium salts. For example, strongly concentrated solutions of hydrochloric or nitric acid may precipitate barium chloride or nitrate respectively. Both salts dissolve, however, on the addition of water (distinction from the sulphate). If these acids are present in large quantities it is preferable to remove them by evaporation, before testing with barium chloride.

Lead sulphate is obtained by precipitation with lead salts. Its properties are described in § 66.

To detect sulphuric acid in insoluble compounds the following methods may be employed: (*a*) The salt is fused with sodium carbonate, and after the fusion product has been dissolved, the solution is tested as above. (*b*) When a sulphate is fused with sodium carbonate and carbon (or on a charcoal support in the inner flame of the blow-pipe) the sulphuric acid undergoes reduction and a sulphide forms. If the fusion product be placed upon a silver coin and moistened with water, a black spot is obtained (Hydrogen sulphide, § 95). The reaction is convenient as a confirmatory test of the first reaction.

Sulphurous Acid and Sulphites

The hydrated acid is unknown. Sulphur dioxide, SO_2, the anhydride, is a gas possessing a suffocating odour, and condensing to a liquid at – 10° C. It dissolves readily in water, to a solution which has the same smell and an acid reaction (it bleaches Brazil-wood paper). The sulphites possess the general formula R_2SO_3, and are decomposed by acids with formation of sulphur dioxide. Only the alkali sulphites dissolve in water, but those of the other metals are readily soluble in acids. Both sulphurous acid and the sulphites are powerful reducing agents. Several of the reactions which they cause will be described below, and we have already observed the use of a few in analysis (Reduction of ferric salts, § 34, of arsenic acid, § 79, etc.) Sulphites are converted to sulphates by chlorine and other oxidising agents.

Reactions of Sulphites.—Certain of the reduction reactions afford characteristic tests. The reduction may be in either of two directions. The sulphurous acid may be used as a reducing agent, when it passes into various other sulphur acids; or it may itself be reduced to hydrogen sulphide or sulphur. Its salts are less characteristic.

Barium sulphite, $BaSO_3$.—The addition of barium chloride to a neutral solution causes a white precipitate of barium sulphite, which is readily soluble in acids. The lead salt shows a similar behaviour.

Reduction reactions.—1. Those caused by sulphurous acid have already been discussed. The reduction of chromic acid, of manganic acid, and of mercuric to mercurous chloride, and the conversion of the halogens to their hydrogen acids are employed as qualitative reactions.

2. The reduction of the sulphurous acid itself is more characteristic. It is decomposed by hydrogen to hydrogen sulphide. The test is made in a small apparatus for generating hydrogen from zinc and hydrochloric acid: moistened lead acetate paper becomes black when held in the issuing gas:

$$SO_2 + 6H = H_2S + 2H_2O.$$

Stannous chloride in presence of hydrochloric acid precipitates stannic sulphide, SnS_2, but not immediately.

Hydrogen sulphide precipitates sulphur from sulphurous acid, the reaction being accompanied by the formation of pentathionic acid:

$$4SO_2 + 3H_2S = H_2S_5O_6 + 2S + 2H_2O.$$

Thiosulphuric acid and the thionic acids.—The reactions of these acids resemble in many ways those of sulphurous acid. The acids do not exist in the free state (a few are known in solution). The properties of barium thiosulphate place thiosulphuric acid in the first group of acids (see § 105). This salt is precipitated from neutral solution by barium chloride, and is difficultly soluble in water, but easily so in acids. All the barium polythionates dissolve readily in water. The solutions of all polythionates are precipitated by silver nitrate as the white silver salts, the latter quickly decomposing, however, to silver sulphide (sulphuric acid is then found in solution). The decomposition to sulphur or sulphurous or sulphuric acid (by the action of acids) characterises them all, and explains the reducing action which their compounds exert. On the other hand, they resemble sulphurous acid in being reduced to hydrogen sulphide by hydrogen. Thiosulphuric acid is distinguished from sulphurous by its behaviour toward hydrochloric acid. When acted upon by the latter the thiosulphates deposit sulphur and evolve sulphur dioxide, which may be detected by its odour. Thiosulphuric, tetrathionic, and trithionic acids are easily distinguished, when but one of them is in the solution, by their varying behaviour toward silver nitrate and copper sulphate. These reagents do not precipitate thiosulphates. Tetrathionic acid deposits, on the addition of silver nitrate, a yellow precipitate which speedily turns black, and has no action upon copper sulphate. When heated with either reagent, trithionic acid deposits a black precipitate. If sulphides are also present in the solution, they should be previously removed by zinc sulphate, as the sulphide of the latter metal.

NITROGEN

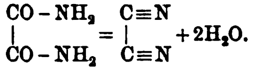
§ **97.** Nitrogen is an odourless gas (sp. gr. = 0·969) which neither undergoes nor supports combustion. Although uniting directly with only a few of the elements (boron, titanium), nitrogen forms compounds which are very diverse. These can be divided into three classes: ammonia and its derivatives, cyanogen compounds, and the compounds of nitrogen with oxygen: the latter include the acids (nitric, etc.) One class of compounds may be converted to another in various reactions.

Ammonia and its compounds have already been discussed (§ 12).

Hydrocyanic Acid, the Cyanides, and Cyanogen

Cyanogen is a colourless gas (condensing to a liquid at − 21° C.) which has a characteristic odour and, when lighted, burns with a violet flame. It is prepared by the ignition of mercuric or silver cyanide.

The cyanides are obtained by the action of nitrogen or its compounds upon carbon in presence of the alkali metals or their oxides and at a high temperature. Potassium cyanide is usually obtained as the product of the reaction, and all the other cyanides are prepared from this salt. Another and equally important method is based upon the formation of cyanides by the withdrawal of water from the amides of organic acids. Thus, cyanogen is formed when the constituents of water are split off from the amide of oxalic acid :



$$\begin{array}{l} CO-NH_2 \\ | \\ CO-NH_2 \end{array} = \begin{array}{l} C\equiv N \\ | \\ C\equiv N \end{array} + 2H_2O.$$

Hydrocyanic acid (Prussic acid) is prepared by distilling cyanides with sulphuric acid. It is a liquid boiling (in the anhydrous state) at 27° C., soluble in water, and having a strong odour of bitter almonds. Hydrocyanic acid is a deadly poison, either in solution or in the gaseous state. The soluble cyanides and simple compounds of hydrocyanic acid are likewise poisonous, and extreme caution must be taken in operations which involve their use.

Cyanides (salts of hydrocyanic acid).—The salts of the metals of Groups I. and II., and of mercury, are soluble in water and alcohol. Their aqueous solutions, however, are unstable; the final products of decomposition being formic acid and ammonia:

$$KCN + 2H_2O = HCOOK + NH_3.$$

The alkali cyanides are stable at a high temperature, but on fusion in the air with oxidising agents (such as the peroxides of manganese or lead) they are converted into cyanates, *e.g.*, KCNO. They also unite directly with sulphur to form the sulphocyanates (KCNS). The employment of potassium cyanide as a reducing agent in the dry way (§ 73) is thus explained. The cyanides of the heavy metals are decomposed by ignition (cyanogen is liberated), and all the salts, including the double compounds (see below), by fusion with potassium nitrate. All cyanides, and also the double salts which are mentioned below, are likewise decomposed by concentrated sulphuric acid, the reaction resulting in the formation of sulphates and evolution of hydrocyanic acid. The action of dilute sulphuric acid, and of hydrochloric and nitric acids, upon the different cyanides is, as we shall see, very diverse.

Double cyanides.—Hydrocyanic acid is characterised by its double salts. They are usually prepared by the solution of metallic cyanides in potassium cyanide, or in soluble cyanides in general, and possess varying formulae (comp. Groups III. and IV.) Some of them are decomposed by dilute acids, with evolution of hydrocyanic acid, and if the metallic cyanide is insoluble in dilute acids it is then precipitated. This class of salts also undergoes decomposition when boiled with mercuric oxide, mercuric cyanide forming, and the oxide of the heavy metal being deposited. The double cyanides which act as above are formed by Mn, Zn, Ni, Ag, Cu, Pd (see these metals). The remaining double salts (those of Fe, Co, Cr, Pt), on the contrary, are stable toward dilute acids, and form acids, such as hydroferrocyanic and hydroferricyanic acids: they are also unaffected by mercuric oxide. We remark again that all the double salts are decomposed by concentrated sulphuric acid (3 parts, H_2SO_4, 1 part, H_2O), and also on fusion with potassium nitrate. In these reactions the cyanogen is driven off (as hydrocyanic acid in the first case, and fully decomposed in the second). Such a decomposition is necessary in the analysis of these compounds, as the metals which they contain can neither be detected nor precipitated by any other means.

Reactions of Cyanides.—These are based in part upon the formation of insoluble salts (simple or double), and partly upon the conversion of cyanides to sulphocyanates. Mercuric cyanide does not show the reactions given below, and the mercury must be previously removed by hydrogen sulphide. Free hydrocyanic acid must be neutralised with sodium hydroxide before being submitted to the tests.

Insoluble salts. Silver cyanide, $AgCN$.—Silver nitrate throws down a white precipitate, which dissolves in an excess of potassium cyanide to form the salt, $AgCN \cdot KCN$. Silver cyanide is soluble in ammonia, but insoluble in nitric acid. It is distinguished from silver chloride in evolving hydrocyanic acid (easily recognised by its odour) when boiled with hydrochloric acid. On ignition it becomes black (with formation of silver paracyanide), and cyanogen is set free (it can be lighted).

Ferric ferrocyanide (Prussian blue), $Fe_4(Fe(CN)_6)_3$.—As the properties of this compound were discussed in § 34, attention will here be paid only to its preparation from cyanides. If ferrous sulphate and ferric chloride be added to a soluble cyanide (as the formula shows, both a ferrous and a ferric salt are necessary), and the solution then precipitated by caustic potash, a precipitate of the iron hydroxides is obtained, and potassium ferrocyanide forms in the solution. If hydrochloric acid be next added, the hydroxide dissolves, and a blue precipitate of ferric ferrocyanide is deposited. When very small quantities of cyanides are present the liquid merely turns green on addition of the hydrochloric acid, and the precipitate separates only after long standing.

This reaction is used to detect nitrogen in organic compounds. If the latter be fused with metallic potassium, the cyanide of the latter is obtained (see the formation of cyanides). The fusion is next treated with water, which converts the excess of the metal (with evolution of hydrogen) into potassium hydroxide, and the detection of the cyanogen (and therefore of the nitrogen) is then accomplished as above.

Ferric sulphocyanate, $Fe(CNS)_3$.—The properties of this compound are described in § 34. In order to employ its formation as a test for hydrocyanic acid, however, the conditions necessary for the conversion of cyanides into sulphocyanates must be studied. The solution of the cyanide is treated with a large excess of yellow ammonium sulphide, which contains sulphur, and, after the addition of a few drops of ammonia, the mixture is evaporated on the water-bath in a porcelain dish until all the ammonium sulphide has been driven off, and a dry white residue is obtained. (The operation must be repeated several times if necessary.) Ammonium sulphocyanate is thus formed, and after acidifying with hydrochloric acid, the addition of ferric chloride to its solution produces a deep-red colour:

$$(NH_4)CN + S = (NH_4)CNS.$$

If free hydrocyanic acid is to be detected by this method, it must first be neutralised by potassium hydroxide, and then evaporated with ammonium sulphide. This reaction forms the most delicate test for hydrocyanic acid.

REMARK.—*Hydroferrocyanic acid*, $H_4Fe(CN)_6$. The conditions under which this compound is formed have already been mentioned. The acid is soluble in water (its solution may be prepared by the action of dilute acids upon potassium ferrocyanide). Its reactions are as follows: on the addition of ferric chloride, ferric ferrocyanide, or Prussian blue, is formed (§ 34): copper sulphate precipitates cupric ferrocyanide (§ 64). Silver nitrate also causes a white precipitate of the silver salt to be deposited, which is soluble in either ammonia or nitric acid, and completely decomposes when its ammoniacal solution is boiled. Insoluble salts are brought into solution by boiling with caustic alkalies (§ 34). They are completely decomposed by boiling with concentrated sulphuric acid, or on fusion with potassium nitrate.

Hydroferricyanic acid, $H_3Fe(CN)_6$, is similar in its properties to the foregoing compound. It is soluble in water. Ferrous salts give with the soluble salts a blue precipitate (distinction from the ferrocyanides). Copper sulphate throws down the green cupric ferricyanide. The silver salt is orange-yellow, and soluble in ammonia (decomposes when boiled). The remaining properties of hydroferricyanic acid are similar to those of the foregoing acid.

Nitric Acid

§ 98. Nitric acid, HNO_3, is a liquid which boils at 86° C., undergoing partial decomposition at the same time; its sp. gr.

at 14° C. = 1·52. It acts as an energetic oxidising agent, and in yielding its oxygen to other bodies is converted into lower oxides of nitrogen. Nitric acid is a solvent for many metals, and in its action upon them evolves either hydrogen (with zinc, etc.), which reduces the acid to nitrous oxide and ammonia, or nitric oxide (with copper, silver, etc.) The application of these properties in analysis is given below. Nitric acid is completely reduced to ammonia by the action of hydrogen in alkaline solution; *i.e.*, by that of zinc, or, preferably, of aluminium, and potassium hydroxide. The normal nitrates are readily soluble in water; the basic salts of some of the metals, however, as well as the salts of certain organic bases, dissolve with difficulty. When ignited, the nitrates decompose, losing oxygen and passing into the oxide of the metal (employed in oxidation-reactions).

Reactions of Nitric Acid and Nitrates.—As nitric acid forms no insoluble salts (except with some organic bases), its detection is effected exclusively by oxidation-reactions. These are all applicable to quantitative analysis. The reactions in which nitric oxide is formed are especially characteristic.

Formation of nitric oxide. Action on copper.—To detect nitric acid by this reaction we use the property which the nitric oxide evolved possesses of turning to brown fumes in the air (union with oxygen: NO_2 is formed):

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

The solution of the nitrate is heated with copper filings and concentrated sulphuric acid (the latter releases the nitric acid); the test-tube becomes filled with reddish-brown fumes, which may be more distinctly observed if viewed through the length of the test-tube.

Action upon ferrous salts (§ 37).—If the concentrated solution of a nitrate be mixed with an equal volume of concentrated sulphuric acid, and after the mixture has cooled a few drops of ferrous sulphate be allowed to flow slowly down the side of the test-tube, so that the two fluids do not mix, a brown line is seen at the point of contact:

$$2KNO_3 + 4H_2SO_4 + 6FeSO_4 = 2NO + K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O.$$

The brown colour is caused by the solution of nitric oxide in the (still unoxidised) excess of ferrous sulphate. If heated, or even if allowed to stand for some time at the ordinary temperature (until the two solutions have become mixed), the colour disappears when all the ferrous salt has been oxidised.

Liberation of iodine (§ 91).—If nitric acid or a nitrate be reduced by zinc (zinc amalgam) and hydrochloric acid, the addition of a drop of the resulting liquid to a potassium iodide solution in presence of starch-paste produces a blue colour. Dry nitrates may be fused with sodium carbonate (they are thus converted to nitrites) and the reaction made with the solution of the fused mixture.

Oxidation of indigo.—Nitric acid decolorises a solution of indigo in sulphuric acid (oxidation of the indigo, C_8H_5NO, to isatine, $C_8H_5NO_2$). The acid must be previously set free by hydrochloric acid, if in the combined state, and the purity of the latter must also be tested, as free chlorine would have the same action. The hydrochloric acid is boiled, a few drops of dilute indigo solution added, and the mixture again boiled. If the reagent proves to be pure, a portion of the solution of the nitrate is next added; the blue colour of the indigo quickly disappears when the solution is boiled. To detect traces of nitrates, a few drops of indigo solution are added to 10 c.c. of concentrated sulphuric acid, so that the latter will be given a very faint blue tint; the substance to be tested (in very concentrated solution if necessary) is then added, and the mixture heated.

If a nitrate be heated with carbon in a glass-tube closed at one end, the carbon ignites and burns in the tube (see Chloric acid, § 93).

Brucine (an organic base, $C_{23}H_{26}N_2O_4$, extracted from *nux vomica*) in sulphuric acid solution causes a red coloration. This reaction is extremely delicate. Dilute solutions are evaporated almost to dryness, an equal volume of concentrated sulphuric acid added, and a crystal of brucine finally dissolved in the solution. The reaction is performed in a porcelain dish.

Diphenylamine, $(C_6H_5)_2NH$, dissolved in sulphuric acid assumes a blue colour on the addition of nitric acid. The operation is performed as in the previous test. The sulphuric acid used in either reaction must first be tested in the same manner.

Nitrous Acid

The anhydride of nitrous acid, N_2O_3, is gaseous at the ordinary temperature (it has a brownish-red colour and condenses at $-15°$ C. to a blue liquid). The nitrites are usually prepared by the action of a high temperature, or of a metal, such as lead, upon nitrates. Nitrites are decomposed by acids, with evolution of nitric oxide, which, on contact with the air, absorbs oxygen and becomes brown.

Reactions of nitrites.—The nitrites are characterised chiefly by reduction reactions.

Silver nitrite, $AgNO_2$, is difficultly soluble in water. It is obtained as a white precipitate by the action of silver nitrate upon nitrites.

The liberation of iodine from potassium iodide, and the consequent coloration of starch-paste, is a very characteristic reaction. (For the method see § 91.) Nitrites must be decomposed by sulphuric acid.

The decolorising effects produced in a potassium permanganate solution in presence of sulphuric acid is also characteristic of nitrous acid.

The action of ferrous salts, which cause a brown zone, is less important (the method is the same as for nitrates). Hydrogen sulphide in acid solution reduces nitrites, with separation of sulphur. The reaction between cobalt salts and potassium nitrite in presence of potassium cyanide will also be remembered (§ 47). With the sulphate of diamidobenzoic acid, $C_7H_4(NH_2)_2O_2H_2SO_4$, nitrites produce a yellow or orange-red colour, according to the quantity present. Diphenylamine, $(C_6H_5)_2NH$, in sulphuric acid solution, produces with nitrites in presence of an excess of sulphuric acid a blue solution.

PHOSPHORUS

§ 99. Phosphorus is known in several modifications. Common phosphorus is colourless, transparent, crystalline (regular system), fuses at 43° C., and boils at about 260° C. It ignites in the air at 75° C., and in burning emits white fumes of the pentoxide, or phosphoric anhydride; if the supply of air be insufficient, the trioxide, P_2O_3, the anhydride of phosphorous acid, is formed. Phosphorus also unites slowly with the oxygen of the air at the ordinary temperature. When exposed to the air it fumes, and is luminous in the dark (see below). Such compounds of phosphorus as are capable of combustion burn with a green flame, the spectrum of which contains characteristic brilliant green lines. Red phosphorus, the second modification, is amorphous,[1] insoluble in carbon

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[1] The name "Amorphous phosphorus" may be improper, as it is stated that the red phosphorus is in fact also crystalline (probably belonging to the hexagonal system).

disulphide (which dissolves ordinary phosphorus), does not oxidise when exposed to the air, and is not poisonous (the other variety is deadly so). It is prepared by heating ordinary phosphorus to 250° C. in a vacuum; when exposed to a higher heat it is reconverted to the first variety. The two modifications form the same compounds.

The property which phosphorus shows of becoming luminous, or phosphorescent, in the dark, is employed for its detection in cases of poisoning. The substance to be examined is submitted to distillation in a current of steam, in a darkened room, in a flask which is connected with a glass condenser. The phosphorus volatilises, and on being carried through the condenser by the steam renders the tube luminous. It loses its power of phosphorescence, however, in presence of mercury salts, and also in that of many organic compounds.

Phosphorus forms several compounds with both hydrogen (the hydrogen phosphides) and oxygen (the acids of phosphorus).

There are three compounds with hydrogen. The most common of them, PH_3, is usually called hydrogen phosphide. It takes fire spontaneously in the air (due to the presence of the liquid phosphide, P_2H_4 or $H_2P - PH_2$). It produces black precipitates of metallic phosphides with lead and copper salts, and throws down metallic silver from its compounds. A hydrogen flame in which hydrogen phosphide is also burning possesses a beautiful green tint, which is more distinctly seen if the flame be allowed to burn against a porcelain disk. Hydrogen phosphide, like carbon monoxide, is absorbed by cuprous chloride solution.

Phosphoric Acid

Phosphoric acid is found in the soil, in the ashes of plants (especially in the ash of seeds), and in both human and animal bones. Bone-ash is composed of calcium carbonate and calcium and magnesium phosphates. Phosphoric acid also occurs in nature in several minerals, such as apatite (calcium phosphate), wavellite (aluminium phosphate), etc., which are soluble in nitric acid. Wavellite also dissolves in potassium hydroxide (especially on fusion with the latter). The acid is also found in the so-called phosphorites ($Ca_3(PO_4)_2$).

The properties of phosphoric acid and its salts, as well as their reactions, are described in § 50. We shall here observe the nature of pyrophosphoric and metaphosphoric acid, and their conversion into the ortho-acid; their formation from the latter, and the properties of their respective salts, have already been noticed (§ 50).

Pyrophosphoric acid and pyrophosphates.—Pyrophosphoric acid is converted to orthophosphoric acid when its solution is boiled. Only the alkali salts are soluble in water. The acid salts are converted to metaphosphates on ignition. The barium salt, $Ba_2P_2O_7$, is formed on precipitation of pyrophosphates or the free acid by barium chloride (like the orthophosphate, and in distinction from the metaphosphate). The silver salt, $Ag_4P_2O_7$, is a white precipitate. Magnesium pyrophosphate is also a white precipitate, obtained by the action of magnesium sulphate, and soluble in excess either of the acid or of magnesium sulphate. Ammonia does not reprecipitate the salt from the resulting solution at the ordinary temperature, but completely from boiling solution (method for the detection of pyrophosphoric acid in presence of the ortho-acid). An albumin solution is coagulated neither by the acid nor its salts (in presence of acetic acid). Ammonium molybdate in nitric acid solution causes no precipitate at first, but after standing for some time the ordinary ammonium phosphomolybdate is deposited.

Metaphosphoric acid.—There are no less than five series of metaphosphates known. Without describing them in detail, we shall mention a few general reactions. Albumin (in presence of acetic acid) is coagulated by both metaphosphoric acid and its salts. The silver salts are white (the various modifications of metaphosphates are not all precipitated by silver nitrate). Magnesium sulphate produces in presence of ammonium chloride either no precipitate or one which dissolves in ammonium chloride. Barium chloride precipitates the solutions of some of the varieties of metaphosphates.

Phosphorous Acid

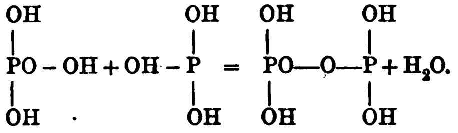
Phosphorous acid, H_3PO_3, crystallises in transparent crystals (it is usually prepared by decomposing phosphorous trichloride with water). It is soluble in water, and readily undergoes oxidation to phosphoric acid. It is distinguished from the latter by its behaviour as a reducing-agent. The alkali phosphites are soluble in water, the others insoluble. Only two of the hydrogen atoms of the acid can be displaced by metals.

Reactions. *Barium phosphite*, $BaPHO_3$.—Barium chloride causes a white precipitate which is readily soluble in acids.

Reduction reactions.—Only a few of the numerous reactions of this nature can be mentioned. Silver nitrate produces a white precipitate (of the silver salt ?) which is speedily turned black by the reduced silver. Mercuric chloride in presence of hydrochloric acid causes no precipitate at first, but in the course of time the white mercurous chloride, HgCl, separates from the solution. Phosphorous acid, finally, when subjected to the action of a high temperature or of hydrogen, evolves hydrogen phosphide.

Hypophosphoric Acid

This recently-discovered acid, $H_4P_2O_6$, is formed during the slow process of oxidation which phosphorus undergoes in the air in presence of water. It may be regarded as an incomplete anhydride of orthophosphoric and phosphorous acids:



$$\underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{PO}}}-\mathrm{OH}+\mathrm{OH}-\underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{P}}} = \underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{PO}}}-\mathrm{O}-\underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{P}}}+\mathrm{H_2O}.$$

The free acid splits up readily into orthophosphoric and phosphorous acids. It has no reducing action, but passes into orthophosphoric acid when heated with potassium manganate. Ammonium molybdate produces, but only in hot solutions, a precipitate of the phosphomolybdate. Silver nitrate causes a white precipitate.

Hypophosphorous Acid

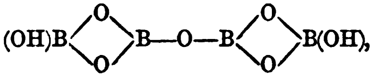
The crystals of hypophosphorous acid, H_3PO_2, melt at 17·5° C. The acid decomposes readily into phosphoric acid and hydrogen phosphide on being heated. It has a reducing action upon numerous substances. The salts contain only one atom of the metal. The barium salt, $Ba(H_2PO_2)_2$, is soluble in water (distinction from phosphorous and phosphoric acids). We shall mention, from among the reduction reactions, only those which are the most characteristic, *i.e.*, which distinguish this acid from phosphorous acid. If a solution of hypophosphorous acid be added to one of copper sulphate, and the mixture gently warmed (not higher than 60° C.), a red-brown precipitate of cuprous hydride, CuH, is formed, which is easily resolved into copper and hydrogen. The reduction reactions mentioned under phosphorous acid are also caused by hypophosphorous acid. Nascent hydrogen produces hydrogen phosphide.

BORON

§ **100.** Boron is known in two modifications, amorphous and crystalline. It is insoluble in acids, and is found in nature only in the form of boric acid and borates.

Boric Acid

Boric acid, H_3BO_3, crystallises in scales which are difficultly soluble either in cold water or alcohol. The acid dissolves more readily in hot water, but evaporates from its aqueous or alcoholic solution on heating, being volatile in the vapour of alcohol or water. When heated alone the crystals lose water and pass into boron trioxide, B_2O_3, which fuses at a red heat and is stable at the highest temperature. In solution, boron trioxide has very weak acid properties, but, owing to its non-volatility, is capable, in reactions by the dry way, of displacing a large number of acids in their salts at a high temperature. The borates, from among which the alkali salts are soluble in water, are also stable at a high temperature, and fuse on ignition to a transparent glass (employment in analysis, § 32, Remarks). Their composition is very complicated, as they correspond, not to the normal hydrate, but to its various incomplete anhydrides. Borax, $Na_2B_4O_7$, for example, is the sodium salt of the anhydrohydrate,



which results when five molecules of water are cut off from four molecules of the orthohydrate:

$$4B(OH)_3 = (OH)_2B_4O_5 + 5H_2O.$$

Reactions of boric acid.—These are found chiefly in the characteristic properties of the acid itself, or of its volatile derivatives, *e.g.*, BF_3; less often in the formation of insoluble borates.

Flame coloration (by volatile boron compounds).—Alcohol is poured over boric acid or its salt (the latter first being decomposed by the addition of sulphuric acid), the liquid warmed, and the escaping alcoholic vapour lighted. The small amount of boric acid which volatilises with the alcohol imparts to the flame of the latter a characteristic green colour, which is sometimes visible only at the edge of the flame. Copper salts and ethyl chloride, C_2H_5Cl (which may form from alcohol if the experiment be made in presence of hydrochloric acid or metallic chlorides), have a colouring effect upon a flame similar to that of boric acid. For the detection of the latter, therefore, the method must be somewhat modified.

The dry boric acid or borate is mixed with four parts of acid potassium sulphate and one part fluor spar (calcium fluoride). If the mixture be moistened with water and brought into the outer cone of the Bunsen's flame, volatile boron fluoride, BF_3, forms and the flame momentarily assumes a green tinge:

$$B_2O_3 + 6HF = 2BF_3 + 3H_2O.$$

Certain boron compounds cause the reaction when simply moistened with hydrofluosilicic acid (or ammonium silicofluoride) and heated. The green boron flame gives a characteristic spectrum, which contains four brilliant green lines, some of them corresponding with the green lines of barium.

Action upon turmeric paper. — Boric acid, and soluble borates in presence of hydrochloric acid, colour turmeric paper a characteristic red, which becomes especially distinct after the moistened paper has been dried. It is due to a compound of the boric acid with the colouring matter of the paper. When acted upon by alkalies or alkaline carbonates the coloration changes to black or dark-green, but returns to red on the addition of hydrochloric acid.

Insoluble borates are but slightly characteristic. *Barium borate* is obtained by the action of barium chloride upon a soluble borate. It is a white precipitate, soluble in acids and ammonium salts, and is not precipitated from acid solution on neutralisation by ammonia.

Silver borate is a white precipitate which dissolves in nitric acid and ammonia. It forms only when the borate solution is concentrated. On addition of silver nitrate to a dilute solution, a brown precipitate of silver oxide is obtained.

SILICON

§ **101.** Silicon is known in both the crystalline and amorphous state. It is obtained by reduction of sodium silicofluoride with sodium or aluminium at a very high temperature. If sodium be used the silicon is obtained as the amorphous variety, but in the second case dissolves in the molten aluminium and crystallises on cooling, as an alloy with the metal (in regular octahedra—graphitoidal silicon). This reduction may also be effected by heating silica with magnesium, the reaction being very vigorous (Beketoff, Gattermann). Crystallised silicon is soluble only in a mixture of hydrofluoric and nitric acids, but its solution may readily be effected by fusion with sodium oxide, with which it forms a sodium silicate. Silicon occurs in nature combined with oxygen as silica (silicic acid), the salts of which are called silicates.

Silicic Acid

Silicon dioxide, SiO_2, is very abundant in the mineral kingdom. Its crystalline modifications (quartz, rock-crystal, amethyst, sand) have the sp. gr. 2·6. If this variety be strongly ignited, however, a lowering of the specific gravity is caused, and the latter becomes 2·2. When artificially prepared by ignition of the hydrate, silica is a white powder which melts at a very high temperature and likewise has the sp. gr. 2·2. The hydrated acid is also found in nature (with varying quantities of water,—opal, chalcedony, agate, flint, etc.) When soluble silicates are decomposed by acids, the hydrate, $H_2SiO_3 = SiO_2 . H_2O$, is precipitated (see below for the conditions). The hydrated acid is somewhat soluble in water, more so in acids (it may be obtained in aqueous solution by dialysis), but when heated (to 130°) it loses water, and with the latter its solubility in either water or acids. This operation is called, in analytical terms, the conversion of the silica to the insoluble state. Silica resists the greatest heat, and at a high temperature drives many acids from their salts. In the hydrated state and at a low temperature, however, it forms one of the weakest of all the acids. It dissolves in alkalies and alkaline carbonates to the soluble potassium and sodium silicates, and is somewhat soluble in ammonia, though insoluble in ammonium carbonate (important characteristic). The silicates of the other metals are insoluble in water, but are easily decomposed by acids, with separation of silica. In the mineral silicates the ratio between the metal and silica varies greatly. The simplest forms are represented by the types, R_2SiO_3, and R_4SiO_4; *e.g.*, wollastonite, $CaSiO_3$ or $CaO . SiO_2$, olivine, Mg_2SiO_4 or $2MgO . SiO_2$. The majority of the silicates are salts of polysilicic acids, $xROySiO_2$, where x and y have different values. The silicates usually contain the following metals: iron (ferrous and ferric), manganese, aluminium, magnesium, calcium, and the alkali metals. These compounds show a widely differing behaviour toward acids. Some of them, like the artificial silicates, are easily decomposed by acids, while upon others the latter have no effect. The decomposition of silicates of the second class is effected by their conversion to alkali silicates (by fusion with potassium and sodium carbonates), or into the barium or calcium salts (by the action of the respective oxides). These operations will be more fully discussed below.

Reactions of Silica and the Silicates.—These consist chiefly in the precipitation of the hydrated silicic acid, which is recognised by its characteristic properties. The formation of silicon fluoride is also employed, but is less important.

Precipitation of silicic acid. By the wet way: action of acids.—*a.* The *soluble* silicates of the alkali metals (*e.g.*, the so-called "soluble glass") are easily decomposed by acids. On the addition of a small quantity of hydrochloric acid, a white gelatinous precipitate of silicic acid is obtained (precipitation is incomplete). If a large amount of hydrochloric acid be added to a solution of potassium silicate, however, no precipitate forms, the silicic acid remaining in solution, and, after standing for some time, the liquid solidifies to a transparent gelatine. The more dilute the solution is, the more silica remains unprecipitated by hydrochloric acid. The properties of the precipitate will be explained later.

b. The silicates which are insoluble in water are divided, in reference to the separation of their silica by acids, into two classes, the one being decomposed, and the other unaffected by acids.

Silicates which are insoluble in water, but decomposed by acids.—To separate the silica from compounds of this class, they are reduced to as fine a powder as possible in an agate mortar, and treated in a dish with hydrochloric acid. The mixture is then heated on the water-bath until complete decomposition has been effected. The silicic acid separates as a gelatinous mass, rarely in the form of powder. The more finely the silicate has been pulverised, the more rapid and complete its decomposition. The operation may be considered finished when no more grains of the mineral are felt upon the residue being stirred with a glass rod.

c. The silicates which are not decomposed by acids form the majority.

Stability toward acids in such silicates may depend upon the crystallisation of the silica. Many of these minerals can be decomposed by acids after strong ignition, which lowers the specific gravity (due, in all probability to the conversion of the crystallised silica to the amorphous state, compare above). Almost all silicates decompose when heated with sulphuric acid to 250° C. in a sealed tube.

Silicates unaffected by acids are usually converted in the first processes of analysis to compounds which are thus decomposed. This is accomplished through fusion with a mixture of potassium and sodium carbonates,[1] with calcium oxide, or with barium oxide. The silicate (very finely pulverised) is fused with four parts of the mixed alkali carbonates in a platinum crucible, heat being applied cautiously until the evolution of carbon dioxide ceases. The ignition may be stronger toward the end of the operation, or when the substance shows no more tendency to effervesce. The fusion converts the silica of the mineral to sodium and potassium silicates, which are then extracted by water (the oxides or carbonates of the metals contained in the mineral remain undissolved).

The solution is then treated with hydrochloric acid, without previous filtration, the acid being added gradually. This causes the silicic acid to separate in the form of a gelatinous precipitate, and brings the basic constituents into solution. If calcium or barium oxide be employed (four parts of which are taken to one of the silicate) the operation is performed in the same manner (though preferably in a silver crucible). This method is usually employed to detect the alkali metals in silicates which are not decomposed by acids. (This is impossible in the first method.)

The alkalies in silicates may also be conveniently determined by fusion of the mineral (1 part) with ammonium chloride (1 part) and precipitated calcium carbonate (8 parts). The substances must be thoroughly mixed, and fused cautiously at first, but afterwards for half an hour before the blow-pipe. The mass is then treated with a small quantity of water, taken from the crucible, and the solution filtered. The

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[1] In molecular proportions. It is usually prepared by igniting potassium sodium tartrate, $KNa(C_4H_4O_6)$, and extracting with water. The mixture is employed because sodium carbonate alone is difficultly fusible.

alkalies are to be found in the filtrate, together with a small quantity of the calcium salts. (They are detected as in § 24.)

d. Conversion of the silicic acid to the insoluble state.—In all the foregoing operations a portion of the silicic acid is obtained as a gelatinous precipitate, and the rest remains in solution. Its separation in this way is therefore imperfect, and such solutions, moreover, are very difficult to filter. To completely remove the silica (by converting it to its insoluble modification) the solution obtained in either of the above operations is treated with hydrochloric acid and evaporated to dryness on the water-bath, with frequent stirring with a glass rod (it is still better to heat the residue for some time at 130°-140° C.) The conversion of the silicic acid to the insoluble state is due to its passage into anhydrous silica. The residue is next moistened with fuming hydrochloric acid, and finally treated with water, which extracts the metallic oxides (of Fe, Al, Ca, etc.) which the mineral contained. The silica remains as an insoluble residue, and, after filtration and washing, is obtained as a light white powder.

The above reactions are employed in the qualitative analysis of silicates, and careful attention must be paid to the last process—the separation of silica by evaporation to dryness—as it may otherwise be found in the precipitates obtained with ammonium sulphide, etc. (especially in that of Al.) The purity of the silica must also be confirmed, as aluminium shows the same behaviour as silicon in many reactions. As a confirmatory test, the separated silica is treated with boiling concentrated hydrochloric acid ; aluminium oxide dissolves, and may be detected in this solution. It may be well to mention that the difficulties with which the perfect separation of silica is surrounded render a test for the latter necessary, in the precipitates obtained in the examination for the metals (especially those of Group III. Division 1). The precipitates are treated with boiling hydrochloric acid, which leaves the silica undissolved. The detection of alkali metals in silicates which are unaffected by acids has already been explained, and will be more fully treated below.

The separation of silica by the dry methods is employed as a preliminary test for its presence, especially in silicates which are not decomposed by acids, and is, therefore, an important reaction. Microcosmic salt is fused in the loop of a platinum wire to a clear bead, and then sprinkled with a few grains of the pulverised mineral. All the constituents of the silicate except silica dissolve ; the latter, being insoluble in the microcosmic salt, swims about in the bead, in the form of the original pieces of mineral (silicon skeleton). The theory and performance of this operation have been explained in § 32.

This reaction, which was at one time undisputed, must, according to the investigations of Haushofer and Hirschwald, be admitted as inaccurate. There are many silicates, such as the zeolites, which dissolve completely in the microcosmic bead, while, on the other hand, it has no effect upon certain minerals, such as apatite, which contain no silica.

Formation and properties of silicon fluoride.—Hydrogen fluoride dissolves silica with formation of silicon fluoride. The amorphous variety is especially soluble in this acid (the reaction is violent). Crystallised silica and the silicates go into solution more slowly, but nevertheless completely. It often happens that no silicon fluoride is evolved, a silicofluoride being formed instead:

$$CaSiO_3 + 6HF = CaSiF_6 + 3H_2O.$$

This is prevented if the reaction be brought about in presence of sulphuric acid, which decomposes the silicofluoride with formation of hydrofluoric acid and silicon fluoride. Ammonium fluoride (3 parts to 1 part of the powdered mineral) or calcium fluoride may be conveniently substituted for hydrofluoric acid. Concentrated sulphuric acid is added to a mixture of the fluoride and the silicate in a platinum dish, and the whole cautiously warmed. If a drop of water be held in a platinum loop above the dish in which the test is made, the silicon fluoride, in coming in contact with the water, decomposes to hydrofluosilicic acid and silica (§ 94), and the latter forms a thin white skin upon the surface of the drop.

The reactions with hydrofluoric acid (ammonium fluoride) in presence of sulphuric acid may be employed with particular advantage for the detection of the alkalies in silicates (which cannot be decômposed by acids). The test is made as above, and when the reaction has ceased (the silicon been removed as silicon fluoride), the metals which the silicate contained are left in the form of sulphates.

SUPPLEMENT

§ **102. Qualitative Analysis of Silicates.**—The presence of silica is usually detected by the formation of its skeleton when the mineral is fused with microcosmic salt (§ 101). For analysis, the finely-powdered silicate is heated for some time with concentrated hydrochloric acid at a temperature near the boiling-point of the latter. The acid decomposes it either (1) fully, (2) in part (*e.g.*, many rocks which contain several silicates), or (3) not at all. The three cases will be separately observed.

1. *The silicate is completely decomposed by hydrochloric acid.*—The mineral is treated with hydrochloric acid, and the silica removed according to § 101 (*b* and *c*). The metals are detected in the hydrochloric acid solution by the usual system; the silica residue must also be examined (§ 101).

The silica often contains, as impurities, titanium oxide (which may also go into solution with the metals), aluminium oxide, and, occasionally, strontium and barium sulphates. The best method of procedure is to treat the residue with hydrofluoric acid, and, after removing the silicon and igniting the residue, to fuse the latter with acid potassium sulphate, and treat the product with cold water. An insoluble residue consists of the sulphate of barium or strontium (the metals are detected as in §§ 19, 20). Metatitanic acid is then precipitated by boiling the solution, and, after filtering, the aluminium hydroxide is thrown down from the filtrate by ammonia.

2. *If the silicate is incompletely decomposed by hydrochloric acid*, it is again treated with the latter as in 1. If no further decomposition ensues, the solution is decanted from the residue, and (after the removal of the dissolved silica) is examined for the metals which it contains. The residue insoluble in hydrochloric acid is washed and boiled with sodium carbonate (to remove the silica already formed). It is then filtered, washed, and treated as in 3.

3. *If the silicate is not decomposed by acids*, a portion is fused with sodium and potassium carbonates according to § 101 *c*. Half of the product is retained (see below), and the remainder treated with water and hydrochloric acid (§ 101 *d*). The silica is then removed (its purity tested as in 1), and the metals detected in the solution by the usual methods (§ 87). Another portion of the mineral is examined for the alkali metals, most simply by ignition with barium oxide (4 parts) for half an hour in a silver crucible. The product is then

dissolved in water and hydrochloric acid, and the solution precipitated by ammonia and ammonium carbonate. The filtrate is next evaporated to dryness and ignited. After resolution of the residue and a second precipitation by ammonia and ammonium carbonate, the alkalies are detected as in § 14. The method of decomposing the silicate, for the detection of alkalies, by fusion with ammonium chloride and calcium carbonate, is given in § 101 *c.*

Silicates often contain not only metals but also certain metalloids. Carbonic acid and hydrogen sulphide are recognised upon treatment with hydrochloric acid, the first according to § 103, the second (from sulphides) by its odour and the reactions explained in § 95. The hydrochloric acid solution, obtained either as in 1 (designated below by 1) or from the fusion product obtained in 3 (designated 3), is subjected, in small separate portions, to the following tests:

Sulphuric acid.—In 1: Precipitation with barium chloride; in 3, the same, after acidifying with hydrochloric acid.

Arsenic and phosphoric acid.—In 1: The solution is diluted with water and treated with hydrogen sulphide (at 70° C.) The filtrate is evaporated to dryness with nitric acid, the residue extracted by nitric acid and water, and the resulting solution precipitated by ammonium molybdate (§ 50). In 3: The solution is acidified with hydrochloric acid and treated as above.

Boric acid.—In 1: The mineral is fused in a platinum spoon with potassium and sodium carbonates, the product extracted with water, and the solution tested with turmeric paper or in the alcohol flame, according to § 100. In 3: As the mineral has already been fused with the alkaline carbonates, the test may be directly made.

Chlorine.—In 1: The mineral is most conveniently dissolved in nitric acid, and the solution tested with silver nitrate (§ 60). In 3: The treatment is the same, nitric acid being first added.

Fluorine.—In 1: The test is made as in § 94. In 3: After the addition of hydrochloric acid and removal of carbonic acid, the warm liquid is saturated with ammonia and filtered into a flask. Calcium chloride is then added to the still warm filtrate, and the latter allowed to stand for some time in the corked flask. The precipitate of calcium fluoride which forms is examined according to § 94.

CARBON

§ **103.** Carbon has several allotropic modifications. In the crystalline condition it is called diamond and graphite, and the amorphous variety is familiar to us as soft coal, anthracite, and lamp-black. The latter substances contain, beside carbon and mineral components (ash), hydrogen, oxygen, and frequently nitrogen. All the modifications of carbon can be converted to graphite at a high temperature. Amorphous carbon readily absorbs gases, and odorous or colouring substances (it is used in the arts, as "Animal-char," to decolorise liquids). Amorphous carbon is black in all its varieties. It is insoluble in acids, and affected by chlorine neither at ordinary nor high temperatures. The latter characteristic may be employed with advantage to distinguish carbon from all compounds of the same colour and from metals. When oxidised by oxygen or the air at a high temperature, carbon burns, more or less slowly, to carbon dioxide (safest test for carbon). The compounds of carbon vary between the widest limits (the so-called organic compounds), and we shall discuss only those with oxygen, particularly carbon dioxide, or carbonic acid.

The so-called *organic compounds* of carbon are recognised by the following general points in their behaviour. The volatile compounds are usually combustible, and when lighted, burn to water and carbon dioxide. Non-volatile compounds are decomposed by gentle heat, leaving a black residue (*i.e.*, carbon separates). If organic compounds be mixed with cupric oxide and heated to faint redness in a glass tube, carbonic acid forms; the latter may be led into a solution of barium hydroxide, and barium carbonate thus precipitated.

Carbon monoxide, CO, is a colourless gas which, when lighted in the air, burns to carbonic acid with a bluish flame (characteristic). As a further peculiar property of this gas, its absorption by a solution of cuprous chloride in hydrochloric acid may be mentioned (the compound $CuCl_2 . CO + 2H_2O$ is formed). If the solution be boiled, or even diluted with water, the carbon monoxide is again evolved. Carbon monoxide precipitates metallic palladium, from palladious chloride, as a black powder, the gas itself becoming oxidised to carbon dioxide:

$$PdCl_2 + CO + H_2O = Pd + 2HCl + CO_2.$$

The mixture of gases to be tested for carbon monoxide is led into a solution of palladious chloride, after being freed from hydrogen sulphide by lead acetate solution.

Carbon Dioxide

Carbon dioxide is gaseous at the ordinary temperature, but condenses to a liquid under pressure (36 atmospheres at 0° C.) and cold. If the fluid dioxide be suddenly evaporated, the temperature falls to $-80°$ C., and a portion is obtained as a snow-like solid. Gaseous carbon dioxide dissolves to a slight extent in water (about one volume is absorbed at the ordinary temperature and atmospheric pressure), and its solution imparts a characteristic dark-red colour to blue litmus paper. Carbon dioxide has no hydrate, and is known only as the anhydride of the acid. It acts as a weak acid; many of the metals form no carbonates at all (*e.g.*, aluminium, etc.), others only basic salts. Of the carbonates, the alkali salts and thallium carbonate are the only ones soluble in water (characteristic of these metals). The salts of other metals are all precipitated by the alkaline carbonates (some as hydroxides, some as basic salts). The alkalies also form acid carbonates, which are easily decomposed by heat, with evolution of carbon dioxide and formation of the normal carbonates. Water containing carbonic acid also dissolves the carbonates of barium, strontium, calcium, and magnesium. All carbonates except those of the alkali metals and barium are decomposed on ignition, yielding as a rule the metallic oxide.

Reactions of Carbon Dioxide and the Carbonates.—Free carbon dioxide can occur in analysis either as the gas or in solution. The carbonates may exist in solution or as solid substances.

1. Carbon dioxide as the *gas*, and also in solution, may be detected with a solution of calcium or barium hydroxide. It forms with these reagents the respective carbonates, which are insoluble in water but dissolve readily in acids.

2. *Soluble carbonates* are precipitated by calcium chloride. The properties of calcium carbonate have already been described.

3. *Carbonates insoluble in water* are recognised by their behaviour toward weak hydrochloric acid. The latter liberates carbon dioxide, the properties of which have been given above.

The liberation of carbon dioxide from the carbonates is easily effected, being caused by all acids except hydrocyanic, boric, and hydrogen sulphide. If hydrochloric or some other acid be added to a carbonate the carbon dioxide escapes with effervescence, especially if heat be applied. The generated gas is colourless, and turns moist blue litmus paper cherry-red. For a confirmatory test, it is led into a solution of barium or calcium hydroxide, as above.

HYDROGEN, OXYGEN

§ **104. Hydrogen** is a colourless gas, and has the lowest specific gravity of any substance known (sp. gr. = 0·06926). It burns when lighted in the air (characteristic), undergoing oxidation to water. A mixture of hydrogen and oxygen or air, in certain proportions, is highly explosive (detonating gas). Hydrogen reduces many metallic oxides and chlorides at a high heat, and even at the ordinary temperature it effects many reductions, if acting in the nascent state,—in the moment of its generation from zinc and hydrochloric acid, or zinc in alkaline solution, etc., before its atoms have combined to molecules.

Oxygen is a colourless gas, sp. gr. = 1·10525. It is incombustible, but supports combustion. If a glowing chip of wood be held in an atmosphere of oxygen, it takes fire (this is used as a test for oxygen; nitric oxide gives the same reaction). Oxygen combines with many easily oxidisable substances, even at the ordinary temperature, and this property is taken advantage of in the determination of oxygen in a mixture of gases (phosphorus or a solution of pyrogallol, $C_6H_3(OH)_3$, in potassium hydroxide is employed). The quantity of oxygen dissolved in a solution (in water analyses, for example) is determined most readily by sodium hyposulphite, $Na_2S_2O_4$ (indigo being used as an indicator). A good absorption-medium for oxygen is found in chromous acetate, $Cr(C_2H_3O_2)_2$, which is prepared from chromic chloride, $CrCl_3$, by reduction with zinc and hydrochloric acid in presence of sodium acetate. The experiment is made in a flask fitted with a rubber valve. The blue solution is converted by the oxygen absorbed to a green one of the chromic salt.

Ozone is a modification of oxygen, which is formed when an electric spark is passed through the latter gas, and results, together with oxygen, from the decomposition of certain peroxides. It is also formed when phosphorus is oxidised in the air in presence of water. The density of ozone is one-third greater than that of oxygen. When heated it passes into oxygen, but at the ordinary temperature is a much more powerful oxidising agent than the latter. The liberation of iodine from potassium iodide by its means is especially characteristic. To make this test for ozone we use paper which has been soaked in starch-paste and potassium iodide; if ozone is present the paper becomes blue (the test must be made in the absence of the nitrogen oxides).

Hydrogen and oxygen are quantitatively estimated (gas analysis) by exploding the gas with oxygen or hydrogen, and determining the change in volume (contraction) which the gas has undergone in forming water. If only small quantities of oxygen and hydrogen are present in a mixture of gases, this is the most accurate method for their detection.

Water

The properties of water are too well known to require explanation in detail. It is a fluid which crystallises at 0° C. (ice, snow) and boils at 100°. Solutions to be analysed are usually aqueous, and it is therefore unnecessary to examine them for the presence of water. Qualitative tests for it are usually required only in solid substances. The water may be present either as water of crystallisation, or as a mechanical constituent of the substance (hygroscopic water). Less frequently, the compound to be examined contains hydrogen (*e.g.*, in acid salts, etc.), which can be distinguished as such only through quantitative determinations.

To test for water, the substance to be examined is subjected to the action of a high temperature. All salts which contain water of crystallisation are by these means more or less readily decomposed. The test is made in a glass tube sealed at one end. Heat is applied to the substance, and the presence of water shown by a thin film of moisture which forms in the cold section of the tube, and collects into drops if the quantity of water be large.

Hydrogen Peroxide

With the preparation of hydrogen peroxide on a large scale (in about a 3 per cent solution) its use in qualitative and quantitative analysis has also become more frequent. Hydrogen peroxide is detected by the following method. Dilute sulphuric acid, zinc iodide, starch-paste, two drops of a 2 per cent solution of copper sulphate, and a small quantity of ferrous sulphate in 0·5 per cent solution are added to about 5 cm. of the liquid to be tested. If hydrogen peroxide be present the liquid assumes a blue colour, either immediately or in the course of a few hours. This is due to the fact that in *very dilute solutions*, zinc iodide and copper sulphate yield the soluble compound, CuI_2, which is decomposed in the reaction, with liberation of iodine. We emphasise once more that the test is to be made only with extremely dilute solutions.

SYSTEMATIC COURSE FOR THE DETECTION OF ACIDS

§ 105. We have now learned the individual reactions of the various acids, and the next task is to elaborate a system for their detection. Although the acids are recognised by special reactions, it is advantageous, in view of their great number, to simplify the questions of analysis by showing the absence of the majority of the acids, and testing only for those which are included in the remainder.

There are several methods of doing this, all of which are generally used in each analysis.

First method.—The reactions caused by the addition of hydrochloric acid and precipitation with hydrogen sulphide, in the examination for metals, are observed as closely as possible. The systematic course of analysis given in § 87 includes the detection of those acids which (1) yield gaseous anhydrides on acidulation with hydrochloric acid, and those (2) which are reduced by hydrogen sulphide, or are precipitated as sulphides (*e.g.*, arsenic and arsenious acids).

1. (*a*) *If acidulation with hydrochloric acid* is accompanied by effervescence and evolution of a gas, carbonic acid, sulphurous acid, and hydrogen sulphide may be present. Carbon dioxide is detected by its action on a solution of barium hydroxide (§ 103); sulphurous acid and hydrogen sulphide by their odour and the test with lead acetate paper (§ 95). Hydrocyanic acid may also be recognised by its odour at this point. (See below for the necessary confirmatory tests.)

(*b*) If the addition of hydrochloric acid causes an opalescence in the liquid, or throws down a pale-yellow precipitate of sulphur, and at the same time sulphurous acid escapes (recognised by its odour), the solution contained thiosulphuric acid. If the solution be heated after the addition of hydrochloric acid, and chlorine then escapes, this indicates iodic, chloric, chromic, or nitric acid.

2. *The precipitation with hydrogen sulphide.*—The following acids, in addition to nitric and a few others which cause no change in the colour of the solutions, are decomposed, sulphur being deposited at the same time:

(*a*) Chromic acid (the solution was yellow or red): the solution becomes green. Confirmatory tests; precipitation of the lead and silver salts (chromium is detected among the metals).

(*b*) Iodic acid: the solution is coloured brown by the liberated iodine. The latter is converted to hydriodic acid by an excess of hydrogen sulphide, whereupon the liquid loses its colour.

Second method.—This method is based upon the properties of the salts of the various metals which have been ascertained as present. If the metals contained in the substance are known, and also the reaction of the original solution (neutral, *i.e.*, an aqueous, or acid, solution in an acid), it becomes possible to strike out certain acids as absent, or, in other words, to omit certain tests. This may be made more clear by an example. Let us suppose that barium has been detected; it follows that if the solution was neutral or acid, sulphuric acid is absent. If silver was present, the (acid or neutral) solution contained no hydrogen acids, and also none of a large additional number (see p. 270). To simplify such deductions, a table of the solubility of the more common salts in water and acids is annexed. In this table, salts which are soluble in water are designated by 1; those which are insoluble in water, but soluble in acids, by 2. The numbers 1,2, denote salts which dissolve sparingly in water, but readily in acids; 3, salts which are insoluble in acids; 2,3, insoluble or difficultly soluble in water, difficultly soluble in acids. For the sake of brevity, the acids are written as anhydrides. The small numbers refer to the notes below the table:—

TABLE OF SOLUBILITIES

Salt	CrO_3	SO_3	P_2O_5	B_2O_3	$C_2H_2O_4$	Fl	CO_2	SiO_2	Cl	Br	I	CN	Cfy[1]	Cfdy[1]	S	N_2O_5	Cl_2O_5	As_2O_3	As_2O_5	Salt
K . .	1	1	1	1	1	1	1	1	1[2]	1	1	1	1	1	1	1	1	1	1	K
Na . .	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	Na
NH_4 . .	1	1	1[3]	1	1	1	1	...	1[4]	1	1	1	1	1	1	1	1	1	1[3]	NH_4
Ba . .	2	3	2	2	2	2,3	2	2	1	1	1	1,2	1,2	...	1	1	1	2	2	Ba
Sr . .	1,2	3	2	2	2	2,3	2	2	1	1	1	1	1	...	1	1	1	2	2	Sr
Ca . .	1,2	2,3	2	2	2	2,3	2	2	1	1	1	1	1	1	1[5]	1	1	2	2	Ca
Mg . .	1	1	2	1,2	1,2	2,3	2	2	1	1	1	1	1	1	1	1	1	2	2	Mg
Al . .	...	1	2	2	2	1	...	2,3	1	1	1	...	...	...	...	1	1	...	2	Al
Cr . .	2	1	2	2	1,2	1	...	2	1[6]	1[7]	1	2	...	...	...	1	1	...	2	Cr
$Fe(Fe_2O_3)$	1	1	2	2	2	1	...	2	1	1	1	...	3	1	...	1	1	2	2	$Fe(Fe_2O_3)$
Fe(FeO)	...	1	2	2	2	1,2	2	2	1	1	1	2,3	3	3	2	1	1	2	2	Fe(FeO)
Mn . .	1	1	2	2	1,2	2	2	2	1	1	1	2	2	3	2	1	1	2	2	Mn
Zn . .	1	1	2	2	2	1,2	2	2	1	1	1	2	2,3	2	2	1	1	...	2	Zn
Ni . .	2	1	2	2	2	1,2	2	2	1	1	1	2,3	3	3	2[8]	1	1	2	2	Ni
Co . .	2	1	2	2	2	1,2	2	2	1	1	1	2,3	3	3	2[8]	1	1	2	2	Co
Ag . .	2	1,2	2	2	2	1	2	...	3	3	3	3	3	3	2[9]	1	1	2	2	Ag
$Hg(Hg_2O)$	2	1,2	2	...	2	...	2	...	2,3	2,3	2	...	...	...	...	1[10]	1	2	2	$Hg(Hg_2O)$
Hg(HgO)	1,2	1[11]	2	...	2	1,2	2	...	1[12]	1	2	1	...	...	2[13]	1	1	2	2	Hg(HgO)
Cu . .	1	1	2	2	2	2	2	2	1	1	2,3[14]	2,3[14]	3	...	2	1	1	2	2	Cu
Cd . .	1	1	2	1,2	2	1,2	2	2	1	1	1	2	...	...	2	1	1	...	...	Cd
Pb . .	2,3	2,3	2	2	2	2	2	2	1,2	1,2	1,2	2	2	1,2	2	1	1	...	2	Pb
Bi . .	2	1	2	2	2	1	2	...	1[15]	1,2	2	...	...	...	2	1[15]	1	...	2	Bi
Sn(SnO)	2	1	2	2	2	1	...	...	1	...	1	...	3	3	2	1	1	...	...	Sn(SnO)
$Sn(SnO_2)$	...	...	2	...	...	1	...	...	1	...	1	...	3	...	2	...	...	2	2	$Sn(SnO_2)$
$Sb(Sb_2O_5)$	2	2	2	...	2	1	...	...	1[16]	1[16]	1,2	...	...	...	2	...	...	...	2	$Sb(Sb_2O_5)$
Au . .	...	...	...	...	...	...	...	...	1	1	2	1	...	...	2[17]	...	...	...	...	Au
Pt . .	...	1	...	...	...	...	...	...	1[4]	1	3	1	...	...	2[17]	1	...	...	...	Pt

[1] Denote hydroferro- and hydroferricyanic acids respectively.
[2] Platinichlorides, 2,3.
[3] Ammonium magnesium salt, 2.
[4] Platinichloride, 2,3.
[5] $Ca_3(SbS_4)_2$, 1,2.
[6] Anhydrous $CrCl_3$, 3.
[7] Anhydrous $CrBr_3$, 3.
[8] NiS, CoS, only in *aqua regia*.
[9] Ag_2S, only in nitric acid.
[10] Basic salt and amido-compound, 2.
[11] Basic salt, 2.
[12] Amido-compound, 2.
[13] HgS only in *aqua regia*.
[14] Cuprous salts.
[15] Basic salts and BiOCl, 2.
[16] SbOCl, 2.
[17] AuS and PtS_2 only in *aqua regia*.

Third method. Classification of the acids into groups.—(*a*) The first two methods suffice only for a few of the acids which the given solution may contain. The remainder are systematically detected as follows. The various acids must be in solution as salts of the alkali metals or metals of Group II. Such solutions are prepared thus. The test with hydrochloric acid (see above) having been made, a separate portion of the liquid is precipitated, first with hydrogen sulphide (the accompanying tests may again be made), and then with ammonium sulphide. The solution in which the metals have been detected and separated may also be employed. The sulphides are filtered off, the excess of hydrogen sulphide and ammonium sulphide removed by boiling, and hydrochloric acid added. Such a solution, of course, cannot be used for the detection of arsenic acid, etc., hydrochloric acid (which has been added), or chloric acid (which decomposes when boiled with the latter). The tests for sulphuric and nitric acids are also more or less inexact. To detect these acids the solution must be prepared as follows.

(*b*) The second method of preparing the solution is more convenient than the first (the test for carbonic acid with hydrochloric acid must be made in a separate portion). The boiling solution is precipitated by sodium carbonate in slight excess, and filtered. The filtrate, containing the various sodium salts, is subjected to the reactions given below. Both methods are open to the objection that salts which are deposited from acid solutions on neutralisation (*e.g.*, phosphates, etc.), may also be precipitated. In such cases, and also when the substance to be analysed is insoluble in water or acids, fusion with sodium carbonate must be employed (§ 107, Remark).

The detection of the acids may be commenced directly in the first solution; that prepared by the second method must first be neutralised, by hydrochloric or nitric acid, as the case may be.

Before taking up the course of analysis itself, it may be well to discuss the classification of the acids into groups. This is based upon the solubility of the various barium and silver salts in water (and, to a certain extent, in acids). Barium chloride, added to the neutral solution, is the general reagent for Group I., silver nitrate in nitric acid solution, that of Group II. Group III. is composed of acids, the barium and silver salts of which are soluble in water.

Group I.—Barium chloride precipitates from neutral solution the barium salts of the following acids: chromic, thiosulphuric, iodic, carbonic, silicic (these are all detected in the course of analysis for the metals), sulphuric, hydrofluosilicic (barium salts are insoluble in acids), phosphoric, boric, hydrofluoric (barium salts are soluble in acids). To these may be added arsenious and arsenic acids, which, however, have been detected among the metals. The silver salts of the acids of Group I. are insoluble in water, but dissolve in nitric acid.

Group II.—Silver nitrate precipitates in solutions acidified by nitric acid the silver salts of the following acids: hydrochloric, hydrobromic, hydriodic, hydrocyanic, hydrogen sulphide, hydroferrocyanic, and hydroferricyanic.

Group III.—Nitric and chloric acids are precipitated by neither reagent.

We must remark here that these general reagents of the different groups of the acids are not group reagents, in the sense in which we use hydrogen sulphide or ammonium sulphide for the metals. The acids of one group cannot be separated from those of another by the addition of these reagents, and the latter merely indicate the members of a definite group. The acids are always detected by means of their special reactions, and the use of general reagents is important only in the respect that they dispense at once with the necessity of making several tests. The first reagent can detect with accuracy sulphuric acid alone, and the second (silver nitrate) only hydrogen sulphide (see below).

Course of Analysis.—The group to which the acids contained in the substance belong is first determined, and the acids themselves then recognised by their individual reactions. The acids which have been detected in the preliminary tests (with hydrochloric acid and hydrogen sulphide) are not included in the following course of analysis. Unless directions to the contrary are given, each test is to be made in a new portion of the solution.

1. Barium chloride is added to the solution (in the presence of silver, lead, or mercurous mercury, barium nitrate is substituted): acid solutions must be previously neutralised

with ammonia. If no precipitate appears, the absence of the acids of Group I. is proved (with the exception of small quantities of boric or hydrofluoric acid). If a precipitate ensues which does not dissolve on addition of hydrochloric (or nitric) acid—barium sulphate—sulphuric acid is indicated. The remaining acids of Group I. are detected by the reactions which follow, the test described in 2 being first made.

2. A portion of the solution prepared by the second method, and neutralised by nitric acid, is precipitated by silver nitrate. The non-formation of a precipitate indicates the absence of acids of Group II. In this case it is convenient to follow with a general test for the acids of Group I. Ammonia is cautiously added, care being taken that the layers of the two liquids do not mix. If no precipitate (or turbidity) appears at the point of contact, the absence of phosphoric, chromic, arsenic, arsenious, silicic, and oxalic (and concentrated solutions of boric) acids is proved.

3. If a precipitate formed in 2, more nitric acid is added. Complete solution of the precipitate indicates that the acids of Group II. are absent, and that only the acids of Group I. were thrown down. If on the contrary it does not redissolve, acids of Group II. are present (the presence of those of Group I. is still undetermined, and must be ascertained by special tests; see below). We shall first discuss the detection of the acids of Group I., taking up those of Group II. in No. 7.

4. *Phosphoric acid.*—Ammonium chloride, ammonia, and magnesium sulphate are added to a portion of the solution (§ 50). Small quantities of phosphoric acid are more safely and accurately detected by ammonium molybdate. If the solution was prepared through precipitation by sodium carbonate, it must first be acidified and treated with hydrogen sulphide, to remove arsenic acid. This is necessitated by the fact that the above reagents show the same reaction with arsenic acid as with phosphoric acid.

5. *Hydrofluoric acid.*—Ammonia is added to a new portion of the solution until the reaction is alkaline, and then calcium chloride. The precipitate is treated with acetic acid. If insoluble, it is dried, and a portion tested for fluorine with sulphuric acid (etching glass, § 94).

6. *Boric and silicic acids.*—A portion of the solution is

acidified with hydrochloric acid, and tested with turmeric paper according to § 100 (chloric, chromic, and hydriodic acids must be previously removed if present: chromic acid may be reduced by sulphurous acid, and iodic acid precipitated by silver sulphate). To detect silicic acid, if it has not already been found during the examination of the metals of Group III. (§ 52), the hydrochloric acid solution is evaporated to dryness and the residue extracted with hydrochloric acid. Silicic acid remains behind (confirmatory test with microcosmic salt, § 101).

7. Tests are made for the acids of Group II., if a residue insoluble in dilute nitric acid was obtained in 3. If the precipitate was black (silver sulphide) *hydrogen sulphide* is indicated (or, in general, a metallic sulphide). A confirmatory test must be made by precipitation of the original solution with lead oxide in caustic potash solution (§ 95).

8. *Iodine, bromine.*—A new portion of the solution is tested for iodine according to §§ 90 and 91 (with potassium nitrite and starch-paste), and for bromine (with chlorine-water, or preferably, by § 91), the iodine being first removed as cuprous iodide.

9. *Cyanogen* is detected by the odour emitted when the solution is acidified with sulphuric acid, and according to § 97 (formation of ferric ferrocyanide and sulphocyanate). The absence of ferro- and ferricyanides is required in this test. They are detected through the formation of precipitates with ferric and ferrous salts (§ 97).

10. If the results of the foregoing tests (8, 9) are negative, the precipitate consisted of silver chloride (detection of chlorine). Confirmatory tests according to § 60, and reactions for chlorine in the original solution (§ 89).

Chloric and nitric acids.—A portion of the dried substance is moistened with sulphuric acid. In presence of chloric acid the latter becomes yellow. If chloric acid is present, it must be removed by ignition of the substance, and a test made for nitric acid (or, more correctly speaking, for nitrous acid) with ferrous sulphate (§ 98). Chromic and hydriodic acids influence the reaction, and must be removed as in 6.

We remark again that if the metals which the substance contains are known, a little deliberation will allow the analyst to dispense with the tests for many of the acids, and thus to relieve himself of much fruitless experiment. Careful notes on the reactions, and deliberation as to the impossibility of the presence of this or that acid, are to be recommended here as in the analysis of the metals (§ 87).

SECTION III

PRELIMINARY OPERATIONS IN QUALITATIVE ANALYSIS

THE study of the reactions of the metals and metalloids through which we have just passed has enabled us to elaborate a systematic method for analysing *solutions.* Analyses of this class are the most simple, and in the more complicated cases, therefore, the substances are so treated as to render the same method applicable. In this Section we shall not deal with new facts, but merely apply those which we have already discussed to the solution of the more difficult problems of analysis.

§ **106. Analysis of Solutions.**—A drop of the solution is first evaporated on platinum foil, to ascertain whether the liquid really contains dissolved substances (the residue can be investigated as below). The solution is then tested with litmus paper, the reaction enabling certain definite conclusions to be drawn as to the constituents present.

Neutral solutions.—Solutions which show a neutral reaction toward litmus paper can contain but a limited class of compounds, as neutral solutions characterise only the neutral salts of the metals of Groups I. and II. The neutral salts of the heavy metals and of the earth metals (Group III.) have, as a rule, an acid reaction, even when in aqueous solution.

Acid solutions contain free acids, acid salts, or neutral salts of the heavy metals. A drop of the solution is placed upon a watch-glass, and one of dilute sodium carbonate added. If no precipitate appears, or if one forms for the instant, but again dissolves, an acid (or acid salt) is indicated. Turbidity or the separation of a precipitate points to the presence of a neutral salt. Too much reliance, however, must not be placed upon this test.

Alkaline solutions can contain only the oxides, carbonates, and sulphides of Groups I. and II., and the soluble thio-salts.

The first step in the analysis of solutions is the detection of the metals, according to § 87, where the treatment of the various solutions has already been explained. It need only be added that the acidulation with hydrochloric acid and the reaction with hydrogen sulphide (§§ 80 and 105) must be so performed as to serve at the same time for the detection of certain acids. The metals having been detected, the solution is next examined for its acids (§ 105).

§ 107. Analysis of Solid Bodies which are Soluble in Water or Acids.—Before testing the solubility of the substance in water or acids, it must be ascertained whether the substance itself contains water. For this purpose a portion is heated in a tube sealed at one end. If water is present it condenses on the cold sides of the tube (§ 104). The reaction of the water given off is tested with litmus paper.

The behaviour of the substance while being heated in a glass tube must be noticed as carefully as possible, as it may afford important information in addition to that of the presence of water. The following phenomena may be observed:

1. *Change of colour.*—A large number of metallic oxides become yellow when hot, such as ZnO, SnO_2, PbO, Bi_2O_3, etc. Certain salts which contain water of crystallisation also change colour; copper sulphate, for example, becomes white.

2. *Fusion of the substance.*—The salts of the alkali metals and of the metals of Group II. are fusible.

3. *Evolution of gases or vapours.*—The escape of oxygen (recognised by means of a glowing match, § 104) indicates the presence of peroxides, nitrates, or chlorates (the latter two detonate; test with charcoal, §§ 93 and 98). *The odour* of the gas enables the detection of sulphurous acid (often resulting from the decomposition of sulphates), hydrogen sulphide (from hydrated sulphides) and ammonia (ammonium salts and cyanogen compounds). *Colour* of the gas: brown fumes indicate nitrogen dioxide (also recognised by its smell—nitrates of the heavy metals), chlorine, bromine (brown gas), iodine (violet fumes and black sublimate). *Combustibility* of the gas. Carbon monoxide burns with a blue, cyanogen with a violet, flame (CN also recognisable by its smell).

4. *Formation of a sublimate.*—Sulphur (from sulphides) sublimes in red drops which become yellow on cooling. Iodine—violet sublimate (see above); mercury and its salts, § 61; arsenic and arsenic sulphide, § 78; ammonium salts, § 13.

The residue obtained by the evaporation of the solution upon platinum foil (see above) can also be examined by heating in a glass tube.

Solution in water (analysis of substances which are soluble in water).—The preliminary tests having been made, the powdered substance is treated with 10-15 parts of water in a flask and heated to boiling. If complete solution ensues, the metals are first detected as in § 87, and the acids according to § 105, and by the observations made in the examination for metals. If the substance is not entirely soluble, the remainder is allowed to subside, and a drop of the clear solution evaporated on platinum foil. A residue indicates the partial solubility of the substance; the latter is then boiled with water a second time, and filtered, the filtrate examined as in §§ 87 and 105, and the insoluble residue treated as follows.

Solution in acids (analysis of substances soluble only in acids).—A portion of the residue obtained in the foregoing test is treated with dilute hydrochloric acid, heat being applied if its solution is not effected in the cold. If dilute hydrochloric acid fails to bring about complete solution, the liquid is decanted, and the residue heated to boiling with concentrated acid. If the substance then dissolves, the ensuing solution is added to that of the dilute hydrochloric acid.

We repeat that on addition of hydrochloric acid, attention must be paid to the remarks in § 105 concerning the detection of acids by this reaction, and also that peroxides generate chlorine from hydrochloric acid.

If the substance has now dissolved completely, it is investigated by the usual methods (§§ 87 and 105). On solution in hydrochloric acid, sulphur is often deposited (the liquid becomes turbid or a white precipitate separates), and silica is also thrown down (gelatinous precipitate). These substances must be subjected to confirmatory tests (§§ 95 and 101).

If the solution in hydrochloric acid was incomplete (the tested portion is held for further examination; see below), a new portion of the substance (insoluble in water, or of what remained after extraction with water) is treated with boiling nitric acid, and water then added.

If solution is accompanied by the evolution of nitric oxide, oxidation is taking place; the presence of lower degrees of oxidation is thus obvious.

If all the substance is now in solution (sulphur and silica may act as above) it is investigated directly according to §§ 87 and 105. If a portion still remains undissolved, the residue is treated with boiling *aqua regia*, the contents of the test-tubes in which the action of hydrochloric and nitric acid was tried having first been added. Complete solution is sometimes effected only on a second treatment with *aqua regia*, and sometimes only when the solution has been poured off and the residue diluted with water. All these tests must therefore be made. If all has finally dissolved, it is mixed with the solutions obtained in the previous tests, and the metals and acids detected as usual (§§ 87 and 105).

REMARK. *Testing for metals.*—If a solution in hydrochloric acid has been prepared, the acidulation with hydrochloric acid prior to precipitation by hydrogen sulphide may be dispensed with. (If the substance contained silver, etc., these metals are detected later on in the examination; see below.) The solution is diluted with water, and treated directly with hydrogen sulphide. If, on the contrary, solution was effected with nitric acid, and no test was made with hydrochloric acid, the first step in the examination of the metals is the addition of hydrochloric acid. Heed must also be given to the possible presence of phosphates, silicates, etc., in the acid solutions of the metals of Group III. The degrees of oxidation cannot be determined in solutions obtained by treatment with nitric acid or *aqua regia*, as only higher oxides can then be present. Special tests of the original substance must therefore be made to determine the degrees of oxidation.

Examination for acids.—Chloric acid cannot be present in substances which are insoluble in water, but soluble in acids (since all its compounds dissolve in water). Carbonic acid and hydrogen sulphide are found by the preliminary tests; and the behaviour of the substance in the glass tube suffices for the recognition of nitric acid. To detect the remaining acids, the substance is fused with four parts of sodium and potassium carbonates (and potassium nitrate, if sulphides are present) in a platinum crucible. In presence of easily fusible metals (lead, tin, etc.), a porcelain crucible must be substituted. The fused mass is then boiled with water which contains a few drops of nitric acid, and the resulting solution examined for acids according to § 105. If a porcelain crucible be employed, silica cannot be detected (since porcelain is attacked on fusion with alkali carbonates). Fluorine, phosphorus, and sulphur are best detected in separate portions of the substance; fluorine directly as in § 94, and phosphorus and sulphur according to § 105, after they have been obtained in acid solution (with nitric acid in the first case, for the ammonium molybdate reaction, with hydrochloric in the second).

The analysis of alloys and metals.—Alloys and metals form, analytically, a separate class of substances which are insoluble in water but soluble in acids. They are easily recognised by their external appearance. Alloys are treated with hot nitric acid (sp. gr. 1·2), whereupon gold and platinum remain undissolved (§ 86), and stannic acid and antimonic acids and, to a certain extent, arsenic acid, are left as insoluble white precipitates. When lead alloys are treated with concentrated nitric acid, lead nitrate may also remain undissolved as a white crystalline powder which is soluble in water. The other metals go into solution as nitrates, and are detected by the usual method (§ 87).

§ **108. Analysis of Substances which are Insoluble in either Water or Acids.**—The residue left after treatment with *aqua regia*, and, in general, substances which are soluble neither in water nor acids, are analysed by special methods based upon the properties of the insoluble compounds. Among the latter are:

1. The sulphates of barium, strontium, calcium, lead (as lead and calcium sulphates are slightly soluble in both water and acids, they may be detected in part in the solutions of each solvent).
2. Silver compounds: silver chloride, bromide, iodide, cyanide (and ferrocyanide; to a certain extent, lead chloride also). Silver cyanide and ferrocyanide may partly go into solution (as they are decomposed by some acids).
3. The fluorides, especially calcium fluoride.
4. Certain phosphates and arsenates.
5. The mineral sulphides and arsenides (pyrites, blendes, etc.)
6. Oxides: tin dioxide (tinstone), ignited or mineral chromic oxide (chrome-iron ore), and aluminium oxide (clays).
7. Silica and many silicates.
8. Sulphur and carbon.

It may be well to discuss the methods upon which the analysis of these compounds is based. The substances are either neutral metallic salts, or weak bases and weak acids. The operations by which they are brought into solution consist (1) in fusion with sodium carbonate, the universal agent for the conversion of insoluble into soluble compounds (alkali salts). The same reaction is also employed in the preparation of salts (*i.e.*, solution) of the weak acids, such as silicic, and of a few bases, of which aluminium oxide is an example. (2) The second method, by which insoluble compounds of a basic character (chromic oxide, aluminium oxide) are brought into solution, is based upon the use of sulphuric acid or, preferably, of acid potassium sulphate. The sulphides and arsenides, finally, must be oxidised, and for this purpose they are fused with sodium carbonate and potassium nitrate. We shall see below how these reactions are combined in analysis.

The choice of methods is determined by the following preliminary tests for sulphur, silver chloride, lead sulphate, and silica. The substance is tested for silica (by fusion with microcosmic salt on a platinum wire, § 101). If silica be found, the substance is a silicate, and analysed according to § 102. Sulphur is detected by heating in a glass tube sealed at one end (brown fumes and drops—see also § 107). Carbon is easily recognised by its physical properties and by combustion on platinum foil (it may leave an ash). Tests for the presence of silver chloride and lead sulphate alone remain to be made. For this purpose a new portion of the substance is heated in a test-tube with potassium cyanide and water, filtered, and the filtrate tested with hydrogen sulphide for silver. Its presence is indicated by a black precipitate of silver sulphide. The residue insoluble in potassium cyanide is washed and digested with hydrogen sulphide water. If it becomes black, lead is present. These preliminary tests determine the subsequent method of procedure. If their results are negative (absence of sulphur, lead sulphate, and silver chloride), the substance may be fused directly; if these are present, on the contrary their removal must first be effected. An amount of substance requisite for the complete analysis is taken, and the lead sulphate removed from it by heating with a concentrated solution of ammonium acetate. The resulting solution is tested for lead, chlorine, and sulphuric acid. The residue from this operation is then thoroughly washed and heated with potassium cyanide and water, to remove the silver (the reaction must be brought about in the cold if sulphur is present). The solution in potassium cyanide should be subjected to confirmatory tests for silver (see Remark) and sulphuric acid (which may have passed into solution through decomposition of lead sulphate by the potassium carbonate, which potassium cyanide almost invariably contains). The residue from the potassium cyanide solution is washed, dried, and ignited in a covered porcelain crucible until all the sulphur has been driven off.

Fusion.—The residue, or, if no sulphur, lead sulphate or silver chloride is present, the original substance itself, is fused with 4 parts of sodium and potassium carbonates and 1 part of potassium nitrate in a platinum crucible. The operation is continued until the reaction has subsided and the mixture is in a quiet state of fusion. The red-hot crucible is then placed upon a thick iron plate, which causes it to cool quickly and prevents the substance from adhering to the sides of the vessel. The cake is next removed from the crucible, boiled with water, and the residue washed until the wash-water shows no precipitate on the addition of barium chloride. The solution and residue are subjected to examination separately.

Examination of the solution.—The following tests for acids are made in separate portions of the solution, the latter having first been neutralised with either hydrochloric or nitric acid, according to the conditions present: (1) for sulphuric acid, with barium chloride; (2) for phosphoric acid, with ammonium molybdate solution; (3) for arsenic acid, with hydrogen sulphide; (4) for chromic acid, by precipitation with lead nitrate; (5) for silica; and (6) fluorine. The conditions given in § 105 (and in part in § 102) must be observed in making the tests.

Examination of the residue.—The residue consists of the bases which the original substance contained. It is dissolved in hydrochloric acid (if an insoluble residue remains, tests are made to ascertain whether it is stannic acid), and the solution investigated for the metals (§ 87). If the substance contained silica the examination of this solution is more easily accomplished after the silica has been removed by evaporation to dryness, and extraction of the residue with water.

REMARK.—The residue insoluble in hydrochloric acid (which may very probably contain stannic oxide) can also consist of undecomposed fluor spar and chrome-iron ore. The former is detected with sulphuric acid according to § 94, the latter by fusion with acid potassium sulphate or with sodium carbonate and potassium nitrate (§ 32).

Examination of the silver salt.—The residue left after the tests of the solubility of the substance in acids (§ 107) or, in general, any insoluble substance in which silver has been detected by the operations explained in this paragraph (see above: choice of methods) is subjected to further treatment for the detection of the bromine, chlorine, etc. which are probably present.

For this purpose a fresh portion of the substance is treated, first with water and then with nitric acid, as in § 107. Tests for silver are made anew in separate portions of the residue thus obtained (with cyanide of potassium and ammonium sulphide, § 108). If these yield positive results, the remainder of the residue is boiled with sodium hydroxide to remove the ferrocyanide and ferricyanide (they may be detected in the solution, after hydrochloric acid has been added, as in § 97). This operation may also bring part of the halogens into solution. The insoluble residue is then washed, and digested for ten minutes with dilute sulphuric acid and zinc (which may be added either in the form of filings or strips of zinc foil). This decomposes the silver compounds, and after the removal of the zinc by sodium carbonate and filtration the solution is tested for chlorine, bromine, iodine, and cyanogen, according to § 105, or, if only one halogen was present, as in § 92.

We bring the study of qualitative analysis to a close with the remark, already made in § 14, that when the data obtained in the qualitative examination of a substance are to be used for quantitative determinations, it is necessary to obtain some idea of the quantities in which the single constituents are present (much, little, or traces). It is therefore best to start out with a quantity of the substance, the approximate weight of which is known, and, by employing precipitation-reactions, to draw the necessary conclusions from the amounts of the several precipitates obtained. Colour-reactions, obviously, do not allow us to form such estimates.

SUPPLEMENT

1

THE BLOW-PIPE

§ 109. With the introduction of the Bunsen's gas-burner the blow-pipe has almost completely disappeared from the laboratory, and operations with the latter, therefore, have been excluded as much as possible from the study of analytical methods which we have just finished. Convenient as the blow-pipe is in the hands of an expert, to the beginner it is very hard to draw conclusions from the data obtained by its use. The phenomena are complicated, and as the knack of using the apparatus can be acquired only after long practice, and the results obtained by the beginner are consequently often incorrect, it is clear why its use has not been introduced hitherto. It may be well, nevertheless, to acquaint the student with the general purposes of the instrument, and especially so in this section of the book, since, if employed in analysis at all, it is usually used for the preliminary tests.

The blow-pipe consists of a metallic tube (the length varies; it is usually 8-10 inches), fitted at one end with a mouthpiece through which air is blown from the mouth. This tube is connected with a cylindrical attachment (a "Drum") into which, and at right angles with the main tube, is screwed a smaller tube terminating in a platinum cap which has a very fine opening. If air be blown through the apparatus into a luminous flame (of gas, a candle, or alcohol), both a reducing and oxidising flame are obtained (see § 32, Remark). If a gas-burner be used, access of air to the gas must be shut off, or, better still, a tube the upper end of which has been flattened and cut off obliquely is placed over the inner gas holes of the burner. The reducing flame is obtained by introducing the blow-pipe into the edge of the flame and forcing a moderate current of air through it. The flame takes an inclined direction, and between the outer blue and the inner, barely visible, cone lies the luminous zone of the reducing flame. To get an oxidising flame, the flame of the burner is lowered, the end of the blow-pipe placed directly in the flame, and a stronger current of air driven through the apparatus than in the foregoing case. The apex of the external mantle is the oxidising flame. The air is forced into the tube by the cheek muscles alone, and as their movement causes no interference with breathing, a steady current can be maintained for a long time without exertion.

The blow-pipe is employed to test the substances for their fusibility and volatility, and also for their behaviour in the oxidising and reducing flames. Its analytical use is chiefly for the production of beads and incrustations.

Beads.—These are prepared equally well in the gas-burner, and their formation has already been frequently employed (§§ 32, 47, etc.) The preparation of the bead and the method of making the experiment are exactly the same as when the gas-burner is employed, and we shall therefore merely compare the behaviour of the different metals in this reaction.

The following metals give coloured beads: cobalt, blue (§ 47); copper, blue while hot, green on cooling (if heated in the reducing flame its bead becomes red when cold). Chromium yields an emerald green bead, which undergoes no change in the reducing flame. Iron, bottle-green in the reducing flame, in the oxidising flame brown, and on cooling yellow. Manganese, violet in the oxidising, colourless in the reducing flame. Antimony, aluminium, zinc, cadmium, lead, calcium, magnesium, and barium, give colourless beads which (those of aluminium and antimony excepted) have an opaque and enamelled appearance on cooling. Silica (stannic oxide also) is very sparingly soluble (silica skeleton, § 101).

The fusibility of the substance is tested upon small square sticks of charcoal. As the charcoal absorbs the fused substances the test should be made upon the side which intersects the grain of the wood transversely. A small cavity is made in the charcoal, in which to place the substance, and the latter is then subjected to the reducing flame of the blow-pipe, the support being held in the left hand. If the substance fuses and is partly absorbed by the charcoal, partly left as a molten globule, an alkali salt is indicated (nitrates and chlorates detonate ; §§ 93 and 98). An infusible residue (sometimes left after fusion in water of crystallisation) is a mark of the oxides of calcium, strontium, magnesium, zinc (these four emit an intense light on ignition), barium, aluminium and silicon. If the residue be moistened with a solution of cobaltic nitrate, ignited afresh, and a blue coloration observed, aluminium oxide is indicated ; if green, zinc (§ 39). If an incrustation forms, conclusions may be drawn from it only after the following test has been made.

Incrustations.—The substance is rubbed together with anhydrous sodium carbonate, a drop of water being added to effect a more perfect mixture. The mixture is then placed in the cavity of a charcoal support and heated in the reducing flame. The reduced metal is partly volatilised, and its vapours become oxidised in passing through the mantle of the oxidising flame, the oxide formed being deposited upon the charcoal as an incrustation. Gold and copper leave globules, but yield no incrustation (platinum, iron, nickel, and cobalt, also suffer reduction, but without being left as globules). Arsenic gives a white incrustation which is deposited at a distance from the substance, and an odour resembling that of garlic is at the same time emitted. Antimony, white incrustation and metallic (brittle) globule, which gives off fumes, even after being removed from the flame. Zinc, white incrustation, turning yellow on cooling. The incrustations of the above metals may easily be driven from one spot to another by the flame. Tin forms a pale-yellow incrustation, which is yellow when cold and cannot be moved about ; the metallic globules are soft. Lead gives a lemon-yellow incrustation and soft globules. Bismuth, orange-yellow incrustation, becoming lemon on cooling, and brittle globules. Cadmium, red-brown incrustation which in thin layers appears orange-yellow. Silver, faint dark-red incrustation (in presence of lead and antimony, cherry-red).

To investigate the residual metallic globules, they are removed, together with the surrounding charcoal, by means of a knife, and the mixture crushed in an agate mortar. If water then be added, and the charcoal separated by lixiviation, the heavier metallic granules remain in the mortar.

We have already remarked that in qualitative analysis the data obtained by means of the blow-pipe are valuable in connection with the tests of the solubility of the substance in water and acids.

2

BUNSEN'S FLAME REACTIONS

§ **110.** It was stated above that the Bunsen's burner is a complete substitute for the blow-pipe. Its use is perfected in the flame reactions which Bunsen elaborated, and by means of which reduction and oxidation reactions and the formation of incrustations can be observed, the advantages of the blow-pipe thus being entirely equalled. We shall give a brief description of the necessary manipulations, which have been excluded from the general course for the same reason as the blow-pipe.

The flame of the gas-burner.—The dark (blue) inner cone of the flame has, as we already know (§ 94), a low temperature ; it is therefore used to cool off strongly-heated substances, or to test those which readily volatilise. At a height almost equal to the apex of the inner cone, but in the outer mantle, lies the point where the temperature is the highest (its position has already been shown, § 9). In this part all tests requiring a great heat are made—fusion, volatility, etc. The remaining sections—the oxidising and reducing flames—have already been described in § 32 (Remark).

There are also subdivisions of the oxidising flame, each of which has its special advantages. As explained in § 32, the highest temperature of this flame lies in the lower third of the outer mantle, and in its outer edge (lower oxidising flame). This section is principally used for oxidation reactions with the borax bead, etc. The upper oxidising flame is at the apex of the outer flame, which presents a lesser degree of heat and is therefore used for such reactions as do not require a high temperature, *e.g.*, combustion (of sulphides, etc.)

The reducing flame is subdivided into upper and lower flames. The lower (the position of which is given in § 32 ; to procure it the supply of air is lessened) is used for the reduction of the bead and in reactions with charcoal. The upper reducing flame is the luminous apex of the inner dark cone. In this section of the flame metals are reduced and incrustation obtained.

The operations employed in analysis by Bunsen consist : (1) in testing the action of a high temperature upon the different bodies ; and (2) in causing reduction and oxidation reactions (formation of an incrustation).

1. The behaviour of the substance at a high temperature is observed by means of a very thin platinum wire (one decimeter must weigh no more than 0·034 gr.), or upon a long, fine asbestos thread. If heat must be applied for a longer time, one end of the wire or asbestos is fused into a small glass tube and the latter fastened to a support. The degree of heat can be approximately estimated by the colour of the glowing platinum wire ; the substance being successively tested in the various portions of the flame, from the coldest to the hottest point. Notice is taken of (1) the fusibility ; (2) volatility (rate of volatilisation) ; (3) flame coloration ; and (4) the luminosity of the substance ; as has been explained in the previous paragraphs. We are already to a certain extent familiar with the flame coloration reactions (see also Supplement 3).

2. *The reduction reactions* are obtained in several ways. (1) A mixture of the substance with lamp-black, sodium, and magnesium is heated in a small, thin glass tube (test for Hg, S, Se, P). (2) The metal may be reduced with carbon and sodium carbonate as follows : the wood of an ordinary match is dipped in molten crystallised sodium carbonate and ignited in the flame ; the wood thus becomes carbonised and at the same time absorbs the fused soda. A drop of fused sodium carbonate having been poured over the substance under examination and pulverised, the mixture is placed upon the end of the match and heated in the reducing flame. It is then transferred to an agate mortar, where it is rubbed to

pieces and the reduced metal lixiviated with water. The methods by which the minute quantity of metal obtained is subjected to characteristic tests are given below.

3. *Incrustations upon porcelain.*—Bunsen detects the metals by means of incrustations of the metal itself, and of its oxide, iodide, and sulphide. The first two incrustations are directly prepared, and afterwards converted to the iodides, which are again changed to the sulphides. To obtain a metallic incrustation, the substance is introduced into the upper reducing flame (the luminous point) on an asbestos thread, directly above which is held a small porcelain dish filled with water. The oxide incrustation is obtained in the same way, but the substance is subjected to the upper oxidising flame (the apex of the outer cone). The iodide incrustation is prepared from that of the oxide by treating the latter with hydriodic acid gas, in an exsiccator containing phosphorus iodide. To get the sulphide incrustation, that of the iodide is submitted to the action of a current of air saturated with ammonium sulphide. The manner of investigating the incrustations is explained below.

4. *Oxidation reactions* (with minute quantities of the substance). One end of a platinum wire of a hair's thickness is wound into a sufficiently flat spiral, so that it forms a small spoon, the diameter of which is 2-3 mm. This is filled with a mixture of the substance and sodium carbonate, or sodium carbonate and potassium nitrate, and heated. The product is examined by a special method, which will be explained later.

5. Coloration of the borax bead or microcosmic salt. These tests are made as usual.

The Examination.—We will now consider how the foregoing methods can be connected for the examination of a great number of compounds. Bunsen's classification will be retained.

I. *Preparation of the incrustation* (with platinum wire or asbestos thread, see 3). Incrustations are formed by: Te, Se, As, Sb, Bi, Hg, Pb, Tl, Cd, Zn, In. Metallic and oxide incrustations are obtained, and the latter converted, after their examination, into those of the iodide and sulphide successively. The metallic incrustations are treated with dilute nitric acid (20 per cent anhydride. Operation denoted by 1 in the table). The oxide incrustations are tested by reduction with stannous chloride (denoted by 2 in the table). If no reduction occurs, a drop of sodium hydroxide is added to the stannous chloride (3). The incrustation is moistened with silver nitrate and subjected to a draught of air saturated with ammonia (for this purpose a wash-bottle is used, the tubes of which have been inverted, *i.e.*, the outlet of which is the shorter tube); if a precipitate forms, its solubility in ammonia is tested (4). Iodide incrustations; solubility in water, tested by the breath; sometimes reappear on drying (5). Action of ammonia and air (6). The iodide incrustations also show the same reactions as those of the oxides. The sulphide incrustations are tested for their solubility in water (by the breath) and in ammonium sulphide (7). The latter test is made either in a current of ammonium sulphide (as with ammonia) or by moistening with the reagent. The solutions are added by means of a capillary tube. The reactions are compared in the accompanying table :—

TABLE OF INCRUSTATIONS

	Metallic incrustation.	Oxide incrustation.	Iodide incrustation.	Sulphide incrustation.
Te	Black, brown edge. 1. Sparingly soluble	White. 2. Black. 3. Black. 4. Yellowish tint	Brown, t. vanishing. 6. Vanishing	Black, black-brown. 7. t. vanishing
Se	Cherry-red, brick-red edge. 1. Sparingly soluble	White. 2. Brick-red. 3. Black. 4. White	Brown, not completely vanishing. 6. Not vanishing	Yellow, orange-yellow. 7. Orange-yellow, t. vanishing
As	Black, brown edge. 1. Sparingly soluble	White. 2. White. 3. White. 4. Yellow-brown solution	Yellow. 5. t. vanishing. 6. Vanishing	Yellow. 7. Vanishing
Sb	Black, brown edge. 1. Sp. soluble	White. 2. White. 3. White. 4. Black, insoluble in NH_3	Orange-yellow. 5. Becoming yellow, t. vanishing. 6. Vanishing	Orange-yellow. 7. Vanishing
Bi	Black, brown edge. 1. Difficultly soluble	Yellowish. 2. White. 3. Black. 4. White	Brown, reddish edge. 5. Reddish-yellow. 6. t. vanishing	Brown. 7. Not vanishing
Hg	Gray, not cohering. 1. Difficultly soluble		Red and yellow. 5. Not vanishing. 6. t. vanishing	Brown. 7. Not vanishing
Tl	Black, brown edge. 1. Difficultly soluble	White. 2. White. 3. White. 4. White	Yellow. 5. Not vanishing. 6. Not vanishing	Black, bluish-gray edge. 7. Not vanishing
Cd	Black, brown edge. 1. Dissolves instantly	Black-brown, white edge. 2. White. 3. White. 4. White, turning black	White. 6. White	Yellow. 7. Not vanishing
Pb	Black, brown edge. 1. Dissolves instantly	Yellow. 2. White. 3. White. 4. White	Bright yellow. 5. Not vanishing. 6. t. vanishing	Brown, then black. 7. Not vanishing
Zn	Black, brown edge. 1. Dissolves instantly	White. 2. White. 3. White. 4. White	White. 6. White	White. 7. Not vanishing

1. In HNO_3.
2. On reduction with $SnCl_2$.
3. " " " and NaOH.
4. On moistening with $AgNO_3$ and NH_3.

5. On treatment with H_2O.
6. " " " HNO_3.
7. " " " $(NH_4)_2S$.
t. Temporarily.

II. *Reduction test* with the carbonised match and sodium carbonate (see 2, p. 284). Incrustations do not form, but the metals are reduced. Treatment in the mortar and lixiviation with water.

1. *A globule is not formed.*—*a.* Magnetic metallic powder, Fe, Co, Ni. The powder is collected by means of a magnetised knife-blade and dissolved on filter paper in a drop of nitric acid. The colour of the solution is observed, and a drop of potassium ferrocyanide (for iron) and of sodium hydroxide and bromine water (for nickel and cobalt) added. Coloration of the borax bead by the metals. *b.* The powder is not magnetic: Pd, Pt, Rh, Ir.

2. *Globules are formed* by Au, Ag, Cu, Sn. Solution in nitric acid on filter paper, for copper (potassium ferrocyanide). Gold is dissolved in *aqua regia* (tested with stannous chloride—Cassius' purple); silver and tin are treated on a watch-glass, the former with nitric acid (test with HCl), tin with hydrochloric acid (test with $Bi(NO_3)_3$ and sodium hydroxide). The borax bead may also be used to detect copper.

III. *Fusion on the platinum spiral* with sodium carbonate (see 4, p. 285) for Mo, W, Mn; with sodium carbonate and potassium nitrate for Cr and V. The fusion is dissolved in a few drops of water, the solution taken up with filter paper, and the different reagents added by means of a capillary tube. Molybdenum and tungsten yield a blue coloration with stannous chloride (they are distinguished through the action of HCl and potassium ferrocyanide—Mo becomes brown). Chromium is recognised by the red colour which it produces with $AgNO_3$, and the green one with stannous chloride. Manganese gives a green solution.

IV. Ti (Ta, Nb), Si, U are recognised by their behaviour toward the borax bead. The metals of Groups I. and II., by the flame coloration, volatility of the salts, etc.

V. *Reduction in a glass tube with magnesium*; P, S.—Phosphorus is detected through the formation of phosphorus hydride on moistening with water. Sulphur, by its action on silver foil (black spot).

The following example will serve to show how convenient the above method is for certain analyses. The detection of tin and antimony in small quantities, which by the usual process of analysis is well known as a difficult problem, becomes, on the contrary, very simple when the following method is employed. About 0·3 grams of the sulphides of the metals, obtained in the usual manner, are heated in a small glass vessel. The residue is taken up on an asbestos thread, a metallic incrustation prepared, and the latter dissolved in a few drops of nitric acid. The presence of antimony is indicated by the formation of a characteristic black spot with silver nitrate and ammonia. The tin is found by means of a borax bead very slightly coloured with cupric oxide. If such a bead be heated in the lower reducing flame, a ruby-red coloration is obtained, due to the reduction of cupric to cuprous oxide.

To students who wish to become more familiar with these methods of analysis, we recommend Bunsen's original article on Flame Reactions, in the *Annalen der Chemie und Pharmacie* (1866), vol. cxxxviii. pp. 257 ff.

3

SPECTRUM ANALYSIS

§ 111. When bodies are heated to a high temperature they become luminous. If the rays emitted by a glowing fluid (*e.g.*, a molten metal) or by a glowing solid be passed through a prism they afford a continuous spectrum (certain exceptions to this statement will be pointed out later). Gases or volatile substances (which may be fluid or solid at the ordinary temperature) yield, on the other hand, an interrupted spectrum, which contains a greater or less number of bright or dark lines. Absorption-spectra, as those with dark lines are called, are obtained when the rays pass through a coloured transition medium, such as coloured fluids or gases.

The apparatus by means of which spectra are obtained and examined is called a spectroscope. We shall describe only that which is most frequently employed in the laboratory. It was invented by Kirschoff and Bunsen, who were the originators of this method of analysis.

The spectroscope of Bunsen and Kirschoff.—A glass prism with a refraction angle of 60° is fastened to a small stand. The rays of the coloured flame pass through a tube supplied with an adjustable slit and an objective, are dispersed by the prism, and the resulting spectrum is observed through a telescope which has a magnifying power of about six times the object. The position of the bright lines is determined by comparison with the spectrum of the sun or of some other luminous object. For this purpose a small prism is placed before the upper half of the slit, in such a manner that the rays of the standard light undergo total refraction in passing through it. They are then dispersed by the large prism and yield a spectrum below that which is to be examined. The two spectra, one above the other, can thus be compared on looking through the telescope. The lines may also be determined by means of the image of a scale cast on the spectrum, and which permits the lines to be numbered. For this purpose the apparatus is fitted with a third tube, containing a millimeter scale reduced to $\frac{1}{15}$ the actual measurement. This scale is photographed upon a glass disc, the faces of which are covered with tin-foil, leaving only the engraving visible, and illuminated by a candle or some other luminous flame. The image of the scale is reflected from the large prism and cast upon the spectrum, so that it may be seen through the telescope. The division 50 is usually made to correspond with the dark line D of the sun's spectrum, or, which amounts to the same thing, to the yellow sodium line.

The spectroscope of Bunsen and Kirschoff has been improved upon in another apparatus which affords a larger image of the spectrum. This advantage is obtained by the use of several prisms (usually six), which are fastened to the support in a semicircle. The telescope magnifies six times and may be adjusted in an exactly horizontal position by means of levelling screws. This arrangement is necessitated by the fact that only one portion of the spectrum can be examined at a time. Such an apparatus shows 3000 dark lines in the sun's spectrum.

Reversal of the spectrum.—The bright lines of the spectra of metals can be reversed to black lines. If a flame coloured by the salt of a metal, such as sodium, which yields only one yellow line, is illuminated by a more powerful source of light which gives a continuous spectrum, *e.g.*, by a Drummond light, a black line is seen in the position of the bright yellow one of sodium. If the experiment be performed with a substance which contains several metals, the spectrum obtained shows many black lines, which correspond in position to the bright lines of the emission-spectra of the same metals.

The phenomena of the bright lines and their reversal are explained by Kirschoff by the following hypothesis. The power of emitting and of absorbing rays of a given wave-length and at a given temperature is the same for any one substance. If a flame has a greater power for emitting rays of one wave-length than of others, a bright line appears at the corresponding point of its spectrum. On the other hand, the flame will absorb the same rays if illuminated by another and stronger source of light which yields a continuous spectrum, because its power of absorption is greater for rays of this wave-length than for others. It thus appears, since the remaining sections of the spectrum are given unaltered, as if dark lines were produced.

The coincidence between the bright lines of the metallic spectra and the dark Fraunhofer's lines of the sun's, together with the reversal of bright lines into dark, led to the idea that their origin was identical. Comparison between the spectra of the sun and of the metals has given us very conclusive theories as to the composition of the sun's atmosphere. The self-luminous stars yield spectra which contain bright lines.

The spectrum of a *compound* of a metal shows the same bright lines as the metal itself. The electro-negative constituents of the compound need not be considered under the ordinary conditions of experiment (see below).

The spectrum of a compound which contains several metals is composed of the spectra of the single metals. It is therefore clear that spectrum analysis should be employed chiefly to detect metals with only a few and brilliant lines. If a mixture be examined, the lines of the different metals will be seen to appear gradually, according to the comparative volatility of the compounds taken. The delicacy of this method is remarkable, and an exceedingly minute quantity of a salt of any metal is sufficient to produce brilliant lines. Sodium can be detected if only a millionth of a milligram be present, and its bright-yellow line is therefore seen in all observations with the spectroscope, even if no sodium salt was used in the experiment. The dust of the air itself shows the sodium line.

Dependence of the spectrum upon the conditions of the experiment.—The number of bright lines in a spectrum, as well as their intensity, is dependent upon the temperature to which the vapour of the metal is heated. If various compounds of a given metal be held in the flame of a gas-burner, no alteration is seen in their spectra, and the latter are exactly similar to that of the metal itself when directly produced. The conclusion might be drawn from this fact that the constituents of the salt other than the metal, sulphuric acid in a sulphate, chlorine in a chloride, have no influence upon the appearance of the spectrum. This is indeed true as long as we work with the Bunsen's burner: but in altering the conditions we alter the spectrum. If the temperature which the vapour attains be raised, certain lines which were very brilliant when produced by means of the burner begin to lose their intensity; feeble lines become bright, and, finally, new lines appear. The spectrum of lithium, for instance, when obtained by the oxyhydrogen flame, contains a new blue line. At a very high temperature, lines may become visible which belong to the non-metallic constituents of the salt. When heated in the flame of the Bunsen's burner the metal separates from its salt, probably because of the action of the carbon in the gas. At this temperature the spectrum of the metal alone is seen. It would naturally be supposed that, if a compound were not decomposed in the flame, its vapour would yield a spectrum varying from that of the metal which it contains. It can give no spectrum at all. This, however, is not the case with the chlorides, which are usually used in experiments, as they suffer dissociation. In the examination of gases, the dependence of the spectrum upon the conditions is still more evident (nitrogen shows two, and perhaps three, different spectra).

Owing to the connection between the spectrum and temperature, the methods of spectrum analysis vary according to the heat which must be employed. We shall therefore describe briefly the flame-spectra, spark-spectra, phosphorescence-spectra, and, finally, absorption-spectra.

Flame-spectra.—A Bunsen's burner is employed for the experiment; many of the tests, however, may be made with an alcohol lamp. The spectroscope having been arranged, *i.e.*, the spectrum and image of the scale having been focused, and the slit so arranged that the former is sharply drawn, the experiment is commenced. The substance is first introduced into the flame of the burner, the latter being placed in front of the slit. If the substance be a solid, it is taken up in the loop of a platinum wire, which is fused into a small glass tube and held quiet by a support. Solutions are tested in glass tubes which are drawn out at the lower end and contain a small bunch of fine platinum wires. The thin wires thus remain continually moistened with the liquid. If an alcohol lamp be used instead of a gas-burner, the substance is placed in the alcohol which feeds the flame.

For the following metals the flame-spectra are very well adapted. The position (and in part the breadth) of the lines is denoted by figures. Division 50 in the above scale corresponds with the D line of the sun's spectrum: the distance between the lines A (15) and H (165) = 150 divisions.

Potassium is characterised by the red line α (15) and the indigo-blue β (160).

Sodium.—Almost complete absorption of all but the yellow: the single, very brilliant yellow line, α (50), corresponds to Fraunhofer's line D, and consists, like the latter, of several narrower lines.

Cæsium.—Especially characteristic lines in the blue, α (111) and β (109), which are very intense and sharp. It shows less brilliant lines in the green, orange, and yellow. That in the orange, β (42 and 44), consists of two lines.

Rubidium.—Very brilliant indigo-blue lines, α (142) and β (140). The red lines, γ (13) and δ (11), are also characteristic: those in the yellow, orange, and green are less important.

Lithium shows a very simple spectrum: a brilliant carmine-red line, α (30), and a feeble one in the orange, β (45).

Barium.—Brilliant green lines α (74-76) and β (77-79): the yellowish-green line γ (60) is less conspicuous. There are also several lines, of feebler intensity, in the green, yellow, and red.

Strontium.—The strontium spectrum is rich in characteristic lines. In the orange-red, α (44-47) is very broad: there are also lines in the red, β (31-33) and γ (34), and in the blue, δ (107-108). The latter especially distinguishes the Sr-spectrum from those of Ba and Ca.

Calcium.—A conspicuous blue line, β (60-62), and a sharp line, α (41-43), in the orange. There are also several lines between these.

Thallium, like sodium, has only one line, α (70). This is emerald, and extremely brilliant.

Indium.—The spectrum contains only two blue lines, α (115) and β (154).

The analysis is made as follows:

Group of the alkali metals and thallium.—In a substance containing all these metals, the lithium, sodium, and thallium can be detected without previous separation, even when present in mere traces. To detect the potassium, rubidium and cæsium, the concentrated solution is precipitated with platinic chloride, and the precipitate boiled twenty or thirty times with very little water. After each fifth boiling a portion of the residue is wrapped in filter paper and examined in the flame. The potassium lines first appear, those of rubidium and cæsium being seen only after longer treatment with water.

Group of the alkaline earths.—To test for small quantities of barium and strontium in presence of an excess of calcium, the nitrates are gently heated with absolute alcohol. The residue is washed with alcohol, wrapped in filter paper, and ignited. It is then moistened with a drop of hydrochloric acid and its flame examined. Small quantities of strontium and calcium, when mixed with a large amount of barium, are detected after the chlorides have been extracted with alcohol and treated as above.

The spectroscope has as yet received little attention in analytical work. The reason for this lies in the confined nature of its advantages, the difficulties involved in the analysis of complicated mixtures by its means, and the inapplicability of the spectroscope to all the problems of analysis. The same objections still exist, although Bunsen has done much to overcome them. The exceptional delicacy of spectroscopic methods, nevertheless, gives the instrument an inestimable value as a means of detecting traces of the various elements. Rubidium, cæsium, thallium, indium, and gallium, were all discovered by its means.

Spark-spectra.—The spectra of very many metals must be obtained by means of the electric spark, as their salts are non-volatile at the temperature to which they are raised by the flame of the gas-burner. Bunsen[1] has invented for this purpose an instrument in which the spark from a

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[1] Poggendorf's *Annalen*, vol. clv. pp. 230 and 366.

Ruhmkorff's coil passes between two pointed carbon tips, which are soaked in a solution of the salt to be examined, usually a chloride. The apparatus of Lecoq de Boisbaudran[1] is still simpler. The solution is contained in a small test-tube, in the bottom of which is fused a platinum wire. The end of the latter must not reach the surface of the liquid. A second platinum wire (1 millimetre in diameter) is held over the surface of the solution, and connected with the positive pole of a Ruhmkorff's coil. The spark passes between the points of the two platinum wires. The spectra of the metals, when so obtained, always contain that of the air, *i.e.*, the oxygen and nitrogen lines. Auer von Welsbach has also constructed for this purpose an apparatus which possesses many advantages.[2]

Gases are examined in a so-called Geissler's tube. This is a glass apparatus, into the ends of which are fused two platinum wires. The gases become luminous when a spark passes between the two platinum electrodes. The tube is filled with rarified gas, which facilitates the passage of the spark. The spectrum obtained varies with the gas used.

We shall rest satisfied with the description of the spectra of magnesium and the cerite metals, for which this method of analysis is exceptionally convenient. The tests are made with the chlorides. The slit must be so adjusted that the red yttrium lines are sharply divided. Only the most conspicuous of the numerous lines are mentioned.

Magnesium.—A single blue line, 74·5.

Erbium.—Very sharp lines at 41·5, 60, 63, in the orange and green (see § 53).

Yttrium.—41-44, a group of lines which have a violet tint; another group at 45-48. Exceptionally brilliant lines at 60, 65·5. Two lines at 73·5-74; 88, 89, and many others which are less conspicuous.

Cerium gives several lines, of which those at 67·5 and 71 are very brilliant.

Lanthanum.—The most characteristic lines lie at 53, 53·5, 62, 64, 67, 70, and 87.

Didymium.—The spectrum is simple. It has two brilliant lines near 70, and less important ones at 69, 70·5, 72.

As was explained in § 53, the majority of these spectra belong, not to the pure elements, but to mixtures.

Group of the cerite metals.—Spectrum analysis is especially convenient for the qualitative examination of the cerite minerals. An analysis of gadolinite by Bunsen may be cited as an example. After removal of the silica (§ 53) he examined the hydrochloric acid solution. The absorption spectrum of didymium (see below) was seen, the line at 55 being exceptionally distinct. The absorption spectrum of erbium was much weaker, though the line at 35 was plainly visible, and there were less conspicuous lines at 65-68. Introduced into the flame on a platinum wire, the substance yielded the spectra of sodium and calcium. The spark-spectrum showed yttrium to be present, as it contained several bright groups of lines between 40 and 50. Cerium was indicated only by the characteristic line 70·9, and the lanthanum spectrum was not visible.

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[1] Lecoq de Boisbaudran, *Spectres lumineux*, Paris, 1874.

[2] *Monatsheft für Chemie*, Bd. V. S. 1.

The mineral, therefore, contained the metals yttrium, erbium, didymium, cerium, calcium, and sodium.

Spectra of certain gases.—The Geissler's tube containing the rarified gas is placed in a vertical position before the slit of the spectroscope. Only the spectra of hydrogen, nitrogen, and oxygen will be described. The latter two are of especial importance, as the atmospheric lines always enter into spectra obtained with the electric spark, being caused by the nitrogen and oxygen of the air.

Hydrogen.—The spectrum contains only three lines, one each in the orange, 34, in the blue, 89·5, and in the violet, 127·5.

Nitrogen yields very many lines in the orange, green, blue, and violet.

Oxygen.—The lines 34·5, 50, 82·5 are especially brilliant. Those at 42·5, 44, 49, 55·6, 56, 57, 59, 61, 62·5, 63·5, 64, 68, 71, 75, 81, 101·5-105, 117-120 are less conspicuous.

Phosphorescence-spectra were first investigated by E. Becquerel, who used for the purpose such substances as become phosphorescent in the sunlight (calcium and strontium sulphides). The spectra of these phosphorescent compounds were not broken by lines, but at the same time contained only small sections of the sun's spectrum. Crookes has recently employed phosphorescence-spectra in analytical work, and has discovered that an electric spark passed over certain solid substances in a Geissler's tube causes them to become phosphorescent. The spectra of such substances are sometimes uninterrupted by lines, but they more frequently contain bright bands. The spectrum of yttrium sulphate, for example, is characterised by a citron yellow band. A thorough examination of the latter spectrum has led Crookes to believe that yttrium is a mixture of several elements (§ 53). The recent introduction of this method, however, with which, beside Crookes, only Lecoq de Boisbaudran has experimented, has thus far prevented a confirmation of his views.

Absorption-spectra.—If a ray from a source of light which gives a continuous spectrum be passed through a coloured solution or coloured gas, and then examined in the spectroscope, an absorption-spectrum is seen. The spectrum obtained when a ray is passed through the vapours of nitrous oxide contains a remarkable number of dark lines. The vapours of chlorine, bromine, and iodine have a similar effect. There are also many coloured liquids which yield absorption-spectra. The majority of dyes form solutions individually characterised by their absorption-spectra, and one is also shown by blood. The spectroscope can be used in all such cases, not only for the detection, but even for the quantitative determination of the coloured solutions of these substances.

An even greater interest, if possible, is attached to the absorption-spectra caused by rays which have passed through the colourless solutions of certain metallic salts. The experiments of Bunsen and Bahr have shown that solutions of erbium and didymium are characterised by very peculiar absorption-spectra. This class of spectra has of late received the attention of several chemists. A short history of their investigations, together with the most recent results of Krüss and Nilson, who believe that they have found no less than twenty different elements in the salts of erbium and didymium, has already been given in the Supplement to Group III.

PART SECOND

QUANTITATIVE ANALYSIS

Quantitative analysis is concerned with the determination of the weights of the elements in a given compound. Its problems, like those of qualitative analysis, are solved through the application of the properties of chemical compounds. Quantitative analysis is inseparably bound to general chemistry, since the more thoroughly any element and its compounds are investigated, the more exact become the methods for its quantitative estimation.

The determination of the amount of an element contained in a given compound can be determined either by *Gravimetric* or *Volumetric* analysis. In the former, the quantity of the element is determined by weight. In volumetric analysis, on the contrary, the estimation is based upon the measurement of the *volume* of a solution, the strength of which is known, which is necessary to complete a given chemical reaction.

The principal methods of quantitative analysis may be more clearly studied if classed in three divisions.

Section I. Gravimetric Analysis.
„ II. Volumetric Analysis.
„ III. Analysis of Organic Compounds (ultimate analysis).

SECTION I

GRAVIMETRIC ANALYSIS

§ **112.** In gravimetric analysis the element is isolated from the given substance, either as such or as one of its compounds, and weighed. In the first case, the weight obtained shows directly the quantity of the element previously in the substance; in the second, when the element is in the form of a compound the constitution of which is known, its weight is found by calculation. The elements in a compound can be determined as elements very rarely, however, since this is often prevented not only by the conditions under which the separation is effected, but also by the properties of the elements themselves. The method most frequently used is to dissolve the substance in some medium (if it is not already in solution) and precipitate the element to be determined, in the form of an insoluble compound. Although this operation seems at first very simple, it in fact presents many complications. Every method of gravimetric determination must satisfy several conditions. The following will make this point clear.

The choice of a compound in which this or that element can be estimated is not easily settled. If the compound is to be obtained by precipitation, it must be insoluble, or at least rendered very sparingly soluble by the conditions under which the reaction is caused. Otherwise the precipitation will not be complete, *i.e.*, the element will not be quantitatively separated. Precipitation, the first operation of an analysis, is followed by the washing of the precipitate; this removes the liquid in which the precipitation was made. The washing-medium (water, alcohol, dilute nitric acid) must neither dissolve the precipitate nor have any chemical action upon it. The next steps, drying and igniting, serve to drive off the water, or other fluid, used in washing. The precipitated compound must withstand a high temperature without undergoing change. The last and most important requisite is a well-defined and unchangeable composition in the final compound, by means of which it is possible to calculate from the weight of the compound that of the element which it contains.

To actually satisfy all these conditions is extremely difficult, and for this reason gravimetric analysis is complicated. If the conditions be accurately determined by careful study of the compounds, however, their intricate nature has no effect upon the exactness of the analysis. The majority of quantitative methods contain an error, due to the non-observance of some one or more of the necessary conditions: *e.g.*, the slight solubility of the chosen compound leads to incomplete precipitation (loss); or its change on ignition causes inaccuracy (gain or loss). The error of a good method is small (usually about 0·2 per cent), and, furthermore, its magnitude can be almost exactly determined, and its influence thus rendered harmless.

§ **113.** We have already seen that gravimetric analysis is based upon single reactions. Quantitative separations, like the qualitative, however, depend upon a combination of reactions. The reactions of quantitative separations require the same conditions as those of estimation. Quantitative determinations can be divided into the following three classes.

Direct estimation is the most usual, and also the most accurate method of quantitative analysis. The element to be determined is precipitated and weighed (usually as one of its compounds), or, if it forms a suitable volatile compound (*e.g.*, ammonium salts, carbonic acid, nitric acid), it is driven off in the form of the latter, and the weight of the element calculated from the loss resulting from its volatilisation.—Direct estimation from the loss.

Indirect determinations, though nearly as common, are less accurate than the direct methods. They are used in case an element is to be determined for which the direct separation methods are either inexact or difficult. The indirect method consists in uniting both the elements to be separated to a third, for example, chlorine and bromine to silver, potassium and sodium to sulphuric acid. The combined weight of the two compounds (silver chloride and bromide, potassium and sodium sulphates) is first ascertained; let us call this weight a. The quantity of the metal or acid which is common to both compounds is then determined (silver or sulphuric acid in this case); let this value $= b$. We now have two equations for the solution of the two unknown quantities, x and x', m and m' representing the constituent common to both compounds:

$$x + m + x' + m' = a,$$
$$m + m' = b.$$

The solution of these equations by means of the difference in the molecular weights of the two compounds, and also a second method of deriving the equations in indirect determinations, will be explained in connection with the first group of metals. It may be stated here, however, that indirect methods can be employed only when the elements to be separated bear a certain ratio to each other. Their incorrect use may lead to very inexact results.

Estimation from the difference.—The complications and difficulties involved in fulfilling the conditions necessary for a direct determination are such that quantitative analysis affords no direct means of estimating certain of the elements. The principal members of this class are boron (boric acid) and oxygen. In instances where such elements are present, and also when the methods of separating elements are inexact (*e.g.*, as in the case of iron from aluminium), we determine by the difference. This method consists in finding by gravimetric analysis the quantities of all the elements present, with the exception of the one for which no method of determination exists. The amount of this or that compound in which the element in question was present is found simply by subtracting the weights of all the other elements obtained from that of the substance taken for analysis. Determinations by the difference cannot be as exact as by direct methods. It has already been stated that every direct method has its error. If several distinct determinations must be made, therefore, for which various methods (each with its error) are employed, all the inaccuracies will be concentrated in the value found for the element determined from the difference. It may, of course, be possible that the several errors will balance one another, but this is not necessarily the case, and determination by the difference is therefore never so trustworthy as the direct methods.

The methods of gravimetric analysis which follow are arranged according to the classification which we have employed in qualitative analysis. To enable the student to learn those which are more important in a practical way, and also to simplify his work, illustrations of these methods are given in the chapter on Examples of Gravimetric Analysis.

§ **114. Calculation of Results.**—As the elements are usually weighed in the form of compounds of known composition, the operations of an analysis are followed by the calculation of the quantity of the determined element from the data obtained. Knowledge of the molecular weight of the compound and the atomic weight of the element to be determined is required. This may be more easily explained by an illustration. Suppose the analysis of a certain barium salt is to be made. This is accomplished by precipitation with sulphuric acid, and the quantity of barium found on weighing its sulphate must obviously represent all that which was present in the salt analysed. To ascertain how much barium the latter contained, therefore, we calculate the amount of the metal in the quantity of its sulphate, a, obtained. As the molecular weight of barium sulphate = 233, and the atomic weight of barium = 137, the following proportion is obtained:

$$233 : 137 = a : x. \qquad x = a \times \frac{137}{233}.$$

The amount of barium by weight, x, is expressed in grams and fractions of a gram. The weight thus found is next calculated to 100 parts, *i.e.*, the percentage ascertained. The error of the method is expressed in the same way, and thus if a known substance is analysed, and the results obtained be expressed in percentage, the magnitude of the error made in the analysis is at once apparent. The value x is calculated to percentage. Continuing with the same example, if the amount *b* of the barium salt has been taken for analysis, this is accomplished by multiplying x by $\frac{100}{b}$:

$$x = a \times \frac{137}{233} \times \frac{100}{b}.$$

The calculation is carried out to the second decimal place; additional figures have no value, and even the second figures are usually unreliable (see below).

The above explanations may be thus summarised. To find the amount of an element (x), the value found by weighing is multiplied by a fraction, the numerator of which is the atomic weight of the element in question, and the denominator the molecular weight of the compound as which the element was weighed. The data obtained in the analysis are calculated to the element, as we have seen. The oxygen in oxides is never directly determined, but obtained by the difference found in subtracting the total weight of the remaining elements from 100 (the values having previously been reduced to percentage). The metals were formerly, and very frequently still are, calculated to their oxides—the metalloids to their acids, or, more correctly, to their acid anhydrides. In such calculations the molecular weight of the metallic oxide or acid anhydride is substituted for the atomic weight of the element; in the foregoing illustration, for instance, the amount of barium oxide (mol. wt. = 153) and of sulphuric anhydride (mol. wt. = 80) are ascertained:

$$233 : 153 = a : x.$$

The amount of barium oxide, $x = a\frac{153}{233}$,

and of sulphuric anhydride, $x = a\frac{80}{233}$.

In the calculation of analysis of very complicated substances (soils, mineral water, etc.) it is generally understood that the metals are to be expressed as their oxides and the acids as their anhydrides. The values are finally given in the form of salts (the equivalent weights of acids and metals having first been calculated, see below), the acids being assigned to the bases by more or less arbitrary methods. If, for instance, chlorine, sulphuric acid, and potassium are contained in a substance, they are expressed as potassium chloride and potassium sulphate.

A check upon the data of the analysis, which possesses more or less accuracy, is usually possible. It is entirely reliable in the analysis of chemical compounds (with the exception of certain compounds of almost equal percentage composition, and with high molecular weights). Let us turn to the example which we have already used, and assume that barium chloride has been analysed and the results calculated. Barium chloride has the molecular weight 208, and contains in 208 parts 137 parts of barium. Calculating to percentage, we have:

$$208 : 137 = 100 : x,$$

$$x = \frac{208 \cdot 100}{137}.$$

The value x (per cent of barium) must be equal to the x obtained in the analysis, *i.e.*, to the percentage of barium found.

Error in gravimetric analysis. — The two values obtained for x never exactly agree in practice, as every method of quantitative analysis has its individual error (the cause of which was explained in § 112). Errors are involved not only in neglect of the requisite conditions, but also in the practical operations of filtration, washing, etc. The data of an analysis are nevertheless to be relied upon, for the error of every good method lies within definite limits. To determine it, an accurately weighed quantity of the given compound, in the purest state possible, is analysed, absolute exactness in the operations being assumed, and the percentage of metal or acid calculated from the results. Pure barium chloride, for instance, is precipitated with sulphuric acid, and the quantity of barium found from that of its sulphate. If we suppose that of 1000 parts barium only 999 have been recovered, the error of the analysis is 0·1 per cent. When the values are expressed in percentage, the third, and very often the second, decimal places have no worth—speaking, of course, of the ordinary operations. If the greatest precaution be observed, the personal error is reduced. In Stas's determinations of the atomic weights the correctness of the results is assured even to the third decimal. They have been proved by coincidence between the values obtained by methods which exhibited the widest variations among themselves.

The analysis of substances which possess no definite chemical composition can rarely be accurately controlled. Analyses of alloys and substances, all the components of which have been determined, can be checked by the approximation of the sum of results to 100, but even if they are exactly equal to this figure, the possibility of incorrect determinations of the single constituents is not excluded, and such errors remain undetected. To check complicated mixtures (of salts, or silicates, for example) the metals and acids are calculated to bases and acid anhydrides, and the sum of the equivalent weights of the bases compared with those of the acid anhydrides. These two values must always agree. To illustrate this by an example, let us suppose that an isomorphous mixture of copper and ferrous sulphates has been analysed, with the following percentage results:

$$CuO = 25{\cdot}56;\ FeO = 23{\cdot}12;\ SO_3 = 51{\cdot}38.$$

These values are next converted to equivalents (by dividing by the molecular weights of the respective compounds):

$$CuO = \frac{25{\cdot}56}{79{\cdot}4} = 0{\cdot}322.$$

$$FeO = \frac{23{\cdot}12}{72} = \frac{0{\cdot}320}{0{\cdot}642.}$$

$$SO_3 = \frac{51{\cdot}38}{80} = 0{\cdot}642.$$

The coincidence between the equivalent values of the two bases and sulphuric acid assures us that the analysis was correct.

This method of confirming an analysis is also open to certain objections. The silicates, for instance, often contain a greater quantity of silica than the metals found require. Silica forms several polysilicates, and the computations of the mineralogist are calculated from the ratio of the oxygen of the bases to that of the acids. Finally, the state in which certain oxides (aluminium oxide, boric acid, etc.) are present in the substance is uncertain, *e.g.*, aluminium oxide may be present as an acid, or boron as a base.

To derive the formula of a chemical compound from the data of the analysis, the equivalent quantities are deduced from the percentage results, as above. We may use as an illustration the calculation of the formula of the double iron and copper sulphate which has just been given. In order to avoid new calculations (the constituents of the salt were expressed as bases and acids; the method is obviously the same if we employ the elements themselves), we shall take the values assumed above:

$$CuO = 0{\cdot}322 = 1,$$
$$FeO = 0{\cdot}320 = 1,$$
$$SO_3 = 0{\cdot}642 = 2.$$

The equivalent quantities therefore stand in the ratio of 1 : 1 : 2, and the compound contained one equivalent part of CuO, one of FeO, and two of SO_3, *i.e.*, it had the molecular proportions of the double salt $FeSO_4 + CuSO_4$.

§ **115.** *The atomic weights.*—In ordinary analytical calculations the atomic weights used need contain only one decimal, without danger of any appreciable error. The computation of more delicate operations, such as atomic weight determinations, requires most exact values for the atomic weights, both empirical and calculated. The foundation of the periodic system of the elements has recently called for new determinations of certain elements. The atomic weights in the table at the end of this volume follow the calculations of Ostwald. They are given with one more decimal than is guaranteed by the accuracy of the determinations, and are based upon the hypothesis that that of oxygen is 16, as the ratio between the atomic weights of oxygen and hydrogen is not yet fully ascertained. It is not as 1 : 16 at any rate, but lies between the ratios 1·002 : 16 and 1·008 : 16, and is still to be determined. Since atomic weights in which H = 1 is taken as the unit are often employed, the values calculated on this basis by Lothar Meyer and Seubert are placed in the second column. In this table we have followed the authors in assuming the ratio between the atomic weights of hydrogen and oxygen as 1 : 15·96.

GRAVIMETRIC DETERMINATIONS AND SEPARATIONS OF THE METALS

GROUP I

POTASSIUM, SODIUM, AMMONIUM

§ **116.** I. **Determination.** — The alkali metals (with the exception of ammonium) are preferably determined as their sulphates, these salts affording very accurate results. The properties of the chlorides and nitrates render these compounds less suitable, as their determination is much more affected by the prevailing conditions and more intricate than that of the sulphates. Estimation in the form of these compounds is possible only with the salts of readily volatile acids. Salts of acids which are volatilised with difficulty or withstand a high temperature require either the removal of the acids (sodium; the operation will be explained in the paragraphs on the respective acids) or determination as platinichlorides (potassium and ammonium, possible only when the acid is soluble in alcohol). The platinichlorides are principally used in separations. As the silicofluorides, though suitable for determinations, are almost never employed (except in single separations), this method will not be considered. The ammonium of ammonium salts is usually determined as its platinichloride, or, when this is impossible, it is driven from its compound and estimated by the difference.

Determination of sodium and potassium as their sulphates.— The alkali salt (of a volatile acid) is converted to the sulphate by evaporation on the water-bath with a quantity of sulphuric acid sufficient to displace the acid of the salt. Too great an excess of sulphuric acid must be avoided, as its removal is somewhat difficult. The strongly concentrated solution of the acid sulphate of sodium or potassium is next poured into a platinum crucible, the evaporating dish carefully rinsed, the rinse-water added, and the solution evaporated to dryness. The superfluous sulphuric acid is removed by cautiously heating the upper part of the crucible, which should be placed obliquely and covered. To remove the last traces of sulphuric acid small parts of ammonium carbonate must be thrown into the crucible. Stronger heat may be applied toward the end of the operation, but care must be taken that no potassium sulphate is lost by spirting, and when exposed to a red heat the crucible must be covered. Complete removal of the sulphuric acid may be assumed when the weight of the crucible undergoes no change after repeated ignition. All of these operations can be very conveniently performed in a muffle, the bottom of which has two openings, one for the crucible, the other for the lamp (Lieben), or in an open, cup-shaped air-bath. The determination of the alkali metals as chlorides or nitrates is accomplished in the same manner, but the heating and ignition require greater caution; the nitrates may be heated until they begin to fuse, the chlorides to a dark-red heat, in a covered crucible. It is also possible to estimate ammonia as ammonium chloride, the salt being dried at 100° C.

Determination of potassium and ammonium as platinichlorides.—The solution of the chlorides is mixed with platinic chloride in a porcelain casserole, and evaporated almost to dryness on the water-bath. The residue is then digested with a mixture of 3 parts alcohol and 1 part ether, brought on a filter which has previously been dried and weighed, washed with alcohol and ether, and dried at 100° C. to constant weight. A weighed portion of the precipitate is then heated to 130°, and its loss of weight at that temperature calculated to the entire precipitate, and the result subtracted from the weight of the platinichloride. A more accurate method is to decompose the previously dried platinichloride by ignition. The salt must be wrapped in the filter paper, to prevent its being carried away mechanically, and very carefully ignited (the filter must first be carbonised and then burned), either in a hydrogen stream or after the addition of a few crystals of oxalic acid. The potassium chloride is removed by water, preferably through decantation, and the platinum dried and weighed. Each atom of platinum corresponds to two of potassium. The estimation of ammonia is effected in the same way. Ammonium platinichloride yields pure metallic platinum on ignition. To avoid the always inaccurate use of a weighed filter in estimating the alkali metals as platinichlorides, the potassium salt, dried at 100° C. as usual, may be dissolved in boiling water and evaporated to dryness in a weighed platinum dish or crucible. The residue is then dried at 130° C. to constant weight. In determinations as platinichlorides, the metals must be present as chlorides. The nitrates are converted to the latter by evaporation to dryness with hydrochloric acid and re-solution in water. Sulphates are treated for the same purpose with barium chloride, the least excess of the latter being avoided. If nitrates and sulphates are both present, they are converted entirely to the sulphates by treatment with sulphuric acid, and then into chlorides as above.

The determination of ammonia by means of its liberation from compounds can be accomplished by various methods, of which only one need be given. To estimate it by boiling the ammonium salt with caustic alkalies, a flask is employed, which is connected with a condenser and receiver. The latter is filled with dilute hydrochloric acid (if the ammonia is to be determined as ammonium platinichloride), or with a standard solution of sulphuric acid (for its volumetric determination). The ammonium salt is weighed in a small glass tube, and, without being taken from the latter, dropped into the flask, in which potassium or calcium hydroxide has already been placed. The flask is then quickly joined to the condenser, and the ammonia liberated by boiling, and caught in the receiver.

§ **117.** II. **Separations.**—When ammonium is to be separated from sodium and potassium, it becomes advantageous to determine it in a separate portion of the substance, by conversion into ammonia under the conditions given in § 116. Ammonium salts may be estimated from the loss on ignition, but the method is less accurate, and can be employed only when the following conditions prevail. 1. All the salts, both of the alkalies and of ammonia, must be of one and the same acid. 2. It must be possible to dry the salts at 100° C. without loss of ammonia. These conditions having been secured, the mixture is weighed in a platinum crucible, the latter covered, and at first cautiously warmed, then ignited at a gentle heat. If the sulphates were used, a small excess of sulphuric acid remains, and must be removed before the weighing. This is effected by the addition of small pieces of ammonium carbonate to the residue, and subsequent ignition. The loss of weight which the crucible undergoes gives the quantity of the ammonium salts.

Potassium and ammonium from sodium as their platinichlorides. The conditions necessary are the same as in the single determinations (§ 116). An excess of platinic chloride must be employed, and after the washing with alcohol and ether the filtrate must be yellow. A colourless solution indicates the presence of too little platinic chloride, and the consequent possibility of an error, since, if all the sodium chloride is not transformed to the platinichloride, the unaltered portion remains on the filter with the potassium salt, being insoluble in alcohol. If the combined weight of the chlorides or sulphates from which sodium is separated by this method is known, the quantity of sodium is determined by the difference, as direct methods for its estimation under the prevailing conditions are very intricate.

Potassium from sodium. Indirect determinations. — To ensure the correct use of the indirect determinations, we will supplement the discussion of this method in § 113 by the following remarks. Let us assume that an element, x, of the atomic weight P, is to be separated from another, y, the atomic weight of which is Q, and that for this purpose both of the elements have been combined with the same acid, R. Let the sum of the salts PR + QR be a, and the quantity of acid which they contain $m + n = b$. We have the equations:

$$x + m + y + n = a,$$
$$m + n = b.$$

But $\frac{x}{m} = \frac{P}{R}$ and $\frac{y}{n} = \frac{Q}{R}$. Eliminating m and n from the equation:

$$x = \frac{R}{R(Q-P)}\,(b[Q+R] - aR),$$

$$y = \frac{Q}{R(Q-P)}\,(aR - b[P+R]).$$

Indirect determinations may be made in various ways. For the alkali metals, the sum of the sulphates or chlorides is first found, and the sulphuric acid or chlorine subsequently estimated. The methods for the latter determinations will be found in the respective paragraphs. These two values suffice for the calculation of the sodium and potassium. The most suitable conditions for indirect determinations may be made clearer by the illustration of another method of calculating the results. The sum of the chlorides is again denoted by x, and their chlorine by b. If the quantity of chlorine, b, be calculated entirely to potassium chloride, according to the proportion $35{\cdot}5 : 74{\cdot}6 = b : x$, we obtain the value c, which is greater than the combined weight of the two chlorides taken for analysis, since the molecular weight of sodium chloride is less than that of the potassium salt. The difference, $c - a$, stands in the same ratio to the quantity of sodium, as the number 16·1, the difference between the molecular weights of the chlorides (74·6 − 58·5), bears to the molecular weight of sodium chloride. The proportion is therefore

$$16{\cdot}1 : 58{\cdot}5 = c - a : x,$$

x being the quantity of sodium chloride in the compound.

An examination of these formulae for indirect determination shows that the use of the method becomes the more satisfactory, (1) the lower the atomic weights of the metals to be separated, and the greater the difference between the atomic weights; (2) the greater the molecular or atomic weight of the body with which the metals are combined, and (3) the nearer the ratio between the respective metals is to that of their atomic weights.

GROUP II

BARIUM, STRONTIUM, CALCIUM

§ **118.** I. **Determinations.**—Barium is determined, whenever possible, as the sulphate; this method is very accurate.

Strontium is also determined as the sulphate in the majority of instances, but occasionally as strontium carbonate: calcium, almost exclusively by precipitation as the oxalate and final conversion to the oxide or carbonate. In the calcium salts of organic acids, the metal can also be determined as sulphate (see § 171). All these methods are exact, and others are employed (in separations, etc.) only when their use is not permitted. The remaining methods will be discussed in connection with the separations.

Estimation as sulphates.—This method is inexact in the presence of metaphosphoric or concentrated sulphuric acid, of citric and other non-volatile organic acids, and also when large quantities of any ammonium salt (*e.g.*, the nitrate) are present, the precipitation being incomplete under these conditions. In presence of alkali salts the values obtained are always too high, as small quantities of these salts are held back by the precipitate.

1. *Determination of barium.*—Barium sulphate is precipitated by dilute sulphuric acid, both the solution and precipitant having first been heated to incipient boiling (a large excess of free acid influences the accuracy, though the presence of some hydrochloric acid is required). When precipitated from cold solutions the barium sulphate is not crystalline, and passes through the filter. The heat is maintained for some time, the glass being placed on the water-bath until the precipitate has subsided, and the supernatant liquid then decanted through a filter. The precipitate is again treated with boiling water, stirred, allowed to settle, again decanted, and this operation repeated once or twice more. The salt itself is finally brought on the filter, washed with hot water, dried, and ignited.

2. *Determination of strontium and calcium.*—The solution of strontium or calcium is first precipitated in the cold with dilute sulphuric acid, and an equal volume of alcohol then added. The latter lessens the solubility of the sulphates. The precipitate is filtered after twelve hours, dried, and ignited. If the addition of alcohol is impossible or inexpedient, the precipitation may be made with an excess of dilute sulphuric acid, but the latter method is far less satisfactory than the former.

Strontium.—The carbonate is more suitable than the sulphate for accurate determinations. The moderately concentrated solution of the strontium salt is treated with a small excess of ammonium carbonate in presence of ammonia, and allowed to stand for several hours at a gentle heat. The precipitate is then filtered, dried, and ignited. Ammonium salts influence the solubility of strontium carbonate, and the method is therefore slightly inaccurate in their presence. Calcium and barium are determined by this method only in separations. When barium is to be weighed as the carbonate, protracted ignition in the air must be avoided, as a loss is thus involved, which is due, according to the experiments of H. Struve, to the formation of barium peroxide.

Determination of calcium by precipitation as calcium oxalate. —The hot solution of the calcium salt is treated with an excess of ammonium oxalate and ammonia, enough of the latter being added to impart a strong odour to the solution. The covered glass is then gently warmed for at least twelve hours, or until the precipitate has fully settled. The supernatant liquid is filtered, and the precipitate washed several times by decantation, and finally on the filter. In washing on the filter a second quantity of water must not be added until the filter is empty. The filter is dried with the precipitate, and the calcium determined either (1) as its carbonate, or (2) its oxide. 1. If it is to be weighed as the carbonate the precipitate is placed in a platinum crucible, the filter being burned alone and its ash dropped into the crucible. The latter is then covered, and heated very gently at first, but subsequently until the bottom becomes dull red. This temperature is maintained for ten minutes. Careful ignition is best secured by holding the lamp in the hand and slowly moving it around the crucible. After being allowed to cool in an exsiccator, the crucible is weighed. A test must then be made to ascertain whether the calcium is in the form of its carbonate alone, and not partly converted to the oxide. The contents of the crucible are for this purpose moistened with a few drops of water, and tested with turmeric paper. If the latter turns brown, calcium oxide has been formed. In this case the paper must be rinsed off with water, a piece of ammonium carbonate placed in the crucible, and the water driven off on the water-bath. The crucible is then cautiously ignited and again weighed. If the operation has changed the weight, the treatment with ammonium carbonate must be repeated, until two consecutive weighings show no difference. 2. The estimation as oxide is much simpler. The precipitated oxalate is heated before the blow-pipe for twenty minutes or longer, according to the quantity of the salt. The crucible is then allowed to cool, weighed, and again ignited for ten minutes. The second weighing must give the same results as the first; if any loss has ensued, the ignition is repeated again, or, in general, until the weight remains constant.

§ **119.** II. **Separations.** (*a*) *Barium from strontium and calcium.*—This is always effected by precipitating the barium as its chromate. The necessary conditions, which are given below, must be exactly fulfilled. The method formerly recommended by Rose, which consists in treating the sulphates with a mixture of potassium carbonate and sulphate, has been proved inaccurate by the experiments of R. Fresenius. The method of separating barium as its silicofluoride is also inexact.

Separation as barium chromate.—The neutral solution is acidified by a few drops of acetic acid, heated, and precipitated with ammonium monochromate (for the preparation of this salt, see § 17). After becoming cool again it is filtered off, and the precipitate dissolved in a barely sufficient quantity of nitric acid of sp. gr. 1·20. This solution is then diluted with 200 c.c. water and 5 c.c. of a 10 per cent solution of ammonium acetate, and again precipitated with ammonium chromate. The barium chromate is then washed and *very gently* ignited. Strontium and calcium remain in the filtrate as their chromates.

Strontium from calcium. Separation based on the insolubility of strontium nitrate in alcohol.—The nitrates of the two metals are thoroughly dried on the water-bath, and afterwards for some time at 130°, in a flask provided with a stopper. The residue is digested, in the same vessel, with equal volumes of absolute alcohol and ether, the mixture being still less a solvent for strontium nitrate than alcohol alone. The residual salt is washed with alcohol and ether on a filter protected by a glass plate. Both the strontium and calcium are finally determined as their sulphates (§ 118).

Indirect determination.—There are several indirect methods, of which only the following will be described. The strontium and calcium are precipitated as their carbonates (§ 118), their combined weight ascertained, and the amount of carbonic acid estimated from the loss on ignition at a white heat. The strontium and calcium are calculated from these data by the formulae given in § 117.

(*b*) *Separation of barium, strontium, and calcium from the metals of Group I.*—A distinction will be made, in the description of separations, between the general and special methods. By general separations we mean those in which all the metals of one group or division are separated from another group in a single operation. The special methods are employed to separate the single metals from one another. They are always the more accurate, and are to be employed whenever possible; the general methods give inexact results, which are due to the complicated conditions involved, and at the same time very difficultly secured; and they are to be used only when special methods are inapplicable. Cases in which they must be employed seldom occur in practice, however, and the special methods are therefore almost always expedient.

Special methods.—Barium is separated from the alkali metals by means of sulphuric acid whenever possible (§ 118), calcium as calcium oxalate (§ 118), and strontium as its carbonate (§ 118).

General methods.—If barium and calcium cannot be separated by special methods, all three metals are precipitated as their carbonates by ammonium carbonate and ammonia. If magnesium is present, ammonia cannot be employed, and the method is consequently inaccurate.

The operations necessary in this case are explained in the separation of magnesium. Ammonium must be determined in an extra portion of the substance.

MAGNESIUM

§ **120.** I. **Determination of Magnesium.**—Magnesium is almost invariably precipitated as ammonium magnesium phosphate (except in occasional separations, see II.) Its solution is mixed with ammonia and ammonium chloride (if a precipitate appears, more of the latter is added) until it smells strongly of ammonia; the solution is then precipitated by an excess of sodium phosphate (sodium ammonium phosphate has recently been employed to advantage), and, after being stirred with a glass rod, which must not touch the side of the vessel, it is covered with a watch-glass and allowed to stand for twelve hours. The precipitate is then brought upon a filter and washed with a mixture of 3 parts water and 1 part ammonia, until the filtrate gives no turbidity with silver nitrate in presence of nitric acid. Washing for a much longer time than necessary may lead to a small error. The precipitate is next dried, removed from the filter, and ignited, cautiously at first, in a platinum crucible. A stronger heat is applied as soon as the water and ammonia have been driven off. The filter is burned by itself and its ash added to the contents of the crucible. Magnesium pyrophosphate, $Mg_2P_2O_7$, remains after the ignition, and is weighed in this form.

II. **Separation of Magnesium.**—*From Group II., Division* 1 (barium, strontium, and calcium). The general method is to precipitate the solution with ammonium carbonate in presence of ammonia and a great excess of ammonium chloride. The mixture is then slightly heated or allowed to stand for twelve hours in a warm place, when the precipitated carbonates of barium, strontium, and calcium are filtered and washed with water and ammonia. The method is not entirely exact, as ammonium chloride dissolves traces of barium and calcium carbonates. To obviate the error involved, the filtrate is treated, before the precipitation of magnesium, with a few drops of dilute sulphuric acid, the barium sulphate filtered off, and ammonium oxalate is then added, to precipitate the traces of calcium. The solution is then re-filtered, and magnesium thrown down by sodium phosphate, or sodium ammonium phosphate. *The special methods* are much more accurate. The above method is used only for strontium (§ 118), barium being separated by means of sulphuric acid (§ 118), and calcium with ammonium oxalate in presence of ammonia and ammonium chloride (§ 118). Since the calcium oxalate carries down traces of ammonium magnesium oxalate in the first precipitation, the precipitate must be redissolved in dilute hydrochloric acid after being washed, and again thrown down by neutralisation with ammonia. In all special methods the magnesium is precipitated from its solution by sodium phosphate, the precautions mentioned in I. being carefully observed, and is finally weighed as magnesium pyrophosphate.

Separation from Group I.—The methods of separating magnesium from the alkali metals are based upon the formation of magnesium oxide, which is insoluble in water, or of the carbonate or phosphate. The last of these methods, although the most circuitous, nevertheless gives the most trustworthy results. Whichever method be employed, the alkalies are determined by evaporation (and ignition, if ammonium salts are present), as the chlorides or sulphates.

(*a*) *Separation as magnesium hydroxide.* — Magnesium hydroxide is precipitated by baryta-water, lime-milk, or mercuric oxide. Ammonium salts must be removed by ignition before the precipitation. 1. Baryta-water is added to the solution as long as it causes a precipitate. The solution is then boiled, filtered, and the magnesium hydroxide washed with hot water. To bring it into a state suitable for weighing, it is dissolved in hydrochloric acid, the excess of barium precipitated with sulphuric acid, and, after filtration, the magnesium with sodium phosphate (§ 118). 2. Lime-milk can be substituted for baryta-water. The magnesium hydroxide having been washed and dissolved in hydrochloric acid, ammonium oxalate and ammonia are added to free the solution from calcium, the precipitate washed, and the magnesium thrown down as phosphate. 3. If mercuric oxide is to be employed, both the alkalies and magnesium must be in the form of chlorides, and ammonium salts must first be removed by ignition. The residue is dissolved in water, hydrochloric acid added, and the solution digested with moist mercuric oxide. The operation is performed in a porcelain crucible, which is heated on the water-bath for an hour or two, the mixture being frequently stirred in the meantime. The solution is evaporated to dryness under a hood, and the residue ignited in a covered crucible until the mercuric salts have completely volatilised. The alkali salts are then extracted by water, and the insoluble magnesium oxide washed, ignited, and weighed. The most accurate of these three methods is that with mercuric oxide. In all of them a trace of magnesium oxide goes into solution (it is sparingly soluble), but its quantity can always be determined after the weighing of the alkali sulphates. For this purpose the latter are dissolved in a small amount of water, filtered, and the residual magnesium oxide ignited and weighed.

(*b*) *Separation as ammonium magnesium carbonate.*—The neutral solution is precipitated with *ammonia and ammonium carbonate* and set aside for twenty-four hours. The precipitate of ammonium magnesium carbonate must be washed with water containing ammonia and ammonium carbonate. It is then ignited and weighed as magnesium oxide. If potassium was present, the oxide obtained must be washed with water (potassium carbonate, which is carried down as a double salt, is thus extracted) and its ignition repeated.

(*c*) *Separation as ammonium magnesium phosphate* is the most exact method of isolating magnesium from the alkalies. Ammonium chloride is added to the ammoniacal solution, and the latter then precipitated by *ammonium phosphate.* The ammonium magnesium phosphate obtained is filtered, ignited, and the residue weighed. The ammonia is removed from the filtrate by evaporation, and lead acetate then added to get rid of the excess of ammonium phosphate used. After the excess of lead has in turn been precipitated by hydrogen sulphide or ammonia and ammonium carbonate (for conditions, see Lead), the solution contains only the alkalies and the excess of ammonium salts, and the former are determined as usual (§ 116). The excess of phosphoric acid may be advantageously removed by silver nitrate instead of lead acetate, the surplus silver being then precipitated by hydrochloric acid. The alkalies are thus obtained in the solution as chlorides, and weighed as such.

GROUP III

ALUMINIUM, CHROMIUM, IRON

§ **121.** I. **Determination.**—Aluminium, chromium, and iron are usually determined as oxides, the latter being precipitated with ammonia. The alkalies cannot be employed as precipitants, as it is impossible to wash the hydroxides free from the latter. In separations, as will be seen later, the hydroxides of these metals are precipitated by ammonium sulphide and barium carbonate. Chromium can also be oxidised to chromic acid and weighed as barium or lead chromate, but these two methods are usually employed only in separations.

Determination as oxides. Aluminium.—The hot solution, to which ammonium chloride has been added, is precipitated with a slight excess of ammonia and boiled for a short time. The precipitate is first washed by decantation, and finally on the filter, with hot water. It must be dried as thoroughly as possible before ignition. The latter operation is performed in a covered crucible, cautiously at first and subsequently with a stronger flame. A high temperature is necessary to drive off the last traces of water. If solutions containing aluminium in presence of sulphuric acid be precipitated, a portion of the acid is carried down with the hydroxide, and must be removed by ignition before the blowpipe. The fact must be especially held in mind that the presence of organic substances impedes a correct determination of aluminium. The organic acids, sugar, etc., may be destroyed by evaporation to dryness and fusion of the residue with potassium nitrate and sodium carbonate in a platinum crucible. The fusion product is then extracted with water and hydrochloric acid, the solution filtered, and the filtrate precipitated by ammonia. Pieces of filter paper are destroyed by chlorine; the solution is acidified with hydrochloric acid, heated, and a few pieces of potassium chlorate added. When the oxidation is complete, the solution is boiled (to remove the excess of chlorine) and then precipitated by ammonia.

Chromium is also estimated by precipitation with ammonia. The reaction is brought about in a porcelain or platinum dish on the water-bath, and the heat kept up until the solution has entirely lost its colour. The precipitate is washed and ignited in the same manner as aluminium hydroxide.

To determine *Iron*, the solution is precipitated with an excess of ammonia, heated nearly to its boiling-point, and filtered directly. If the solution contained ammonium chloride, as is almost invariably the case, the precipitate must be very thoroughly washed. When ferric oxide is ignited in presence of ammonium chloride, ferric chloride forms, and as this salt is volatile it may result in a loss of substance.

Estimation of chromium in chromic acid and chromates.—Chromium in chromic acid is determined either (1) by precipitation as a suitable chromate, or (2) by reduction of the acid to chromic oxide. 1. The neutral solution of a chromate (or if acid, after neutralisation; preferably after the addition of sodium acetate) is precipitated by barium nitrate. The barium chromate obtained is then dried and very cautiously ignited. Mercurous nitrate is a still better precipitant, the solution having been neutralised with nitric acid, if necessary, before the addition of the reagent. The precipitate is washed with a dilute solution of mercurous nitrate and ignited, the ignition yielding chromic oxide, which is then weighed. 2. The chromate solution is treated with hydrochloric acid and alcohol and boiled; the boiling must be continued, after the reduction has ceased, until all the alcohol is removed, and chromic hydroxide is then precipitated with ammonia as above.

§ **122.** II. **Separations.** A. *The metals of Group III. Div.* 1.—(*a*) *Chromium* from iron and aluminium. When these three metals are present together the first operation is to separate the chromium, by its oxidation to chromic acid with sodium carbonate and potassium nitrate (1 part KNO_3, 3 parts Na_2CO_3). Eight parts of the mixture are taken for every one of chromic oxide present, and the whole ignited in a crucible (one of platinum can be used) until the greater portion of the potassium nitrate is decomposed, and the mass has ceased to effervesce, and is in a state of quiet fusion. The product is then extracted with boiling water. The alkali chromates go into solution, and ferric oxide is left as a residue. If aluminium is to be separated by this method, it must be observed that a large quantity of its oxide will be found in the solution as an aluminate. To recover it, the fused mass is washed into a porcelain dish with hot water, potassium chlorate added, and the solution neutralised by hydrochloric acid, an excess of the latter being avoided. It is then evaporated to the consistency of syrup, potassium chlorate being added from time to time during the operation, until all the hydrochloric acid has been decomposed. Aluminium hydroxide is then precipitated by ammonia or ammonium carbonate, and filtered; the chromic acid is found in the filtrate.

The conversion of chromic oxide to chromic acid is also employed in the separation of chromium from the metals of both the second and third divisions of Group III., but in this case involves certain extra conditions. The oxides of all the metals except chromium are left as a residue, and the solution contains only the alkali chromates. In the separation from manganese the fusion products, after treatment with hot water, are heated for some time with alcohol, which decomposes the manganate formed, and precipitates it as manganese dioxide. This method cannot be directly employed in the analysis of chrome-iron ore. The mineral is first fused with borax or acid potassium sulphate, and finally with potassium nitrate and sodium carbonate. Potassium chlorate is to be preferred to the nitrate as the oxidising agent, although the operation demands greater caution. It is performed in the same manner. The separation of chromium can also be effected by oxidation of its solution. Wöhler proposes to separate it from aluminium by treating the solution of the two oxides in caustic potash with chlorine, decomposing the hypochlorate formed by heating with hydrochloric acid, and precipitating aluminium hydroxide with ammonia. In certain instances it becomes convenient to effect the oxidation by means of potassium chlorate and nitric acid. The substance (chromic oxide, chrome-iron ore) is mixed with a small quantity of potassium chlorate, and heated in a porcelain casserole on the water-bath with 50 c.c. of nitric acid (sp. gr. 1·37). The casserole should be covered by a glass funnel. The addition of a second quantity of potassium chlorate may be necessary. A still simpler method of oxidising chromic oxide to the acid is to neutralise the acid solution, add an excess of sodium acetate and bromine, and warm the mixture. The neutrality of the solution must be maintained by the occasional addition of sodium carbonate. Ferric and aluminium hydroxides are precipitated, and the chromate is obtained in solution (Gibbs).

(*b*) *Separation of iron from aluminium.*—The separation of these two metals involves great difficulties. The gravimetric methods are almost all circuitous, and give no trustworthy results. The most accurate method consists in the volumetric estimation of the iron, after the combined weight of the two oxides has been ascertained. Aluminium is then found from the difference.

1. *Separation with potassium hydroxide.*—The neutralised solution of aluminium and ferric chlorides is added to the boiling caustic potash solution in a silver dish, the operation being accompanied by continual stirring. Ferric hydroxide is precipitated. It is determined after being dissolved in hydrochloric acid and again thrown down by ammonia. The aluminium is precipitated from the alkaline solution, the organic substances having first been decomposed. This method may be modified as follows. The ferric salt is partly reduced by sulphurous acid, and the solution boiled with caustic potash, whereupon the iron separates as the black, magnetic, ferro-ferric oxide. To separate aluminium from nickel and cobalt, the oxides are fused with potassium oxide in a silver crucible.

2. *Separation with sodium thiosulphate.*—The hydrochloric acid solution of iron and aluminium is neutralised with sodium carbonate, and then diluted with water until five hundred parts of the solution contain only one part of the oxides. The cold solution is treated with an excess of sodium thiosulphate and boiled, until the sulphurous acid has entirely escaped. The precipitate of aluminium hydroxide and sulphur is easily washed. The sulphur is removed by ignition, after the precipitate has been dried. The filtrate must next be concentrated by evaporation, and again treated with sodium thiosulphate, to ascertain whether all the aluminium has been removed. The method (Chancel) does not ensure the complete precipitation of the aluminium, and the necessary conditions have not yet been thoroughly studied. If the separation was not complete on the first precipitation, the analysis may be considered worthless, for in this case the aluminium cannot all be obtained by the second or even the third addition of sodium thiosulphate. The iron is determined by precipitation from the acidified solution with ammonia.

B. *Separation of the metals of Division* 1 *from those of Divisions* 2 *and* 3 (manganese, zinc, nickel, and cobalt).—Only the methods which are based upon characteristic compounds of Division 1 will be considered.

General methods. (For the use of general and special methods, see § 119.) 1. *The action of barium carbonate.*—The reaction is brought about under the conditions explained in § 28. If nickel is to be separated, the solution must contain ammonium chloride. Cobalt cannot be accurately separated by this method.

2. *With tartaric acid and ammonium sulphide.*—Tartaric acid is added to the solution, and the latter then precipitated by ammonium sulphide. The conditions are discussed in the separations of the following Division. Operations with ammonium sulphide are so disagreeable, however, that this method is seldom employed.

Special methods.—*Chromium* is separated, as explained in § 122, by its oxidation to chromic acid. *Iron* and *aluminium* are isolated as their basic acetates, formates, or succinates. The solution is neutralised, if acid, with sodium carbonate until it becomes turbid. It is then treated with sodium acetate in fair but not too great an excess, and the red liquid which results is boiled for a few minutes until the precipitate has thoroughly coagulated. The latter is washed, first by decantation, finally on the filter, with hot water which contains a small quantity of ammonium acetate. On ignition of the precipitate aluminium oxide and ferric oxide are left. The metals of Divisions 2 and 3 remain in the filtrate (precautions, § 124). The basic formates are in all respects analogous to the acetates, and are to be preferred, as they can be much more easily washed. If the succinates are employed, the solution must be neutralised with ammonia, the precipitate which forms being redissolved by heat. As soon as the latter has become permanent, and the liquid has a deep red-brown colour, a solution of ammonium succinate is added, and the mixture allowed to cool. The precipitate is then filtered and washed, with cold water at first, and subsequently with warm ammonia to remove the succinic acid. Ferric oxide and aluminium oxide are obtained on ignition of the precipitate. Aluminium, if alone, can also be separated by means of potassium hydroxide (see above A).

C. *Separation of the metals of Division* 1 *from those of Group II.*—Since chromium can be separated by oxidation to chromic acid (§ 122 *a*), and barium and strontium as their sulphates (§ 118), the question becomes limited to the separation of aluminium and iron from magnesium and calcium. The general methods employed for this purpose are: the action of barium carbonate (§ 28 *a*); precipitation with ammonia (§ 121 *a*); with ammonium sulphide; or as succinates (§ 122 *c*). All of these methods have already been described. The following are to be particularly recommended.

1. *Separation with tartaric acid and ammonia.*—Tartaric or citric acid is added to the solution, and the latter diluted and saturated with ammonia. Calcium oxalate is then precipitated by ammonium oxalate, filtered, washed, and the magnesium thrown down from the filtrate as ammonium magnesium phosphate. To determine the magnesium the latter precipitate must be redissolved in hydrochloric acid and again precipitated by neutralisation with ammonia (§ 120). The filtrate, containing the iron and aluminium salts (in absence of magnesium), is evaporated to dryness, and, after the addition of sodium carbonate and potassium nitrate, the residue is ignited. It is then dissolved in hydrochloric acid, and aluminium and iron precipitated as hydroxides by ammonia.

2. *The stability of the nitrates of magnesium and calcium*, and the instability of the corresponding aluminium and ferric salts, affords a very accurate method of separation (Deville). The solution of the nitrates is evaporated to dryness and the residue heated to 250° C. in an air-bath. The heat is maintained until no fumes of ammonium nitrate are formed about a rod moistened with ammonia and held over the dish. Magnesium nitrate also loses a small portion of its nitric acid, and the residue is therefore heated again, this time with ammonium nitrate, to reconvert the magnesium into its neutral nitrate. On extraction with water, magnesium and calcium nitrates go into solution, while ferric and aluminium oxides are left undissolved.

D. *Separation of the metals of Group III., Division* 1, *from the alkali metals.*—This can be effected either by precipitation with ammonia (§ 121 *a*), or by heating the nitrates to 250° C. Ammonium salts are driven off by ignition (§ 116). In estimating ammonia from the difference, however, chlorides must be absent (as aluminium chloride, which is volatile, may otherwise form). Ammonia can also be determined in a separate portion (§ 116).

MANGANESE, ZINC, AND FERROUS IRON

In gravimetric analysis the ferrous compounds are converted to the ferric state (for the estimation of iron as its oxide, see § 121 *a*). We shall therefore consider only the determination of iron as ferrous sulphide and the separation of ferrous from ferric compounds.

§ **123. I. Determination.**—Zinc and manganese are weighed almost invariably as zinc oxide and mangano-manganic oxide respectively, the latter being obtained from manganous carbonate, or, as will be explained in the paragraph on the separations, from one of the higher oxides. In separations, and in general when the sulphides are employed, the determinations are made as the anhydrous sulphides. Both methods are accurate.

Determination as oxides.—Organic acids and ammonium salts hinder complete precipitation. If the latter are present they may be removed by boiling the solution with sodium carbonate. The boiling, very slightly acid solution is precipitated by sodium carbonate, the reagent being added drop by drop. The vessel in which the precipitation is performed (preferably a large platinum dish) must be covered with a watch-glass. As soon as the reaction is complete, the solution is boiled for a few minutes, decanted through a filter, and the precipitate again treated with boiling water and decanted. This operation is repeated several times, and the washing finally completed on the filter. A few drops of ammonium sulphide should be added to the filtrate, to ascertain whether the precipitation was thorough. The carbonate obtained is ignited, the filter paper being burned alone. The further processes of the method vary for the two metals. In the determination of manganese the precipitation is incomplete, and the filtrate must therefore be evaporated to dryness, extracted with water, and the slight quantity of mangano-manganic oxide which remains collected on a small filter. The two precipitates are ignited together at as strong a heat as possible and under complete exposure to the air, and the ignition continued until two consecutive weighings give the same results. Mangano-manganic oxide, Mn_3O_4, is thus obtained. It must then be repeatedly extracted with water (as it probably contains alkali salts), transferred to a small filter, the latter burned, and the residue ignited and weighed. On ignition of zinc carbonate anhydrous zinc oxide (which is yellow while hot) is formed. The filter is moistened with a concentrated solution of ammonium nitrate, dried, and burned. The above method of determining manganese may be modified as follows. The neutral or slightly acid solution of manganous chloride is precipitated by a slight excess of ammonium carbonate in presence of a large quantity of ammonium chloride, and allowed to stand for twelve hours in a warm spot. The precipitate is then brought upon a double filter, washed, and ignited. The method is accurate, but not always applicable.

Estimation as anhydrous sulphides.—This method may also be employed for the determination of iron. *Precipitation with ammonium sulphide:* The solution, neutralised by ammonia, if acid, is precipitated by yellow ammonium sulphide in presence of ammonium chloride (an excess of ammonia or ammonium chloride, and also of organic acids, such as tartaric and oxalic, is to be avoided). The operation is performed in a flask which, after the precipitation, is completely filled with water, closed by a cork, and set aside for twenty-four hours. During the filtration and washing (with ammonium sulphide water) the precipitate must be exposed to the air as little as possible, and while on the filter must be continually covered by water. The funnel should be covered by a glass plate. (If this method is to be supplemented by the first, the moist sulphides are placed in a beaker together with the filter, dissolved in dilute hydrochloric acid, and precipitated with sodium carbonate.) According to Ribau, zinc sulphide can also be precipitated by hydrogen sulphide, if the gas be led into the slightly acid zinc solution after the addition of some sodium thiosulphate. *Determination as anhydrous sulphides* (Rose's method): For this purpose a porcelain crucible is employed, the cover of which has an opening fitted with a porcelain tube for the introduction of a current of dry hydrogen. The dried hydrated sulphides are placed in the crucible, together with the ash of the filter. and covered with a layer of powdered sulphur. Hydrogen is then led into the crucible, and the latter ignited, at first gently, but subsequently with a strong flame. The crucible is allowed to cool in the stream of hydrogen, weighed, and again ignited as before, until the weight remains constant. Instead of the hydrated sulphides, the oxides or carbonates of manganese and zinc can also be converted to the anhydrous sulphides, the treatment being the same as in the foregoing case. The ignition with sulphur must be repeated until a constant weight is obtained. The sulphides have the formulae, MnS, ZnS, and FeS. The sulphur employed should be tested to see whether it leaves a residue on combustion.

Determination of manganese and zinc by electrolysis.—Manganese is precipitated from the solution of its sulphate as the peroxide, which collects at the positive electrode. The solution is contained in a platinum crucible which serves as the positive pole, and for the negative a platinum spiral is suspended in the liquid. The solution is then warmed to 60°-70° C., and an electric current (from 1-2 Bunsen's couples) allowed to pass through it. When the precipitation is complete, the solution is poured off, and the residual manganese dioxide washed, ignited, and weighed as mangano-manganic oxide. To determine zinc, a solution of the double cyanide of zinc and potassium is subjected to the current produced by four Bunsen's couples. The zinc deposits upon a small platinum cone which is employed as the negative pole. When the reaction is finished, the electrode is taken from the liquid, rinsed with water, alcohol, and, finally, ether, and placed in an exsiccator to dry. After being weighed, the zinc is dissolved in hydrochloric acid and the cone weighed again (see Examples of Gravimetric Analysis).

§ **124.** II. **Separations.** (*a*) *Metals of Group III., Division* 2. *Manganese from zinc.*—For the separation of manganese from zinc, either the insolubility of zinc sulphide in acetic acid or the property which manganese possesses of forming higher oxides (zinc has only one degree of oxidation) may be employed. The first method is much simpler than the second, and very accurate. By *means of zinc sulphide:* The solution, in which the metals should be present as acetates if possible (the acetates are obtained in analysis by the double decomposition of the sulphates with barium acetate) is precipitated by hydrogen sulphide in presence of free acetic acid. The zinc is then determined as in § 123. Manganese is determined in the filtrate according to § 123, after the excess of barium has been removed by sulphuric acid. Instead of acetic acid and acetates, formic acid and the formates may be used, and Ribau's method (§ 123) is also applicable. *By the action of bromine:* The solution is made slightly alkaline by sodium carbonate, the precipitate dissolved in acetic acid, sodium acetate added, and the liquid treated with bromine at 70° C. until it has attained a slightly reddish tint. A few drops of alcohol are then added and the manganese dioxide filtered off. The precipitate obtained is not directly ignited, but dissolved in hydrochloric acid and the manganese determined according to § 123. Zinc is estimated in the filtrate from the manganese dioxide, according to § 123 (the bromine must first be removed).

Separation of iron from manganese and zinc; see below, *c.*

(*b*) *Separation of ferrous oxide from ferric oxide.*—The quantitative separation of ferrous from ferric oxide cannot be satisfactorily performed by gravimetric means alone. The chief difficulty consists in the impossibility of preventing the ferrous salt from becoming oxidised by the air during the operations. All the iron in the solution is determined by the usual method (oxidation and precipitation with ammonia § 121), and that which is in the ferrous or the ferric condition is then found in a separate portion of the original substance. The difference between the two results is the iron present as the remaining oxide.

Method of determining ferric oxide.—The solution is treated with barium carbonate as in § 28 *a.* The precipitate must be washed with water from which the air has been expelled by boiling, and which has been cooled off in a closed flask. It is then dissolved in hydrochloric acid, the barium removed, and ferric hydroxide precipitated by ammonia, ignited, and weighed (§ 121).

The methods of determining ferrous oxide are based upon the conversion of ferrous to ferric salts. The volumetric methods for its estimation are more accurate than the gravimetric, and require far less time. If the double salt, $KCl . AuCl_3$, be used as the oxidising agent (auric chloride, $AuCl_3$, is not employed, as it usually contains $AuCl$), the gold deposited is weighed, and the quantity of ferrous oxide calculated from the results. Bunsen recommends the estimation of the chlorine necessary for the oxidation of the ferrous salt. A certain quantity of potassium dichromate is weighed off, mixed with the hydrochloric acid solution of the substance to be analysed, and the amount of liberated chlorine estimated. This value is less than that which corresponds to the potassium dichromate taken, and the difference equals the quantity of ferrous oxide present. To estimate the ferrous and ferric oxides in a compound which is insoluble in water, the substance is fused with borax, dissolved in water, and the determinations made by one of the above methods. A still more accurate method has recently been proposed, which involves the decomposition of the insoluble substance with hydrofluoric acid and dilute sulphuric acid in an atmosphere of carbon dioxide. This method may be modified for the determination of ferrous iron in silicates as follows. The silicate is mixed with fluor spar or cryolite (which must be free from iron) and strong hydrochloric acid is then added until the crucible is two-thirds full. The mixture is then heated on the water-bath, and the resulting solution titrated with potassium permanganate.

(*c*) *Zinc and manganese from the metals of Group III., Division* 1 (aluminium chromium iron).—Since to separate ferrous compounds we always convert them to the ferric state, the separation of iron from manganese and zinc will be discussed in connection with that of Division 1. Ferrous iron is usually oxidised by heating with hydrochloric acid and adding a few pieces of potassium chlorate, $KClO_3$, to the hot solution, until the latter retains the odour of chlorine even after being heated for some time. The ferrous solution may also be saturated with chlorine (when in small quantities, by bromine-water or chlorine-water). If the presence of chlorine would be troublesome in the subsequent treatment of the solution, it can be removed by boiling. If nitric acid be employed as the oxidising agent, the ferrous solution is boiled with a small quantity of the acid (in presence of free hydrochloric) until it assumes a yellowish-brown colour. Other methods of oxidation (as with manganese dioxide, comp. Tin) are rarely used.

We now pass to the various methods of separating the metals of Division 1 from manganese and zinc. *The general method* is based upon the reaction with barium carbonate;

conditions, § 28 *a*. *The special methods* are, as usual, more exact. Chromium is separated through its oxidation to chromic acid (§ 122 *a*); iron and aluminium, as basic acetates, formates, or succinates (§ 122). The filtrate is evaporated, the ammonium salts removed, and the residual zinc and manganese then determined. Ferrous iron must be oxidised before these methods can be employed, the oxidation being effected most advantageously with chlorine. Nitric acid is not applicable, as, unless it be removed by boiling with hydrochloric acid, detonation may occur during the removal of the ammonium salts (due to the action of the nitrates upon the acetates). The foregoing methods may be recommended. Less accuracy is attained when zinc is separated by precipitation as zinc sulphide from its acetate in presence of acetic acid, or when manganese is thrown down through the action of chlorine or bromine. Both of these methods are explained in § 124 *a*. Beilstein suggests that manganese be separated from iron as follows. The solution is neutralised, treated with a concentrated solution of potassium cyanide (in the cold), and iodine is then added until the solution becomes brown. The manganese is thus deposited as its dioxide:

$$K_2MnCy_4 + 10I + 2H_2O = MnO_2 + 4HI + 2KI + 4CyI.$$

Another method consists in dissolving the manganese and iron compounds in nitric acid and treating the boiling solution with potassium chlorate. This precipitates the manganese as its dioxide, which may be determined volumetrically (by Bunsen's method; see Section II. Halogens). Volhard treats the solution with zinc oxide, which throws down the iron, the manganese being determined volumetrically as above.

(*d*) *Zinc and manganese from Groups I. and II. General methods.*—The manganese and zinc are precipitated as their sulphides by ammonium sulphide, under the conditions given in § 123. *Special methods:* Barium, strontium, and calcium are separated by precipitation with sulphuric acid (strontium and calcium from the solution of the chlorides in presence of alcohol), according to § 118. Magnesium and the alkali metals are separated from manganese by Deville's method of heating their nitrates to 250° C. (§ 122 C.), or by oxidising the manganese with chlorine (§ 124 *a*). The separation of zinc from these metals is effected by its precipitation as zinc sulphide (§ 124 *a*). If the metals of Group II. are absent, and manganese and zinc alone are to be determined (the alkalies neglected), direct precipitation with an alkali carbonate may be employed (§ 123). Ammonium is estimated in a separate portion of the substance, according to § 116.

NICKEL AND COBALT

§ **125.** I. **Determination.**—In the quantitative estimation of nickel and cobalt it must be remembered that non-volatile organic acids prevent complete precipitation. They cannot be determined as their anhydrous sulphides, since these compounds are irregular in their composition. Nickel may be very advantageously determined by electrolysis.

Nickel.—Nickel is almost invariably weighed as its monoxide, NiO. The solution is precipitated by an excess of potassium hydroxide (or by a dilute solution of sodium carbonate), and heated to boiling. The precipitate is first washed three or four times by decantation, being boiled up at each washing. A platinum dish is to be preferred for the precipitation. The nickelous hydroxide obtained is dried and ignited. It frequently happens in separations that nickel must be precipitated as the sulphide. This is accomplished with ammonium sulphide, under the conditions in § 123. The reagent must be completely saturated with hydrogen sulphide, and the precipitation performed in presence of a large excess of ammonium chloride. The precipitate is collected (the precautions mentioned in § 123 must be observed), dried, ignited, and dissolved in *aqua regia*, in a beaker. The ash of the filter must be added to the solution. The solution is then precipitated with potassium hydroxide, and the nickel determined as nickelous oxide.

The determination of nickel by electrolysis is similar to that of zinc (§ 123). An ammoniacal solution of the nitrate is employed, and the weighing of the nickel deposited is performed exactly like that of the zinc. The details of the analysis are given among the examples of gravimetric analysis.

The estimation of cobalt is performed in a different manner from that of nickel.

1. *The determination as metallic cobalt* is the most accurate method. The compound is reduced in a stream of hydrogen. Alkalies and difficultly volatile acids, such as sulphuric, must be absent. If the cobalt is in the form of nitrate or chloride, its solution is evaporated to dryness in a platinum or porcelain crucible, into the cover of which is fitted a tube for the introduction of the hydrogen stream (Rose's crucible, § 123). A very gentle heat is at first applied, but must subsequently be increased, to render the metallic cobalt non-pyrophoric. The reduction may be assumed to be complete when the weight has remained unchanged after two consecutive weighings. In presence of alkalies the following operations are necessary. The cobalt solution is heated nearly to boiling in a platinum dish, potassium hydroxide added in slight excess, and the heat continued until the precipitate is dark-brown or almost black. It is washed, first by decantation and finally on the filter, with boiling water. The dried precipitate is then reduced with hydrogen as above.

2. *As sulphate.*—It is often necessary to precipitate cobalt as the sulphide before its determination, the precipitation being effected in exactly the same manner as that of nickel sulphide. In such cases it is most convenient to weigh the cobalt as its sulphate. The solution of the sulphide in *aqua regia*, prepared like that of the nickel salt, is evaporated with an excess of sulphuric acid until the hydrochloric and nitric acids are entirely removed. The solution is then poured into a platinum crucible, evaporated to dryness, and very cautiously ignited until sulphuric acid fumes cease to escape. The flame must be held against the upper half of the crucible. The cobalt sulphate which remains is then weighed. A second weighing is necessary to assure the complete removal of the sulphuric acid. The cobalt in salts of volatile acids can also be determined as the sulphate.

3. *By precipitation as potassium cobalt nitrite.*—This method is accurate, and generally applicable. The cobalt solution should not be too dilute (300 parts water to 1 of the cobalt salt), and, if acid, must first be neutralised by potassium hydroxide. The latter is added in slight excess, the resulting precipitate redissolved in acetic acid, and the liquid then mixed with a concentrated solution of potassium nitrite, which

has been slightly acidified with acetic acid. The beaker is then allowed to stand in a warm place for 12-24 hours. The precipitate should be washed at first with a solution of potassium acetate (1 : 10). It is finally dissolved in hydrochloric acid, and the cobalt determined by precipitation with potassium hydroxide, as in 1.

§ **126.** II. (*a*) *Nickel and cobalt.*—1. The separation of cobalt from nickel as *potassium cobaltic nitrite.* The solution is first concentrated (if necessary) by evaporation, and neutralised with potassium hydroxide. The precipitation is effected as above. Its completeness can be ascertained only by a confirmatory test, and barium, strontium, and calcium must be absent, as these metals form insoluble double salts with nickel nitrite, such as $NiSr(NO_2)_4$. The nickel may be estimated either by the difference, or by precipitation from the filtrate of the double nitrite with potassium hydroxide. 2. *Separation by means of the double cyanides:* The solution, neutralised if necessary, is stirred with a concentrated solution of *pure* potassium cyanide (or potassium hydroxide and hydrocyanic acid) until the precipitate which at first forms is redissolved. The mixture is then treated with bromine, with occasional addition of potassium hydroxide. Nickel separates as the black nickelic hydroxide, and, after filtration, is dissolved in hydrochloric acid, and reprecipitated as in § 125. Cobalt is most simply determined by the difference. 3. Nickel may be very accurately separated from cobalt by the use of nitroso-β-napthol (Ilinski, *Berichte d. deutschen chem. Gesellschaft*, vol. xviii., p. 699).

(*b*) *Cobalt and nickel from the metals of Group III., Division* 2 (manganese and zinc).—*The general methods*, which are based upon the insolubility of cobalt and nickel sulphides in dilute hydrochloric acid, and upon the reduction of cobaltous and nickelous oxides with hydrogen, afford only an inexact separation of these metals from zinc. *The special methods* are much more accurate, especially that of separating *cobalt as its double salt with potassium nitrite.* The method has been described in *a*, and serves for the separation of cobalt from nickel, zinc, and manganese, but only when barium, strontium, calcium, and lead are absent. Cobalt can also be separated from manganese and zinc by means of the double cyanides.

The solution is treated with pure potassium cyanide until the precipitate redissolves, a few drops of hydrochloric acid are added, and the mixture then boiled. Zinc cobaltocyanide is next precipitated by hydrochloric acid, the solution boiled until free from hydrocyanic acid, the precipitate dissolved in caustic potash, and zinc thrown down by hydrogen sulphide. The cobalt is best determined by the difference. *Nickel from zinc:* In Wöhler's method, the solution is treated with an excess of freshly-prepared potassium cyanide (or potassium hydroxide and hydrocyanic acid), and then precipitated with potassium sulphide. Zinc sulphide is thus obtained, and is filtered off and weighed. The filtrate, containing the nickel, is then treated with potassium chlorate and hydrochloric acid, and nickelic hydroxide precipitated with caustic potash. Wöhler's method is less convenient than that of Schmitt and Brunner. In the latter the hydrochloric or nitric acid solution is nearly neutralised with potassium carbonate (it must remain slightly acid), and subjected to the action of hydrogen sulphide. When the separation of the precipitate has ceased, a few drops of sodium acetate solution are added, and hydrogen sulphide again led into the solution. After standing for twelve hours the zinc sulphide is filtered off, washed with hydrogen sulphide water, and the zinc estimated as zinc sulphide (§ 123). The hydrogen sulphide is then removed from the filtrate by boiling, and the nickel precipitated with potassium hydroxide. A method proposed by Beilstein consists in precipitation of the solution with ammonia, solution of the precipitate in citric acid, and treatment of the liquid with hydrogen sulphide. Zinc separates as its sulphide, and nickel is determined in the filtrate by electrolysis. *Nickel and cobalt* may be separated *from manganese* as follows. The solution is first precipitated with caustic potash, and the hydroxides washed, and ignited, in a bulb tube, in a stream of hydrochloric acid gas. The chlorides which thus form are next reduced with hydrogen in the same tube. Manganous chloride, which remains unaffected, is then extracted with water. Manganese can be separated from nickel by one of the methods based upon the formation of higher degrees of oxidation of manganese, of which nickel is incapable. For this purpose the solution may be treated with lead dioxide, or chlorine, in presence of an excess of acetic acid, or with chlorine in aqueous solution. In the last method, the manganic hydroxide is precipitated by barium carbonate. The conditions are explained in § 124 *a.*

(*c*) *Cobalt and nickel from Group III., Division* 1 (aluminium, chromium, iron). It is preferable to use special separations, though the general methods already described may also be employed, *e.g.*, precipitation with ammonium sulphide in presence of tartaric acid. Iron and aluminium are most conveniently separated as their succinates or basic acetates (§ 122). Iron, especially if its quantity be small in proportion to that of nickel and cobalt, can be precipitated by ammonia in presence of ammonium chloride, the nickel and cobalt remaining in solution. Chromium is best separated by its oxidation to chromic acid (§ 122).

(*d*) *Cobalt and nickel from the metals of Groups I. and II.*—The reduction of the chlorides by hydrogen, or, if possible, methods based upon the properties of the metals of Groups I. and II. are employed.

GROUP IV

SILVER, MERCURY, COPPER, CADMIUM, LEAD, AND BISMUTH

§ **127.** I. **Determination.** (*a*) *Silver.*—Silver enters into several compounds suitable for its estimation. It is most frequently weighed as silver chloride (an exceptionally accurate method). When this method is unavailable, the determination may be made as metallic silver, or more rarely as the sulphide or cyanide (as the latter only in separations).

As silver chloride.—The solution is heated to 70° C., and precipitated by a slight excess of hydrochloric acid in presence of nitric acid. To make the precipitate coagulate, the solution must be rapidly stirred or shaken in a stoppered flask. It is then set aside in a dark place for twelve hours, and the supernatant liquor finally decanted through a filter. The precipitate remaining in the flask is washed two or three times with hot water which contains nitric acid, brought on the filter, and washed, first with water and nitric acid, finally with hot water alone. The filter is next dried, separated as completely as possible from the precipitate, and the latter gently ignited to incipient fusion in a porcelain crucible and weighed. The filter is burned by itself, its ash placed in the crucible, and the latter again weighed. The difference gives the amount of metallic silver reduced on ignition of the filter. This value is calculated to silver chloride, and the result added to the weight first obtained. The metallic silver obtained by combustion of the filter can also be converted to the chloride. For this purpose the ash is laid on the cover of the crucible, carefully dissolved in nitric acid, and reprecipitated by a drop or two of hydrochloric acid. It is then cautiously evaporated to dryness and fused. By this method the entire quantity of silver chloride is ascertained in one weighing.

As silver sulphide.—The solution is precipitated with hydrogen sulphide or hydrogen sulphide water. The precipitate is allowed to subside in a closed flask, and finally collected on a weighed filter, dried at 100° C., and weighed. This method is usually employed only in separations. If substances were present which decompose hydrogen sulphide, the precipitate contains free sulphur, and requires purification; either by ignition in a stream of hydrogen (Rose's method) and determination as metallic silver, or as follows. The precipitate is carefully rinsed from the weighed filter into a porcelain dish, warmed with a concentrated solution of sodium thiosulphate, and again brought upon the same filter, which has been re-dried as thoroughly as possible in the meantime. The sulphide may also be dissolved in nitric acid, and the silver estimated as chloride.

As silver cyanide.—The solution is acidified with nitric acid and precipitated with potassium cyanide. The silver cyanide thrown down is then dissolved in an excess of the reagent, reprecipitated by a slight excess of nitric acid at a gentle heat, and collected on a weighed filter. It is then dried at 100° C., and weighed.

As metallic silver.—The method can be used for the estimation of the silver in compounds with volatile acids and in those which decompose on ignition (salts of organic acids, carbonate, oxide, etc.) The compound is cautiously heated in a porcelain crucible and the residual silver weighed (when obtained from organic salts, only after the carbon has been completely destroyed). The silver in compounds which readily undergo reduction in a stream of hydrogen may also be weighed in the metallic state. The method, as we have already said, can be used in connection with the precipitation of silver as the sulphide, and is also applicable to the analysis of the chloride, iodide, and bromide. The operation may be performed either in a Rose's crucible or in a bulb-tube of difficultly fusible glass. It must be continued until the weight remains constant.

(*b*) *Determination of mercury.*—Mercury is generally estimated as its sulphide, or as mercurous chloride. Both methods are exact, and applicable to either mercurous or mercuric compounds. If the chloride is to be precipitated, the mercuric salts must be reduced (see below); if the sulphide, the lower compounds must be oxidised by gently heating with nitric and hydrochloric acids. It must be remembered that if mercury solutions which contain hydrochloric acid be evaporated, mercuric chloride, $HgCl_2$, will volatilise. The determination as mercuric oxide or metallic mercury is less accurate.

As mercurous chloride.—*Mercurous* solutions are sufficiently diluted with water, and the chloride precipitated with sodium chloride. The precipitate is then collected upon a weighed filter, dried at 100° C., and weighed. Insoluble mercurous compounds are dissolved in cold dilute nitric acid, and the solution neutralised by sodium carbonate before the precipitation. *Mercuric* salts are treated with hydrochloric acid (nitric acid does not prevent the reaction) and a solution of phosphorous acid or, more simply, water in which phosphorus has been standing for some time. The liquid is then set aside for twelve hours. The mercurous chloride separates in the crystalline condition, and is finally collected upon a weighed filter, dried at 100° C., and weighed.

As mercuric sulphide.—The method is simple and accurate. The slightly acid solution is treated with hydrogen sulphide or a freshly prepared solution of the gas, and, as soon as it has subsided, the precipitate is collected upon a weighed filter. It is then washed with cold water, dried at 100° C., and weighed. If the precipitate contain free sulphur it may be purified in the same manner as silver; or, after being washed with water and subsequently with absolute alcohol, it may be treated on the filter with carbon disulphide (until a drop of the filtrate leaves no residue on evaporation).

(*c*) *Determination of copper.*—Copper is weighed either as cupric oxide, cuprous sulphide, or the metal. All three methods are exact and convenient if the necessary precautions be observed. The determination as cuprous sulphide is usually employed in separations. When non-volatile organic acids are present, copper cannot be estimated by precipitation as its hydroxide.

As cupric oxide.—The dilute solution is heated to boiling in a porcelain or platinum dish and treated with sodium hydroxide, the reagent being gradually added until precipitation ceases. The solution is then heated to incipient boiling again, and as soon as the precipitate has turned black, it is allowed to settle (which it does quickly), and immediately filtered. The supernatant liquid is decanted off, and the precipitate in the bottom of the dish repeatedly treated with boiling water. It is finally transferred to the filter and washed with hot water. If the removal of all the cupric hydroxide from the sides of the dish is impossible, the particles which remain may be dissolved in nitric acid and the solution poured into the crucible to which the precipitate has been transferred. The whole is then evaporated to dryness and ignited. The ignition (in a platinum crucible) must be very strong, and the filter burned separately. The requisites for an exact determination are: a dilute solution, thorough washing of the precipitate, non-reduction to metallic copper during the ignition, and finally, the cooling of the crucible in an exsiccator. The filtrate from the precipitate must also be tested with hydrogen sulphide, to ascertain whether the precipitation was complete. After being weighed, the cupric oxide is tested for the possible presence of silica (if the analysis was made in a porcelain dish) by solution in hydrochloric acid.

As cuprous sulphide.—The neutral or slightly acid solution, which must contain very little or no nitric acid, is heated to 80° C. and while at that temperature treated with hydrogen sulphide or its aqueous solution. The precipitate is filtered off as soon as it has subsided, washed with hydrogen sulphide water, and dried quickly. It is brought into a state fit for weighing by Rose's method of igniting the precipitate and filter ash with sulphur in a stream of hydrogen. The operation yields cuprous sulphide, Cu_2S. The determination as cuprous sulphide is most frequently resorted to in separations effected by precipitation with sodium thiosulphate or potassium sulphocyanate (see Separations).

As metallic copper.—The determination in this form is both convenient and exact. The solution, free from nitric acid (the nitric acid may be removed, if necessary, by evaporation with sulphuric or hydrochloric acid), is treated in a weighed platinum dish with a few pieces of zinc (which must dissolve in acids without leaving a residue). The evolution of hydrogen must not be too strong. The dish should be covered by a watch-glass; drops of the solution will collect upon the surface of the latter, and must be rinsed back into the dish from time to time. The copper separates, either as a metallic deposit on the sides of the dish or as a spongy red mass. Complete precipitation is effected in from one to two hours. As soon as it has ceased (ascertained by the addition of hydrogen sulphide to a small portion) and the zinc has passed entirely into solution, the copper is washed by decantation with hot water until free from hydrochloric acid. Alcohol is then substituted for water, and the metal is finally dried at 100°. The weight of the platinum dish alone having already been ascertained, the amount of copper is found directly on being weighed. Copper may also be precipitated in the metallic state by other methods, *e.g.*, with a weak galvanic current (see Examples; Determination by electrolysis).

(*d*) *Cadmium* may be determined either as the oxide or, still better, as the sulphide.

As oxide.—The cadmium solution is precipitated by sodium carbonate (in the same manner as zinc; § 123), and the oxide obtained by ignition of the precipitate. The filter is burned separately, and must first be moistened with ammonium nitrate and dried. (Metallic cadmium will otherwise form and volatilise.)

As cadmium sulphide.—The neutral or very slightly acid solution is precipitated by hydrogen sulphide (or sodium sulphide), and the precipitate collected on a weighed filter and dried at 100° C. If the precipitate contains free sulphur, the latter is removed as from silver and mercuric sulphides. The cadmium sulphide may also be dissolved in hydrochloric acid and the cadmium determined as oxide.

(*e*) *Determination of lead.*—Lead is usually weighed as the sulphate. It may also, especially in separations, be determined as sulphide (sometimes as chromate). When existing as a salt of an organic acid it is most frequently determined as lead monoxide.

As lead sulphate.—The fairly concentrated solution is treated with dilute sulphuric acid until the precipitate ceases to form. A volume of alcohol equal to that of the solution is then added, and the mixture allowed to stand for some hours. The precipitate is washed with alcohol, on a weighed filter, care being taken that the sides of the latter are thoroughly washed. It is then dried at 100° C. and weighed. The ignition of the lead sulphate is a more difficult operation. If the circumstances are such that no alcohol can be used, an excess of dilute sulphuric acid may be added, which lessens, but by no means obviates, the error due to the solubility of the salt. Lead salts of volatile acids, the oxides, etc., can be converted to the sulphate by evaporation with sulphuric acid and cautious ignition.

As lead sulphide.—This method is employed more particularly in separations. The precipitation can be made either with hydrogen sulphide (from slightly acid solution) or with ammonium sulphide. The lead sulphide is washed with cold water, and brought into a state suitable for weighing by ignition with sulphur to redness in a Rose's crucible. The composition of lead sulphide is PbS.

As lead oxide.—The precipitation of lead solutions by ammonium carbonate in presence of ammonia, and subsequent conversion of the lead carbonate obtained into the oxide by ignition, is seldom employed, as its accuracy is less than that of other methods. Lead salts of organic acids yield the oxide when ignited, very cautiously at first, in a covered crucible. If the cover be taken off, the contents of the crucible begin to glow, the carbon ignites, and the oxide undergoes reduction to metallic lead. As soon as the crucible has become somewhat cool, therefore, a few pieces of recently-fused ammonium nitrate should be added, and the crucible covered and again ignited. The lead oxide thus obtained is pure and fit for weighing.

(*f*) *Determination of bismuth.*—The most accurate method consists in the precipitation of bismuth oxychloride and weighing as the metal. The determination as sulphide or oxide is less accurate. The latter method may be supplemented by reduction to metallic bismuth.

As oxide.—Hydrochloric and sulphuric acid must be absent, as the corresponding basic salts may otherwise form. The bismuth solution is diluted with water (any precipitate separating may be neglected) and treated with ammonium carbonate. It is then heated for some time almost to boiling, and the precipitate finally filtered off, dried, and ignited.

As sulphide.—The solution is diluted with water, a few drops of acetic acid being added to prevent the formation of basic salts, and is then treated with hydrogen sulphide (aqueous or gaseous) or with ammonium sulphide. The precipitate is allowed to settle, and washed with water containing hydrogen sulphide. It must be filtered through a weighed filter and dried at 100° C. Since it is difficult to prevent oxidation by the air, and consequently, to obtain a constant weight, better results are obtained if the bismuth sulphide be dissolved in nitric acid and the determination made as oxide.

As metallic bismuth.—The oxide may be reduced (the sulphide undergoes reduction less readily); but it is better to employ the oxychloride obtained by precipitation with water. The acid solution is neutralised with potassium hydroxide or ammonia, and sodium chloride added. On dilution with water the oxychloride separates. As soon as the further addition of water produces no more precipitate, the basic salt is allowed to settle and then filtered. It must be washed with cold water and dried at 100° C. As the bismuth oxychloride undergoes partial decomposition during the operation of washing, and has no permanent and definite composition, it must be reduced to the metal before the final determination. The reduction is effected by fusion with five parts of potassium cyanide in a porcelain crucible, the mass being kept in a molten state for some time. On extraction with water metallic bismuth is obtained; it is collected on a filter, washed with water and subsequently with alcohol, dried, and weighed. The filter must be previously dried, and weighed in the crucible to be employed for the reduction. The bismuth must be finally weighed, together with the filter, in the same crucible (this obviates the error which might otherwise be caused by the action of the potassium cyanide upon the crucible). Bismuth oxide is reduced in the same manner.

§ **128.** II. **Separations.** (*a*) Metals of Group IV.—Most of the separations are based upon the same properties as are employed in the determination of the metals, and which have been described in that connection. The various methods of separation will be classified according to these properties. Separations by electrolysis are given in the examples of gravimetric analysis.

Separation of silver.—Silver may be separated from almost all metals as its chloride, under the conditions given in § 127. The separation from mercurous mercury by this method is impossible, and in the presence of lead or mercuric mercury the method is inexact, as the results are effected, in the first instance, by the difficult solubility of lead chloride, and in the second, by the solubility of silver chloride in mercuric nitrate. The error may be lessened by the addition of sodium acetate (which dissolves the lead chloride and makes the silver chloride more sparingly soluble in mercuric nitrate), but it is still preferable to separate the two interfering metals beforehand (see below). In separations from mercury, copper, and cadmium the insolubility of silver cyanide in nitric acid is also employed. The solution (neutralised if acid) is treated with potassium cyanide until the precipitate redissolves, and nitric acid is then added. The silver cyanide thus obtained is determined as in § 127 *a*. Separations from silver which are based on the properties of the other metals will be discussed below.

Separation of mercury.—*Mercurous* compounds are separated (from mercuric mercury, lead, copper, and cadmium) exclusively as mercurous chloride, according to § 127 *b*. *Mercuric* mercury can also be separated (usually from copper and cadmium), as the lower chloride by reduction with phosphorous acid (Rose's method, § 127 *b*). In cases where this method is inapplicable (separation from silver and bismuth), the insolubility of mercuric sulphide in boiling dilute nitric acid is employed. Copper and cadmium may also be separated from mercury by this method. The sulphides are precipitated together, under the conditions explained in § 127 *b*. The chief requisite upon which accuracy depends is the absence of free chlorine. The results obtained by this method in the separation of mercury from lead are not so satisfactory (see separation of bismuth). The volatility of mercuric chloride may be employed for the separation of mercury from silver, lead, and copper (and, in general, all metals the chlorides of which are non-volatile). Hydrogen sulphide is led into the solution (§ 127 *b*), and the precipitate dried at 100° C. and weighed. A portion is then placed in a bulb tube connected with a receiver containing water, and heated in a stream of chlorine. The latter decomposes the sulphides, with formation of the volatile mercuric chloride (and also sulphur chloride), and the non-volatile chlorides of the other metals. The mercuric salt either passes into the receiver or condenses in the posterior portion of the tube, while the non-volatile chlorides remain in the bulb. The mercuric chloride in the tube is then dissolved in water, added to that in the receiver, and the mercury determined according to § 127 *b*.

The separation of lead from mercuric mercury, bismuth, copper, and cadmium is effected by means of its sulphate (§ 127 *e*). When this method is inapplicable, for instance, in presence of mercurous salts, the solution is precipitated with sodium carbonate and then heated for some time with potassium cyanide. The lead carbonate is left undissolved (it cannot be directly weighed, however, as it retains some of the alkali).

Separation of bismuth.—The formation of bismuth oxychloride (§ 127 *f*) permits a very exact separation of this metal from copper and cadmium. The behaviour of bismuth salts toward sodium carbonate and potassium cyanide (comp. separation of lead) is also the basis of accurate separations from mercury, cadmium, and copper (see also the separation of silver, mercury, and lead). In some cases (from cadmium) the insolubility of the chromate and the volatility of bismuth chloride are also resorted to (the operation is the same as in the separation of mercury). The latter method is especially convenient in the analysis of bismuth alloys. Hydrochloric acid is placed in the receiver, and the final determination of the bismuth made by means of its oxychloride. Jannasch and Etz employ an atmosphere of bromine instead of chlorine for the separation of bismuth from lead and cadmium. The details of the method, which gives very satisfactory results, will be found in the *Ber. d. d. chem. Gesellschaft*, xxv. 737.

Separation of copper and cadmium. — The separation of copper from the metals already discussed is usually based upon the properties of the other metals, and not of copper (see separations of silver, mercury, lead, and bismuth). Only those methods in which characteristic reactions of the copper are employed remain to be considered. The separation of bismuth by means of ammonium carbonate, in which the bismuth is precipitated as its carbonate, is inaccurate. Copper can be separated from nearly all metals by means of the ammonium compounds which it forms. When in presence of lead and bismuth, it may be isolated by precipitation with sodium carbonate and treatment of the precipitate with potassium cyanide (see separation of lead). The solubility of cupric sulphide in potassium cyanide yields a method for its separation from silver, mercury, and cadmium. This method is employed almost exclusively, however, for the separation of copper and cadmium. The slightly acid solution (partially neutralised if necessary) is treated with potassium cyanide, and the precipitate dissolved in an excess of the latter. Hydrogen sulphide is then passed through the solution (or ammonium sulphide added). The resulting sulphide of cadmium (silver or mercury) is washed by decantation, and weighed as in § 127 *d*. To determine the copper, the solution is evaporated with sulphuric or nitric acid until the hydrocyanic acid has been removed, and cupric hydroxide or sulphide is then precipitated (§ 127 *c*). Rivot has elaborated a method in which the solution, which must contain neither nitric acid nor free chlorine, is precipitated with potassium sulphocyanate in presence of sulphurous (or phosphorous) acid. The cuprous sulphocyanate which forms is allowed to settle, filtered, and converted to cuprous sulphide (by Rose's method). The cadmium is precipitated from the filtrate as its sulphide (§ 127 *d*). According to Hofmann, the sulphides may be precipitated and boiled with dilute sulphuric acid (1 : 5), in which cadmium sulphide is soluble. The cupric sulphide is then filtered off, and determined according to § 127 *c*.

(*b*) *The separation of the metals of Group IV. from those of Groups I., II., and III.* is always effected by means of characteristic reactions of the metals in Group IV., the methods just described being employed. *A general method* consists in precipitation with hydrogen sulphide, which yields all the metals of Group IV. as sulphides. In the separation from Groups I. and II. by this reaction, the state of the solution is of no importance; in that from Group III., on the contrary, the concentration and acidity must be within certain limits. If the solution be very slightly acid, zinc sulphide may be precipitated, and if it be too strongly acid, cadmium (also lead and other metals) may remain in solution. The acidulation should be effected with hydrochloric acid if possible; if this be inexpedient, and nitric or sulphuric acid be employed, the solution must be highly diluted with water. In the separation of zinc from copper the precipitation must be repeated twice, to obtain the copper sulphide free from zinc. When copper is to be separated from nickel or cobalt a second precipitation is unnecessary if the solution contain a sufficient quantity of hydrochloric acid. In separating cadmium from zinc it is also advisable to repeat the precipitation, the cadmium remaining in solution after treatment with hydrogen sulphide being thrown down by the gas in aqueous solution. In double precipitations the sulphides obtained in the first operation are dried, dissolved in *aqua regia*, the solution evaporated to dryness, the residue dissolved in hydrochloric acid, and again precipitated with hydrogen sulphide. *Special methods. Silver:* By precipitation as the chloride according to § 127 *a*. *Mercury:* Mercurous compounds are precipitated with hydrochloric acid as in § 127 *b*; mercuric salts are reduced by phosphorous acid in presence of hydrochloric acid, as in Rose's method, § 127 *b*. *Lead:* with sulphuric acid, § 127 *c*. Barium sulphate can be separated from lead sulphate by treatment with cold ammonium carbonate. The latter converts the lead salt into the carbonate, which can then be removed by dilute nitric acid. The washed precipitate of the mixed sulphates may also be rinsed into a beaker and digested with cold sodium thiosulphate, which dissolves the lead salt.

(lead is in this case determined as sulphide). *Copper:* The solution is acidified with sulphuric acid, heated to boiling, and precipitated with sodium thiosulphate until the copper has been completely deposited. The further treatment of the precipitate is given in § 127 *e*. In this method, any large excess of hydrochloric or nitric acid must be removed by evaporation with sulphuric acid. The separation of copper from zinc, and also from iron, by means of potassium sulphocyanate is to be especially recommended (separation of copper, § 128 *a*). *Bismuth* is isolated as its oxychloride (except from iron) according to § 127 *f*. *Cadmium*, by means of hydrogen sulphide (§ 127 *d*).

GROUP V

TIN, ANTIMONY, ARSENIC

§ **129. I. Determination.** *Of tin.*—Tin is always determined as stannic oxide, the latter being obtained either directly or after the precipitation of stannic sulphide. Acid solutions which contain hydrochloric acid or chlorides must not be evaporated. *By precipitation as stannic acid.* 1. *With nitric acid:* Metallic tin (alloys), and those of its compounds which contain no non-volatile acids (chlorides, as we have seen, must be absent), are treated with nitric acid (sp. gr. = 1·3) in a small flask, the metal first having been reduced to powder. The acid is gradually added in the cold, and the vessel covered by a watch-glass. Toward the end of the reaction, the flask may be heated on the water-bath until the insoluble residue has turned completely white. The contents of the flask are then rinsed into a porcelain dish, evaporated to dryness on the water-bath, extracted with water, and filtered. The precipitate should be ignited in a porcelain crucible, before a blow-pipe flame. If the sulphide is to be oxidised with nitric acid, it is advisable to add a few pieces of ammonium carbonate to the contents of the crucible during the ignition, to remove the sulphuric acid. 2. *Precipitation by neutral salts:* The tin must be in the stannic form, stannous compounds requiring previous oxidation (with hydrochloric acid and potassium chlorate). The solution is cautiously neutralised by ammonia (if a slight turbidity ensues, a few drops of hydrochloric acid may be added), mixed with a concentrated solution of sodium sulphate or ammonium nitrate, and warmed for some time. The precipitate of stannic acid is first washed by decantation, then on the filter, and finally ignited. Complete precipitation must be confirmed by the addition of sodium sulphate to the filtrate and heating. The method is exact.

Precipitation as sulphide.—(This method is employed only in separations.) Stannous compounds are precipitated by hydrogen sulphide (gas or solution) from a well-diluted and slightly acid solution. When the liquid has become saturated with hydrogen sulphide it is placed aside for half an hour, to allow the precipitate to settle, and then filtered. If stannic compounds are to be precipitated, the vessel is covered, and placed in a warm spot until the odour of hydrogen sulphide has disappeared. It is advisable to wash the stannous sulphide first with a sodium chloride solution, and finally with ammonium acetate and acetic acid, as the precipitate is otherwise very apt to run through the filter. The precipitate is converted to stannic oxide by careful ignition in a porcelain crucible (until no more sulphurous anhydride escapes). A stronger flame is employed towards the end of the operation, and a few pieces of ammonium carbonate added.

Determination of antimony.—Antimony is preferably weighed as antimony trisulphide.

As antimony sulphide.—The solution is acidified with hydrochloric acid, tartaric acid is added, and the solution diluted with water if too concentrated. The precipitation must be made in a flask closed by a doubly perforated cork. In one of the holes is inserted a tube which leads to the bottom of the flask, and serves for the introduction of the hydrogen sulphide; through the other a second thin tube is passed, which extends only a short distance below the cork, and is bent to a right angle above it. This tube is connected with another, which dips below the surface of some water contained in a beaker, the antimony solution thus being effectually protected from the air. The solution is treated with hydrogen sulphide until saturated with the gas, and, if possible, should be in continual ebullition during the latter part of the operation. The precipitate is then allowed to settle, the hydrogen sulphide driven from the solution by a current of carbon dioxide, and the liquid finally filtered through a weighed filter. The precipitate is dried at 100° C., and weighed. It still contains water, and sometimes sulphur, however, and before the final determination a small portion is dissolved in boiling hydrochloric acid. If complete solution results, sulphur is absent, and the precipitate need only be freed from its water. A weighed portion is placed in a porcelain boat, and the latter inserted in a glass tube. It is then ignited in a stream of carbon dioxide until the precipitate has entirely lost its orange colour and become black. The current is continued until the tube has cooled off. The boat having again been weighed, and the quantity of antimony trisulphide which it contains thus ascertained, the amount of trisulphide in the whole precipitate is calculated from this value. If sulphur was present, the heat must be continued until it has entirely volatilised.

The determination of arsenic may be made either by means of ammonium magnesium arsenate or as arsenic trisulphide. Both methods are exact if the proper conditions be observed. Certain other methods are also employed in separations, and these will be described in their proper place (§ 130).

As ammonium magnesium arsenate.—The arsenic must be present as arsenic acid (oxidised, if necessary, by evaporation with nitric acid). The solution is mixed with an excess of ammonia (which must cause no precipitate) and magnesia-mixture is added after some time (§ 136; for arsenic determinations the mixture prepared from magnesium chloride is diluted with one half its volume of alcohol). The liquid, which must smell strongly of ammonia, is allowed to stand for 36-48 hours and then filtered. The precipitate must be washed on the filter, with a mixture of 6 parts water, 2 parts ammonia, and 1 part alcohol, until silver nitrate in presence of nitric acid causes no precipitate. When dried at 103°-105° C., the precipitate has the composition $Mg(NH_4)AsO_4$, and for exact determination must be converted, by very gentle ignition, into magnesium pyroarsenate, $Mg_2As_2O_7$. The filter is burned alone, having first been moistened with ammonium nitrate and thoroughly dried.

As arsenic trisulphide.—Arsenious solutions are precipitated by hydrogen sulphide in the same manner as antimony. The precipitate is collected on a weighed filter, dried at 100° C., and weighed. If the trisulphide contains sulphur as an impurity (which will be the case if the solution contained substances which decompose hydrogen sulphide), it must be converted to arsenic acid. The oxidation can be effected either with chlorine in presence of potassium hydroxide or with concentrated nitric acid. The well-dried precipitate is placed in a porcelain casserole, covered with nitric acid, and, as soon as the reaction has somewhat subsided, heated on the water-bath. The casserole should be kept covered by a glass plate during the operation. The filter must also be decomposed, but apart from the precipitate. The two solutions are then united, and the arsenic determined as ammonium magnesium arsenate. The precipitation of arsenic acid solutions by hydrogen sulphide should be performed at 70° C., or, still better, after sulphurous acid has been added. The precipitate invariably contains free sulphur, and it must therefore be converted to arsenic acid and determined as ammonium magnesium arsenate. The sulphur can also be removed from the arsenic sulphide by washing with carbon disulphide, but only when the precipitation was made from cold solution.

§ **130.** II. **Separations.** (*a*) Metals of Group V., Division 1.—There are many methods for the separation of these metals, each of the latter having characteristic compounds by means of which it can be isolated. The various methods can be more exactly comprehended if discussed in connection only with the metal upon the compounds of which they are based. To speak generally, the separation of antimony is effected by means of the insoluble sodium antimonate, that of arsenic by ammonium magnesium arsenate. Tin is precipitated in neither reaction, and is therefore obtained in the filtrate from the other metals.

Separation of antimony.—The metals (or their alloys) are oxidised in a porcelain crucible by nitric acid (sp. gr. = 1·4), the reagent being added little by little. When the reaction is complete, the solution is evaporated to dryness on the water-bath, and the residue transferred to a silver crucible. The porcelain crucible is rinsed with a solution of sodium hydroxide, the rinse water being poured into the silver crucible, to the contents of which are also added several pieces of solid sodium oxide. The whole is then carefully heated to fusion, and after remaining in a molten state for some time, is finally allowed to cool, and treated with hot water until the residue has become pulverulent. After the addition of dilute alcohol (1 vol. alcohol, 3 vols. water), the vessel is set aside for twenty-four hours. The residue is washed with dilute alcohol (the same mixture), dissolved in hydrochloric acid in presence of tartaric acid, and the solution precipitated by hydrogen sulphide. The determination of the antimony is made according to § 129. Tin and arsenic (in the filtrate from the sodium metantimonate) are precipitated together as stannic arsenate by hydrochloric acid, a few drops of sodium carbonate also being added, and the unfiltered solution is then treated with hydrogen sulphide (§ 129). The sulphides obtained are separated by the following method.

Separation of arsenic.—If arsenic is to be separated only from antimony, it is converted to arsenic acid (with *aqua regia* or potassium chlorate and hydrochloric acid) and, after the addition of ammonium chloride and ammonia, is precipitated with magnesia mixture. The precipitate of ammonium magnesium arsenate is dissolved in hydrochloric acid, and again thrown down by ammonia, to free it from the small quantity of magnesium tartrate which it retains. This method may be modified as follows for the separation of arsenic from tin. The two metals (or their compounds) are oxidised with nitric acid, as in § 129, the solution evaporated, and the residue treated with ammonia and yellow ammonium sulphide. This yields a solution of the thio-salts, from which the arsenic can be precipitated in the usual manner (§ 129), as the ammonium magnesium salt. The tin is thrown down from the acidified filtrate as its sulphide (§ 129). Rose's method of separating arsenic and tin, which is based upon the volatility of arsenic sulphide in a current of hydrogen sulphide, is more complicated than those which have just been explained.

Separation of tin.—We have no good methods which are based upon the properties of the tin, and for this reason it is determined after the other metals have been separated by the methods which have just been considered. The solubility of tin in hydrochloric acid is sometimes employed to separate it from antimony (the two metals first being reduced by zinc), and the same result may be attained by precipitating the antimony with metallic tin. These methods are rarely used, however, and are more or less inexact. *Winkler's method:* The metals must be present in their higher degrees of oxidation. The liquid is diluted to 300 c.c., and a solution of calcium chloride added (about fifteen parts of $CaCl_2$ to one of tin). It is then neutralised with potassium carbonate, and potassium cyanide is added; after which it is again treated with potassium carbonate until the calcium is completely precipitated. The solution is heated to incipient boiling, allowed to settle, and the supernatant liquid decanted through a filter. The precipitate, still in the glass, is then dissolved in hydrochloric acid, and again thrown down by potassium cyanide and carbonate. The second precipitate is transferred to the same filter, washed, dried, and strongly ignited. It is then treated with dilute hydrochloric acid, which dissolves only the calcium carbonate, and the stannic oxide can be filtered off and determined. In this method antimony and arsenic remain in the filtrate.

Stannous and stannic tin.—All the tin present is first determined as stannic oxide in one portion of the substance (§ 129); in another, the quantity which is in the stannous condition is estimated by a volumetric method (see §§ 150, 152).

The separation of arsenious from arsenic acids, and of antimonious from antimonic acids, is effected in the same way. In one portion the total amount of arsenic or antimony is found, and in another the arsenious or antimonious acid (by volumetric methods). In both cases, the quantity of the higher oxide is determined by calculation from the results obtained for the total weight and that of the lower oxide.

(*b*) Metals of Group V., Division 1, from those of Groups IV., III., II., I. *General methods.*—Precipitation of the acid solution with hydrogen sulphide (separation from Groups I., II., and III.), and precipitation of the thio-salts (separation from Group IV.) The precipitation with hydrogen sulphide is effected according to the directions already given (§ 128). The solution must be acidified with hydrochloric acid and well diluted with water, and the directions given in § 129, concerning the precipitation of the sulphides of Group V., must be carefully followed. The precipitation of antimony should be effected from dilute solution and in presence of tartaric acid.

This method does not suffice for the separation of zinc from arsenic acid, as the thio-salt, $Zn_3(AsS_4)_2$, precipitates; the arsenic must therefore be first reduced to arsenious acid (by sulphurous acid). For the separation from Group IV., the sulphides obtained by precipitation with hydrogen sulphide (under the correct conditions) are washed, and treated, while still moist, with yellow ammonium sulphide. The digestion must be prolonged for some time, and the liquid kept slightly warm. The residual precipitate is filtered off, again treated with ammonium sulphide, filtered, and washed with ammonium sulphide water. It consists of the sulphides of Group IV. The solution contains the thio-salts of the metals of Group V., the sulphides of which are precipitated by slow addition of hydrochloric acid. In separations from copper, the ammonium sulphide should be mixed with sodium sulphide. The use of the latter reagent is permitted, however, only when mercury is absent. The separation of Groups V. and IV. can also be effected by the direct addition of ammonium sulphide in excess, instead of previous precipitation with hydrogen sulphide. In this case, likewise, the precipitate must be treated a second time with ammonium sulphide. It is more convenient, when possible, to obtain the thio-salts by fusion (of the oxides, salts, or the like) with 3 parts of anhydrous sodium carbonate and 3 parts of sulphur, in a porcelain crucible. When the contents of the crucible have passed completely into a state of fusion and the excess of sulphur has burned away, the thio-salts of Group V. are extracted with water. The sulphides of Group IV. remain undissolved.

Special methods.—These are in many instances much simpler than the foregoing. 1. The volatility of the chlorides of arsenic, tin, and antimony, affords an easy separation from metals which form non-volatile chlorides (principally from copper, silver, cobalt, nickel). The operation is performed in the same apparatus, and under the same conditions, as that explained in § 128 (separation of mercury, etc.). The same property may be employed in the separation of tin, arsenic, and antimony from Groups I. and II., and the process is in this case much less complicated. The dry substance is mixed with 5 parts of ammonium chloride and ignited in a porcelain crucible fitted with a platinum cover, until all the ammonium chloride and the chlorides of Group V. have volatilised. The ignition must be repeated until the crucible maintains a constant weight. To separate tin and antimony from lead and cadmium, Jannasch and Remmler recommend the use of bromine instead of chlorine. The solution is precipitated with hydrogen sulphide, and the precipitate collected on a weighed filter, washed, and dried. It is then transferred to a porcelain boat, which is inserted in a long glass tube, one end of which is drawn out and passes into a receiver. The other end is connected with a wash-bottle containing bromine, the vapour of which is carried over the sulphides in a current of carbon dioxide. The boat is gently heated by a small flame, and the tin, antimony, and sulphur driven over into the receiver as their bromides. The receiver contains dilute hydrochloric acid. The residue of lead bromide is treated with chlorine water, to convert it to the chloride, and weighed as lead sulphate (§ 127 *e*). The contents of the receiver are evaporated to a small volume with nitric acid, the sulphuric acid driven off in an open air-bath, and, after further treatment with nitric acid, the residue is dried and weighed. Instead of the precipitation with hydrogen sulphide, the metals or salts can be converted directly to the sulphides by fusion with sulphur and a small quantity of iodine, in a stream of hydrogen sulphide. The excess of sulphur is driven off, and the residue treated as above. For this operation the authors recommend a special apparatus, which is described in their original article on the method (*Ber. d. d. chem. Gesellschaft*, xxvi. 1423).

2. *Arsenic and antimony* can be separated from the metals of Groups III. and IV. by means of the soluble salts which they form with the alkalies. Arsenic compounds may be oxidised by fusion with sodium carbonate and potassium nitrate; those of antimony (and also of arsenic) are oxidised in the dry state (in ores, etc.), with chlorine in presence of potassium hydroxide. Arsenic and antimony go into solution, and the residue consists of the metallic oxides of Groups III. and IV.

3. *Tin* is separated (especially in alloys) by conversion to the insoluble metastannic acid on treatment with nitric acid (§ 129). The method is inapplicable when manganese, bis-

muth, or iron are present, and does not afford exact results in separations from copper (in this case the general method is substituted). Tin can be accurately separated from the metals of Groups I., II., and III., and also from copper, by precipitation with sodium sulphate or ammonium nitrate (§ 129).

4. *Arsenic.*—In addition to the employment of ammonium magnesium arsenate, by which arsenic can be separated from copper, iron, manganese, nickel, and cobalt, there are several methods (viz., precipitation as the arsenate of mercury or iron, or as ammonium arsenomolybdate), in which the operations are the same as in the separation of phosphoric acid (see Phosphorus).

GOLD, PLATINUM

§ **131.** I. **Determinations.**—*Of gold.* Gold is always determined in the form of the metal.

1. *By ignition.*—(Analysis of compounds containing no other constituents which resist heat.) The ignition is effected in a closed porcelain crucible; the heat being at first very gentle, but afterwards strong. This is the most exact method.

2. *By precipitation from solution with ferrous sulphate or oxalic acid.*—(In separations, and where the foregoing method is inapplicable.) Whichever precipitant is used, the solution must be free from nitric acid. When the latter is present, the solution is evaporated on the water-bath, and hydrochloric acid added from time to time until the nitric acid has been completely destroyed. Ferrous sulphate, or better still, ferrous chloride, is added to the solution in a porcelain dish, and the mixture then cautiously heated for an hour or two. The precipitate of metallic gold is washed, dried, and ignited. In precipitation with oxalic acid (or ammonium oxalate), the solution should be acidified with hydrochloric acid, and allowed to stand for two days in a covered vessel. The gold separates in metallic flakes, which are washed, dried, and ignited. G. Krüss precipitates the fairly concentrated gold solution by heating it for half an hour with aqueous sulphurous acid. The liquid may be filtered as soon as it has become clear.

3. *By precipitation as gold sulphide* (employed only in separations). The very dilute solution is treated in the cold with hydrogen sulphide, and the precipitate quickly filtered

and washed. After being dried, it is ignited in a porcelain crucible, and the residual metallic gold weighed.

Determination of platinum.—Platinum, like gold, is almost always weighed as the metal. The latter is obtained by ignition of the compound, or by previous precipitation of a platinichloride or platinum sulphide.

1. *By precipitation as the platinichloride of potassium or ammonium.*—Ammonia is added to the concentrated solution until its acid (if present) is almost saturated. The solution is then treated with alcohol and ammonium chloride, and allowed to stand for twenty-four hours in a beaker protected by a glass plate. The precipitated platinichloride is then filtered, washed with alcohol, and ignited. Proper ignition is very important. The precipitate should be wrapped in the filter and placed in a weighed porcelain crucible, which is then covered and very carefully ignited until the ammonium chloride has been driven off. The cover of the crucible is finally removed, and a strong flame applied. If a large quantity of the precipitate was obtained, its reduction is preferably effected in a stream of hydrogen, or in presence of oxalic acid. The estimation as potassium platinichloride is made in the same way, except that the precipitation is effected with potassium chloride instead of the ammonium salt. In exact determinations the platinum should be separated and weighed as the metal. For this purpose the precipitate is dried at 100° C. (on a weighed filter) and weighed. A portion is then introduced into a weighed bulb-tube and heated in a current of dry hydrogen, until the escape of hydrochloric acid gas has ceased. After having cooled off in the stream of hydrogen, the potassium chloride is extracted with water, and the metallic platinum dried and weighed in the same tube.

2. *By ignition.*—In determining platinum by ignition, the directions given for the estimation of gold must be followed. For its reduction from solution, common ferrous sulphate is added to the boiling solution in presence of potassium hydroxide. (The iron hydroxides are extracted with hydrochloric acid.)

3. *By precipitation as platinum sulphide.*—The solution is saturated with hydrogen sulphide, heated to incipient boiling, and the precipitate filtered and ignited.

II. **Separations.**—Platinum is separated as a platinichloride. The solution is treated with ammonium or potassium chloride, as already explained, and the precipitate washed with alcohol and ether. The filtrate contains the gold as ammonium aurichloride. For the details of the operation, see the determination of platinum.

Gold and platinum from the metals of the other groups. 1. *By the action of acids* (analysis of alloys).—The alloy is treated with boiling nitric acid. This method will not answer, however, if it contains less than 80 per cent of silver or lead, and in such cases the substance must be fused with three parts of lead before its treatment with nitric acid. Sulphuric acid (two parts of the acid to one of water) may also be employed. The alloy is heated with the acid in a platinum dish, and extracted with water; gold remains in the residue, and the other metals go into solution as their sulphates. Fusion with acid potassium sulphate is a still more convenient method for the separation of platinum and gold from other metals. Nitric acid cannot be employed when platinum is present, as a small quantity of the metal is very apt to be dissolved by this reagent.

1. *By reduction to the metallic state.*—The separation of gold and platinum can be effected by their reduction from solution, with ferrous sulphate or oxalic acid, and that of platinum by precipitation as a platinichloride. The methods are the same as for the simple determination of the metals. They cannot be employed in presence of silver or lead. In the analysis of certain gold ores, finally (its compounds with antimony, tellurium, etc.), the substance is treated with chlorine: neither aurous nor platinous chloride is volatile.

GRAVIMETRIC DETERMINATION AND SEPARATION OF THE METALLOIDS

HALOGENS

CHLORINE, BROMINE, IODINE

§ **132.** I. **Determination.**—The determination of the hydrogen acids and of haloid salts is almost invariably effected by precipitation of the respective silver compound (that of iodine occasionally by means of palladious iodide). The free halogens are most readily estimated by volumetric methods (see Volumetric Analysis, Section II.)

Chlorine, in hydrochloric acid and chlorides, is most usually determined as silver chloride. The solution is acidified with nitric acid, and precipitated by silver nitrate. The precipitate must be heated and well stirred, to bring about coagulation. Directions for its washing and determination are given in § 127. This method effects the separation of chlorine from the metals in almost all soluble chlorides (the metal is determined in the filtrate from the silver chloride). A very few salts, however, form exceptions to this rule, and in their analysis the processes must be reversed (the metal is first precipitated, and the chlorine determined in the filtrate). To analyse stannic chloride, for instance, the tin must first be thrown down as stannic acid by ammonium nitrate (§ 129). In the analysis of mercuric chloride and of antimony trichloride, the metals are first separated by means of hydrogen sulphide (§§ 127 and 129). A solution of chromic chlorid (the green variety) does not deposit all its chlorine on g, addition of silver nitrate, and the chromium must the be precipitated by ammonia (§ 121) before the chlorine can be determined. In all such cases the chlorine is precipitated from the filtrate in the usual manner. Chlorides which are insoluble in water or dilute nitric acid can be brought into solution by various means: lead chloride, by the prolonged action of sodium bicarbonate at the ordinary temperature; silver chloride, by fusion with the carbonates of sodium and potassium, or by the action of zinc and sulphuric acid; mercurous chloride, by treatment with potassium hydroxide. The chlorine is determined in the filtrate (from the precipitate of the base), after acidulation with nitric acid. If only the metal in a chloride is to be determined, it is convenient to evaporate the solution to dryness with sulphuric acid and weigh the metal as sulphate (not always possible).

The determination of bromine, in hydrobromic acid and bromides (and also the separation from the metals mentioned above) is made in all cases like that of chlorine.

The determination of iodine as silver iodide is made under the same conditions as that of chlorine or bromine. When iodine is to be separated from the other halogens, it is usually estimated as palladious iodide, by precipitation of the solution with palladious chloride, after acidulation with hydrochloric acid. The precipitate is allowed to settle at a gentle heat, collected on a weighed filter, and dried at 80° C. The determination can also be made by ignition of the precipitate and calculation of the iodine from the weight of the residual metallic palladium. Insoluble iodides (PdI_2 and CuI in particular) are brought into solution by boiling with potassium hydroxide, or through the action of nitric acid; the former reaction is to be preferred, as nitric acid may precipitate some of the iodine. Many of the insoluble salts, further, dissolve in sodium thiosulphate. If this method be employed, the metal is precipitated by ammonium sulphide, and the solution evaporated to dryness with sodium hydroxide. The residue is then dissolved in water, ferric chloride and hydrochloric acid are added, and the iodine is distilled into a receiver and estimated volumetrically.

II. **Separation of the halogens** in hydrogen acids and haloid salts.

Separation of chlorine and bromine.—For this object two operations are necessary. In the first, the chlorine and bromine are determined together, by precipitation with silver nitrate in the usual manner. One gram of the substance is then dissolved in 50 c.c. of water and a solution of acid potassium sulphate (3 gr. in 30 c.c. water), and one of potassium permanganate (1 : 50) are added. The bromine is thus liberated from its compound, and is drawn by means of an aspirator into a Will and Varrentrapp's apparatus (see Section III., Analysis of Organic Compounds), which contains a solution of sodium hydroxide (1 : 50). The chloride remains in the flask, and its chlorine can be determined as usual, after the potassium permanganate has been decomposed by alcohol. The bromine carried over into the receiver is also estimated by the usual method, the sodium hypobromite first being decomposed by ammonia and the solution then acidified with nitric acid (*Zeitschrift für analytische Chemie*, 1885, p. 185).

Separation of iodine. 1. *As palladious iodide.*—The sum of the chlorine and iodine is first determined (by precipitation with silver nitrate; § 132, I.), and the iodine in another portion of the substance is then precipitated by palladious chloride, as in § 132, I. The quantity of iodine having been found, that of the chlorine is calculated from the difference. It is advantageous to have the iodine in concentrated solution, and if only a small quantity is present, the liquid should be evaporated to dryness with sodium carbonate and extracted with alcohol. The alcoholic solution is then evaporated to dryness, the residue dissolved in water, and the iodine determined in this solution. If all three halogens are present, the excess of palladium in the filtrate from the palladious iodide is removed by hydrogen sulphide, and the latter destroyed by ferric sulphate (see below). The bromine is then determined by the indirect method. To find the chlorine, all the halogens in another portion of the substance are precipitated together by silver nitrate, and the chlorine estimated by subtraction of the iodine and bromine from the result obtained.

2. *As thallious iodide.*—The solution of the alkali haloids, which must be neutral and dilute, is treated with a saturated solution of thallic nitrate; the reagent should be added gradually (a burette may be employed with advantage), as long as a yellow precipitate continues to separate. The appearance

of a white precipitate which goes into solution again on being stirred indicates that the reaction is complete, and the addition of the thallic nitrate is then stopped. The liquid is allowed to stand for eight hours, filtered through a weighed filter, and the precipitate washed with as little water as possible. It must be dried at 100° C. (Hübner). The chlorine and bromine are determined as above.

3. Chromic acid in dilute solution decomposes only the iodides, according to the equation:

$$6KI + 8CrO_3 = 6I + Cr_2O_3 + 3K_2Cr_2O_7.$$

The reaction is induced in a flask, and the iodine distilled, by means of a current of steam, into a receiver; after which it is volumetrically estimated. (For the details of the method see Volumetric Analysis.)

Indirect determinations. Chlorine from bromine, chlorine from iodine.—The theory of this method was explained in §§ 123 and 117. The total weight of the halogens present is learned by precipitation with silver nitrate, as in § 132, I. A portion of the precipitate is next transferred to a weighed bulb-tube (by fusion and pouring out from the crucible) and weighed. A current of dry chlorine or hydrogen is then passed through the tube, and the latter heated. The operation is continued until the weight of the tube remains constant. If chlorine was used, the substance has now been completely converted to silver chloride (the bromine or iodine has been displaced, and there is consequently a loss in weight); if hydrogen, metallic silver is obtained. The calculation is made according to § 117, and the quantity of silver bromide having been found, and subtracted from the weight of the original silver salts, the remainder gives the weight of the silver chloride. The halogens themselves are then calculated from the respective silver salts. If the silver salts were reduced with hydrogen, the metallic silver is calculated to silver chloride; comparison with the total weight of the silver salts will show the same difference as in the foregoing case, and the necessary data are found in the same way. To make the method generally applicable, *e.g.*, even when the quantity of bromine is small in proportion to that of chlorine, fractional precipitation is employed (Fehling). The sum of the halogens is first determined by precipitation with silver nitrate; another portion of the substance is then treated with silver nitrate, in a quantity insufficient to cause complete precipitation ($\frac{1}{5}$, $\frac{1}{10}$, $\frac{1}{60}$ of the amount necessary for complete precipitation is used, according to the probable quantity of bromine present), and the liquid allowed to stand for several hours, with repeated stirring. All the bromine (or iodine) will then be found in the precipitate, since the silver chloride originally deposited will be converted to the bromide (or iodide) by the prolonged action of potassium bromide (or iodide). It must be remarked that silver bromide does not completely pass into the iodide when treated with the potassium salt of the latter halogen. The precipitate is weighed, and then treated with chlorine as above. The loss of weight is calculated to the whole of the precipitate, and from this value the quantity of silver bromide (or iodide) is found as above. The weight of silver chloride is obtained by subtraction of that of the bromide from their combined weight, and from the silver salts the halogens themselves are calculated.

OXYACIDS OF THE HALOGENS

Hypochlorous acid can be estimated by reduction with zinc and sulphuric acid, and subsequent precipitation with silver nitrate, but gravimetric methods are rarely employed for its determination. Its compounds (chiefly bleaching powder) are principally of technical importance. The volumetric methods are numerous, and are grouped together under the name "Chlorimetry" (only the chlorine which can be liberated from the bleaching powder is important in technical questions). These methods will be more closely studied in the section on Volumetric Analysis.

Chloric acid can be determined gravimetrically (by reduction with zinc and sulphuric acid and precipitation with silver nitrate), but the volumetric methods are much more convenient. In the latter, the amount of iodine liberated in the reaction between potassium iodide and the chlorate in presence of hydrochloric acid is determined:

$$KClO_3 + 6KI + 6HCl = 6I + 7KCl + 3H_2O.$$

To separate chlorates from chlorides the former are converted to chlorides by ignition and the total chlorine then determined by precipitation with silver nitrate. The chloric acid is next estimated, in a second portion of the substance, by a volumetric method, and the quantity of chloride found from these two data.

Iodic acid is estimated volumetrically by the action of fuming hydrochloric acid. The chlorine set free is led into a solution of potassium iodide, and the liberated iodine determined:

$$HIO_3 + 5HCl = ICl + 4Cl + 3H_2O.$$

FLUORINE

§ **133**. The fluorine of fluorides is always determined as calcium fluoride. Acid solutions and free hydrofluoric acid must first be neutralised by an excess of sodium carbonate, and any precipitate which forms filtered off (it must be examined for fluorine). Calcium chloride is then added, and the precipitate allowed to settle, washed by decantation and on the filter, with hot water, dried, and gently ignited in a platinum crucible. To remove the calcium carbonate which it contains, it is treated with acetic acid (in a platinum crucible or porcelain dish), evaporated to dryness on the water-bath, and extracted with water. The calcium fluoride remains undissolved, and after filtration and drying, is again ignited and weighed. Neutral solutions are directly precipitated (in a platinum dish) with calcium chloride, boiled, and the precipitate allowed to settle. It is first washed by decantation, and then treated as above. Insoluble anhydrous fluorides are heated with concentrated sulphuric acid, ignited, and weighed. The hydrofluoric acid is in this case estimated from the difference, the metal being calculated from the weight of its sulphate if the latter is undecomposed. If the salt does decompose on ignition, the metal in the residue must be determined, and the fluorine then calculated. Hydrated fluorides can be analysed in the same manner, but the loss found comprises both the fluorine and water. A determination of the latter is therefore necessary; it can be made by gentle ignition of a new portion of the substance. If some other acid be present which volatilises on ignition, the substance must previously be mixed with an excess of lead monoxide (to hold the acid back). The ignition is effected in a small weighed retort. The weight of the water having been found, that of the fluorine is determined from the data of the two analyses (see Silicon).

Hydrofluosilicic acid.—The salts are most conveniently analysed by treatment with hot concentrated sulphuric acid in a platinum dish, the hydrofluosilicic acid being calculated from the metal in the residual sulphate. The determination of the water in hydrated salts is made as in fluorides. Free hydrofluosilicic acid is estimated by precipitation with potassium chloride, in alcoholic solution (equal volumes of alcohol and water). The potassium silicofluoride is then transferred to a weighed filter, washed, and dried at 100° C. Its formula is K_2SiF_6.

Separation.—Fluorine is separated from the halogens by precipitation with calcium nitrate. The halogens remain in solution, and are determined in the filtrate.

SULPHUR

§ **134.** *a.* **Determination of Hydrogen Sulphide and of Sulphur in Metallic Sulphides.**—According to Mohr, the hydrogen sulphide is precipitated by a weighed quantity of sodium arsenite in excess, and the excess of the reagent then estimated volumetrically with iodine (see Volumetric Analysis). The gravimetric estimation is effected by precipitation with arsenious acid (and weighing of the As_2S_3 obtained, § 129), or by one of the following methods.

Sulphides.—Methods based upon the precipitation of zinc sulphide or arsenic trisulphide are less exact than those in which the sulphur is converted to sulphuric acid.

Oxidation by the dry way.—The sulphides, which must lose no sulphur when heated, are mixed, by means of a glass rod, with 6 parts anhydrous sodium carbonate and 4 parts potassium nitrate, in a crucible of either porcelain or platinum. To clean the rod, the substance adhering to it is rubbed off with sodium carbonate. The crucible is at first gently heated, and the mixture finally brought into a state of complete fusion. It is then extracted with water, filtered, and the sulphuric acid which it contains determined (the barium sulphate must be purified; see below). If the sulphide under analysis parts with sulphur on being heated, it is mixed, in the same manner as above with 4 parts Na_2CO_3, 8 parts KNO_3, and 24 parts NaCl. Fusion with potassium chlorate (or nitrate) is not so expedient, since the potassium chlorate decomposes before complete oxidation has been able to take place, and also because a loss is apt to ensue from spattering. The substance can also be fused with 4 parts of sodium peroxide and 2 parts of sodium carbonate in a thick silver crucible; the latter must remain covered throughout the operation (Hempel).

Oxidation with chlorine.—The substance is placed in a bulb-tube, one end of which is connected with a chlorine generator and the other with a receiver containing water (if the substance contains antimony, the receiver is filled with a solution of tartaric acid). When the air in the tube has been completely displaced by chlorine, and the reaction has proceeded as far as it can in the cold, the bulb is heated. The sulphur chloride which forms distils over into the receiver, and is there decomposed to sulphur and sulphuric acid by the excess of chlorine. The sulphur is then collected on a weighed filter, and the sulphuric acid determined as in *b*. (The method is applicable in the analysis of many mineral sulphides; see Examples of Grav. Anal.) Sauer has elaborated a method in which the sulphides are heated in a stream of air or oxygen, and the sulphurous acid evolved absorbed in bromine water. The sulphuric acid thus formed is determined as in *b* (*Zeitschrift für analytische Chemie*, 1883, p. 581). This method is very well fitted for the estimation of sulphur in pyrites, coals, etc.

Oxidation by the wet way.—The sulphides are weighed in a small glass tube, closed at one end, and placed in a capacious flask, which is provided with a glass stopper and contains enough fuming nitric acid to completely decompose the mineral. When the reaction has subsided, the contents of the flask are shaken about, and if this causes no further reaction the stopper is taken out, rinsed with water, and the flask cautiously warmed. The sulphuric acid is then determined by the usual method. Should a portion of the sulphur remain undissolved, concentrated hydrochloric acid and a few pieces of potassium chlorate must be added, and the flask placed on the water-bath. If this operation does not effect complete oxidation, the sulphur is filtered off on a weighed filter, and its weight determined. The sulphur thus obtained must be burned away in a porcelain crucible after its weighing, to ascertain whether it actually leaves no residue. The sulphides may be directly treated, in the above manner, with potassium chlorate and hydrochloric or nitric acid, the latter being preferred; this method is to be especially recommended. A method in which the sulphur undergoes oxidation more slowly consists in digestion of the finely powdered mineral for some hours with a solution of potassium hydroxide, and final treatment of the latter with gaseous chlorine. The precipitate is then filtered off, the filtrate acidified with hydrochloric acid, and the sulphuric acid determined by precipitation with barium chloride. It should be ascertained in all of these methods that the barium sulphate obtained is pure. The presence of an excess of ferric salts makes the determination inaccurate.

b. **The determination of sulphuric acid** by gravimetric methods (and sometimes by volumetric) is accomplished by means of barium sulphate. *Determination as barium sulphate:* It is much more difficult to estimate sulphuric acid in the form of this salt than to determine barium by its means (§ 118), since when the solution of a sulphate is precipitated by barium chloride, the precipitate is apt to carry down certain soluble salts (especially when chlorates and nitrates are present). The precipitation is made in presence of free hydrochloric acid, as in § 118, and the barium sulphate must be washed with hot water until the filtrate gives no test for barium. When precipitated from such solutions as were obtained in *a*, the salt must be purified after its ignition and weighing. If chlorates or nitrates were present, it is sufficient to boil the precipitate with hydrochloric acid (the latter is removed by evaporation) and wash the residue with water. If potassium or sodium nitrate was present, however, this operation is not enough, even if repeated several times. In such cases it is advisable to fuse the ignited precipitate with sodium carbonate, extract the residue with water, and reprecipitate the solution with barium chloride. Concerning the separation of sulphuric acid from the metals in insoluble sulphates (the soluble salts are analysed as above) the following remarks may be made. The sulphates of barium, strontium, and calcium are fused with five parts of sodium carbonate, in a platinum crucible. When the operation is finished, the crucible is placed in a porcelain dish, boiled with water, and the precipitate filtered and washed with water containing ammonia and ammonium carbonate. The precipitate consists of the carbonates of barium, strontium, and calcium (§ 118), and the sulphuric acid passes into the filtrate. The salts of calcium and strontium also decompose when boiled with sodium carbonate (barium sulphate barely does so). Lead sulphate is converted to the carbonate by sodium carbonate even at the ordinary temperature.

Sulphurous acid and sulphites are converted to sulphuric acid for their gravimetric estimation. The solution may be saturated with chlorine and heated, or the substance be fused with sodium carbonate and potassium nitrate. The sulphuric acid obtained is then determined as above.

Thiosulphates (and also the polythionates) are gravimetrically estimated in the same manner as sulphurous acid.

Separations.—Hydrogen sulphide is separated from sulphuric acid by means of cupric chloride. From the halogens: The solution is precipitated by silver nitrate, and the precipitate, which contains both silver sulphide and the haloid salts, is filtered upon a weighed filter, dried at 100° C., and weighed. The sulphur in a portion of it is then determined according to one of the methods in *a*. If the hydrogen sulphide is simply to be removed from the solution, ferric sulphate may be employed. Sulphuric acid is separated from the halogens by means of a barium salt (the nitrate or acetate), and from fluorine by the usual method. (The purity of the precipitate must be ascertained as above.) Insoluble fluorides must be fused with six parts of the carbonates of sodium and potassium and two parts of silica. The product is then extracted with water, and the solution acidified with hydrochloric acid and precipitated by barium chloride. To separate sulphuric acid from hydrofluosilicic acid, the latter is first thrown down as its potassium salt (§ 133).

NITROGEN

§ **135. Determination of Ammonia.** — The methods have been described in § 116. Cyanogen compounds can also be analysed by conversion to ammonia, the change being effected by the action of soda-lime upon them at a high temperature. (The method is the same as that for the determination of nitrogen in organic substances, according to Varrentrapp and Will; see Section III., Analysis of Organic Compounds.)

Determination of hydrocyanic acid and of the cyanogen in cyanides. Free hydrocyanic acid is determined by precipitation with silver nitrate. The reagent having been added, the precipitate is treated with dilute nitric acid, allowed to settle in the cold, and filtered through a weighed filter. It is then dried at 100° C. and its weight ascertained. It may also be ignited in a porcelain crucible until the weight of the residual metallic silver remains constant.

In *cyanides* which are soluble in water or nitric acid (the latter completely decomposes the double salts) the cyanogen is determined as silver cyanide, according to the above directions. The analysis of mercuric cyanide by this method is impossible, however, and the mercury must first be precipitated by hydrogen sulphide (§ 127). To determine the cyanogen, another portion of the salt is ignited with cupric oxide, and the volume of the free nitrogen formed is measured (after its purification from carbon dioxide; see below). These methods are inapplicable in the analysis of certain double salts, and the latter are therefore treated in the following manner.

Decomposition with mercuric oxide (applicable to the double salts of Ni, Mn, Fe, but not of Co). The salt is boiled for some time with mercuric oxide, and the alkaline solution then almost neutralised by nitric acid. The metallic oxide, the salt of which was decomposed, is obtained with the excess of mercuric oxide in the precipitate: on ignition of the latter the mercuric oxide volatilises, and the metallic oxide is obtained as a residue. The cyanogen passes into solution as mercuric cyanide, and is estimated as above.

Determination of the cyanogen by loss.—The salt is moistened with sulphuric acid (3 parts H_2SO_4, 1 part water) in a platinum dish, and ignited at first gently, then at a greater heat, until all the free sulphuric acid has volatilised. If the resulting sulphate is stable, it can be directly weighed; if not, the metal is determined by the usual methods, the cyanogen being in both cases found from the difference. Neutral mercuric sulphate (6 parts, to 1 part of the cyanide) can be substituted for sulphuric acid. The mixture is ignited cautiously at first, in a platinum crucible, and the heat then raised until the crucible has become red-hot. The final weight must be constant. The residue is the metallic sulphate (or oxide). Certain salts (those of nickel and cobalt) can be more conveniently analysed by ignition with ammonium chloride in a current of hydrogen (which reduces nickel and cobalt to the metallic state).

Potassium ferrocyanide.—This salt can be very readily determined by oxidation with potassium permanganate in presence of sulphuric acid, in the same manner as ferrous salts are volumetrically estimated (see Volumetric Analysis).

All cyanogen compounds can be analysed by the methods employed in ultimate organic analysis. The cyanogen is then found from the quantities of nitrogen and carbonic acid formed on its oxidation.

Nitric Acid.—Free nitric acid is most readily estimated by volumetric methods (titration with sodium hydroxide; see Acidimetry and the Examples in § 149). To determine it gravimetrically, the acid is neutralised by ammonia, evaporated to dryness on the water-bath, and the ammonium nitrate dried at 115° C. and weighed. The determination of the nitric acid in salts is more difficult, and requires practice. After choosing one of the methods, therefore, the student should familiarise himself with its details by analysing some pure nitrate of known composition, before proceeding with that of the substance itself.

Determination from the loss.—From 2 to 3 gr. of pulverised quartz are ignited in a platinum crucible and weighed. The nitrate (about 0·5 gr.), which has previously been fused at as low a temperature as possible, powdered, and again dried just before the analysis, is then mixed with the quartz, and the crucible again weighed. The latter is then covered and heated very gently for half an hour. The loss of weight represents the nitric acid anhydride driven off.

By distillation.—The salt (1 gr.) is mixed with sulphuric acid (5 c.c. H_2SO_4, 10 c.c. H_2O) in a distilling apparatus; a vacuum is then produced in the latter, and the distillation effected by the heat of the water-bath. The use of a paraffin bath (170°) under the atmospheric pressure is not so good. The retort is connected with a receiver, which contains a measured quantity of standard sodium hydroxide solution, and when the distillation is complete (it requires about three hours), the nitric acid is found by retitration of the alkali. If chlorine is present, a sufficient amount of silver sulphate or oxide must be added before the distillation is performed.

By oxidation of ferrous salts.—1. Method of Pelouze and Fresenius: The excess of the ferrous salt is found by titration with potassium permanganate, and the quantity of the nitric acid determined from that of the ferrous salt which has undergone oxidation. $3Fe = 1HNO_3$, according to the equation:

$$3FeCl_2 + KNO_3 + 4HCl = NO + 3FeCl_3 + KCl + 2H_2O.$$

About 1 gr. of piano wire is dissolved in 30-40 c.c. fuming hydrochloric acid, in a tubulated retort of 200 c.c. capacity. The retort is placed upon the water-bath, and a stream of carbon dioxide or hydrogen led through the solution while the reaction is in process. When all the iron has dissolved and the liquid grown cold (in the stream of gas), the stopper is removed, a small tube containing the substance (a quantity corresponding to about 0·2 gr. nitric acid) dropped in, and the stopper quickly placed in position again. The retort is then warmed for fifteen minutes on the water-bath, and the solution finally heated to boiling. When all the nitric oxide has been driven off and the solution has lost its dark tint, the latter is allowed to cool in a current of carbon dioxide. It is then diluted with water, and the quantity of ferrous iron still unoxidised is volumetrically ascertained by means of potassium permanganate. The method of calculating the results is obvious. The strength of the potassium permanganate must first be determined in presence of hydrochloric acid, and under the same conditions in regard to concentration of the solution (the latter must be very dilute, Section II.) as prevail in the nitric acid solution itself. This method may be modified to a certain extent, and the quantity of ferric chloride formed be directly titrated with stannous chloride.

2. Schlösing recommends another method which is based upon the same reaction: The nitric oxide formed is collected

in a cylinder with water, and then converted into nitric acid by the action of oxygen or hydrogen peroxide. The dilute nitric acid solution so obtained is then titrated with sodium hydroxide. In the apparatus employed by Schlösing the analysis is conducted in a mercury bath, but its modification by Reichart (*Zeitschrift für anal. Chemie*, 1870, p. 24) permits the mercury to be replaced by sodium hydroxide. Frankland and Armstrong decompose the nitrate by means of mercury in presence of sulphuric acid, and measure the nitric oxide obtained. This reaction is also employed for the determination of nitric acid by means of Lunge's nitrometer.

By conversion to ammonia.—This method is employed in several modifications, of which the following one is most to be recommended. The nitrate is decomposed by finely pulverised zinc (zinc dust) and iron, in presence of potassium hydroxide; the flask in which the decomposition takes place is connected with a condenser and receiver, the latter containing a measured volume of a standard acid. On boiling the solution, ammonia escapes, and becomes absorbed by the acid in the receiver. The surplus acid is then titrated, and the ammonia estimated from the amount of acid which it has saturated.

Schulze's method: The volume of hydrogen generated by the action of potassium hydroxide upon a known quantity of aluminium, and collected in a special apparatus, is measured. The test is then repeated under the same conditions, but in presence of the nitrate to be analysed. The difference in the volumes of hydrogen obtained in the two experiments represents the quantity of ammonia formed from the nitric acid, and which has passed into solution. The calculation is made according to the equation:

$$HNO_3 + 8H = NH_3 + 3H_2O.$$

Nitric acid can also be quantitatively converted to ammonia in acid solution. The nitrate is heated with tin (50 gr. Sn : 1 gr. HNO_3) and 20 per cent hydrochloric acid (60 gr.), or with iron dust and sulphuric acid. When the reduction is complete, sodium hydroxide is added to the solution, and the ammonia distilled into a receiver filled with standard sulphuric acid. The remaining operations are the same as above.

By conversion to nitrogen.—This method is described in

Section III., Determination of Nitrogen in Organic Bodies. The volume of nitrogen obtained corresponds to the nitric acid originally present.

Titration with indigo solution, although unreliable, is a convenient method, and is usually employed in the estimation of nitric acid in water.

Nitrous acid is determined by conversion to nitrogen, or by its oxidising action upon ferrous salts, the methods being the same as for nitric acid. Its determination by titration of its very dilute solution (1 : 5000) with potassium permanganate is less exact. The reaction involved is as follows:

$$5HNO_2 + 2HMnO_4 = 5HNO_3 + 2MnO + H_2O.$$

The details of the method are explained in the *Zeitschrift für anal. Chemie,* 1883, p. 95.

PHOSPHORUS

§ **136. Phosphoric Acid.**—The free acid in aqueous solution may be evaporated to dryness and ignited with a weighed quantity of lead oxide. Cases where this is permitted, however, very rarely occur. The combined acid is usually thrown down as ammonium magnesium phosphate (often after preliminary precipitation as ammonium phosphomolybdate, mercurous or stannic phosphate). The gravimetric determination as uranium phosphate is likewise exact. Before discussing the various methods, it may be well to call attention to the readily occurring transition of phosphoric acid to the meta- and pyrophosphoric compounds, which result not only on fusion of phosphates, but even when the residue obtained by the evaporation of their solution is heated to 150° C. Since the properties of metaphosphates and pyrophosphates prevent their determination as such, these compounds must first be converted to the ortho-salts. This object is most easily obtained by fusion with 4-6 parts of sodium carbonate, the method being applicable not only to the alkali salts, but in general, to all phosphates which are completely decomposed by fusion with sodium carbonate. The phosphates of the metals of Group II. (with the exception of magnesium) are treated in this manner. Long-protracted boiling with sulphuric acid constitutes another method of converting the meta- and pyro-salts into orthophosphates. This method is convenient for the determination of free meta- or pyrophosphoric acid, or salts which form insoluble sulphates. Any other acid can be substituted for sulphuric, but one should be chosen which will precipitate the metal of the phosphate, so that the phosphoric acid will be in the free state. A large excess of acid and long-continued boiling (or, still better, heating in a sealed tube) assist the transition, but the reaction is quantitatively procured only with difficulty.

1. *By precipitation as ammonium magnesium phosphate.*—The solution of the phosphate is treated with magnesia mixture,[1] in presence of ammonium chloride, as long as a precipitate continues to separate. Ammonia is then added (it must impart a strong odour to the solution and represent at least a fourth of the total volume), and the beaker is covered with a watch-glass and allowed to stand for from twelve to twenty-four hours. The precipitate is then collected on a filter and washed with dilute ammonia (1 part aqueous ammonia, 3 parts water). The final processes of the estimation are explained in § 120. A pure precipitate is usually obtained by this method; if for any reason it seems impure, it should be dissolved in hydrochloric acid and again thrown down by magnesia mixture and ammonia. Phosphoric acid is also reprecipitated as ammonium magnesium phosphate subsequently to its being thrown down according to one of the following methods. The latter are employed only in separations.

2. *As ammonium phosphomolybdate* (inapplicable in presence of reducing substances and of certain organic acids, such as tartaric, etc.)—The reagent used is a solution of ammonium molybdate in nitric acid (1 part of the salt in 15 parts HNO_3 of sp. gr. = 1·2. The liquid is usually called "molybdate

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[1] The so-called magnesia mixture is prepared as follows: 83 gr. crystallised $MgSO_4$ are dissolved in boiling water, and after the addition of 5 c.c. HCl, precipitated with 82 gr. crystallised $BaCl_2$. The solution is then filtered, the filtrate tested for barium (if present, more $MgSO_4$ is added), and solution and wash water evaporated on the water-bath. The concentrated liquid is next poured into a liter measuring flask, 165 gr. NH_4Cl and 260 c.c. NH_4OH are added, and the mixture is then brought up to the liter mark with water. After standing for some days (and refiltration, if necessary) the liquid is ready for use. The same mixture can be more easily prepared by the solution of 100 gr. crystallised $MgCl_2$, 140 gr. NH_4Cl, and 200 c.c. NH_4OH in 1300 c.c. water.

solution "). The solution of the phosphate is concentrated by evaporation if necessary, and a great excess of molybdate solution added (about 40 parts to one of phosphoric acid). The beaker is then allowed to stand for an hour or two at 80°-90° C. The clear supernatant solution is tested again with the reagent, and if the precipitation was complete, is filtered through a small filter, and the precipitate washed with the molybdate solution and water (equal volumes). When thoroughly washed, it is dissolved in ammonia on the filter, and the latter carefully washed with the same reagent. Some hydrochloric acid is then added to the filtrate, and the phosphoric acid precipitated with magnesia mixture as in 1. The method is accurate, but attention should be paid to the fact that the quantity of phosphoric acid to be precipitated must not be large (not more than 0·1 gr.) The presence of either arsenic or silica influences the reaction, and these substances must therefore be removed, if present, before the precipitation is made. The following method is less convenient.

3. *As mercurous phosphate.*—The phosphate is dissolved in nitric acid and heated in a porcelain dish with metallic mercury, the latter being added in such a quantity that a portion remains undissolved. The nitric acid is next removed by evaporation to dryness on the water-bath, the residue treated with hot water, filtered, and washed. The dried precipitate is then rolled up in the filter, placed in a platinum crucible with sodium and potassium carbonates, and ignited until the mercury has entirely escaped. The fusion-product is dissolved in hot water, and the solution neutralised with hydrochloric acid and precipitated as in 1.

As stannic phosphate.—The salt is dissolved in nitric acid, 9 parts of metallic tin added, and the solution boiled for five or six hours. The precipitate is first washed by decantation, then on the filter. It is finally dissolved in nitric acid, treated with ammonia and ammonium sulphide, and the phosphoric acid precipitated directly, according to 1. (This method is often employed in separations.)

4. *As basic ferric phosphate.*—The solution is mixed with a known quantity of ferric chloride (prepared by solution of a weighed piece of piano wire). Sodium acetate is then added and the mixture boiled. Acid solutions must be pre-

viously neutralised by ammonia. The boiling solution is filtered, and the precipitate washed with water (containing ammonium acetate), dried, and ignited in the air. It is next moistened with nitric acid and the ignition repeated. The weight of the precipitate, minus that of the ferric oxide used, equals the weight of the phosphoric acid present in the substance.

As uranyl pyrophosphate (the method cannot be employed in presence of aluminium).—The phosphate should be dissolved in acetic acid if possible. If other acids are present they can be removed by evaporation with ammonia and ammonium acetate (if a precipitate separates, it is to be dissolved in acetic acid). Uranyl acetate is next added, and the solution boiled. The uranyl ammonium phosphate which precipitates is washed by decantation, being boiled up on each addition of the wash water, and finally on the filter with water which contains a small quantity of ammonium nitrate. Ignition of the precipitate yields the pyrophosphate $(UO_2)_2P_2O_7$, which is weighed.

Phosphates.—Not only must the various methods of determining phosphoric acid be learned, but also certain rules concerning their application in the separation of the acid from the metal in phosphates. The method to be chosen often depends upon the requirements of the analysis, *i.e.*, whether only the metal or the phosphoric acid is to be determined, or the analysis is to include both constituents. Phosphoric acid is removed from alkali salts by means of lead acetate (the excess of lead with hydrogen sulphide), or with silver nitrate and carbonate. (The silver is precipitated by HCl.) The precipitate of lead phosphate (and also the barium, calcium, and strontium salts) is next treated with sulphuric acid and alcohol, and the phosphoric acid determined according to 1. The alkalies can also be separated from phosphoric acid by the addition of a known quantity of magnesium oxide in presence of ammonium chloride, evaporation to dryness, and ignition (to remove ammonium salts). The alkali chlorides are then extracted from the ignited residue with water, and the residue again ignited. The gain in weight over that of the magnesium oxide taken shows the quantity of phosphoric anhydride. The separation of phosphoric acid from iron and aluminium is much more arduous, and several methods have been employed for this purpose. The one most usually employed, and which, indeed, is applicable to the separation of phosphoric acid from all the metals (of all groups), is that depending upon its preliminary precipitation as ammonium phosphomolybdate, according to 2. The method involving precipitation as mercurous phosphate (3) affords a separation from all the metals (except aluminium and mercury), but neither this nor the precipitation of the stannic salt is often used To analyse the phosphates of Mn, Zn, Co, Ni, the substance may be fused with sodium carbonate, extracted with water, and the solution acidified and precipitated as in 1. The phosphoric acid in fertilisers and bone-char is usually determined by volumetric methods.

Remark.—Arsenic acid is precipitated as ammonium arsenomolybdate, uranyl ammonium arsenate, and as ferric arsenate, under the same conditions as are required in the corresponding methods of estimating phosphoric acid.

Phosphorous and hypophosphorous acids are determined by conversion to phosphoric acid. This end is readily attained by heating the substance with nitric acid (sp. gr. 1·3) in a sealed tube at 150° C. After having been subjected to this heat for several hours, the tube is opened and the phosphoric acid estimated by the method given in 1. Evaporation with nitric acid and lead oxide gives less satisfactory results. For the indirect determination based upon precipitation of the phosphorous or hypophosphorous acid with mercuric chloride and estimation of the mercurous chloride formed, see § 127 *b* (Rose's method).

Separation.—Phosphoric acid is usually separated from the acids already mentioned by one of the above methods. Its separation from fluorine, however, requires a special method. The solution is precipitated with calcium chloride and lime-water (added until the reaction has become alkaline), in a vessel in which it is protected from the air. The precipitate is washed, ignited, and weighed. A known quantity is then heated with concentrated sulphuric acid until the hydrofluoric acid has been entirely removed, and the phosphoric acid and calcium oxide determined in the residue: the fluorine is calculated from the results and the original weight of the precipitate. In compounds which are insoluble in water, and not decomposed by sulphuric acid, all the other constituents are determined and the phosphoric acid found from the difference (used in the analysis of apatite, phosphorite, etc.)

BORON

§ **137. Boric acid** forms no easily determined and thoroughly insoluble salts; and, in addition to this difficulty, the acid solution (aqueous or alcoholic), of a borate cannot be evaporated without loss ensuing from the volatilisation of the boric acid. The latter impediment may be overcome by the addition of sodium carbonate to the solution, but in the majority of analyses, the other constituents of the substance are first determined, and the boric acid calculated from the difference. The method proposed by Strohmayer, which consists in the formation of the sparingly soluble salt, KBF_4, by the action of hydrofluoric acid and potassium hydroxide upon borates, is inaccurate (in several direct analyses the average error was – 2·0 per cent). For Rosenbladt's method, which is based upon the action of methyl alcohol and sulphuric acid upon the borate, see *Zeits. f. anal. Chemie*, 1887, p. 18. The same principle has also been employed by Gooch (*Chemical News*, **55**, 7), and Moissan (*Comptes Rendus*, **16**, 1087); the two latter methods are to be especially recommended.

SILICON

§ **138. Silica.**—Analyses in which the determination of silica is necessary are usually those of mineral silicates. The points most important in the analysis of silicates are the following: 1. The reduction of the mineral to as fine a powder as possible. 2. The conversion of the silicic acid to the insoluble condition: this is especially important. 3. Cautious ignition (envelopment in the filter). 4. Tests of the purity of the silica obtained (they are given below). The metals contained in the silicate are obtained in hydrochloric acid solution after the silica has been precipitated, and are separated by the usual methods. A departure from this method of separation is explained in the Examples of Gravimetric Analysis.

1. *Silicates which are decomposed by hydrochloric acid* (those

which dissolve, and many which do not dissolve, in water).—The well-pulverised silicate (previously ignited) is thoroughly moistened with a few drops of water, in a porcelain or platinum dish, by means of a glass rod. It is then covered with hydrochloric acid (nitric is substituted if silver or lead be present) and heated on the water-bath, the mixture being repeatedly stirred during the operation. The reaction may be considered finished when no more grains of the unaltered mineral can be felt, and no grating is caused on stirring with the rod. In regard to the duration of time necessary for the decomposition, and also to the external appearance of the silica obtained (pulverulent or gelatinous), the different silicates show a varying behaviour. As soon as the decomposition has been thoroughly effected, the solution is evaporated to dryness on the water-bath: it is necessary to have the residue completely free from hydrochloric acid, and this is sometimes attained only after it has been moistened with water and again evaporated. The operation may be shortened (but with less advantage), if the residue be heated to 130°-140°. The dish is next allowed to cool off, and the residue moistened with hydrochloric acid, stirred, set aside for half an hour, and finally warmed on the water-bath, and treated with hot water. The silicic acid is washed by decantation with hot water, being well stirred each time, and finally transferred to a filter, where the washing is completed (still with hot water). The thoroughly dried precipitate is ignited (it should first be wrapped up in the filter), the operation being cautiously performed at first; stronger heat is applied as soon as the filter has burned away, as hydrated silica is difficultly freed from the last traces of its water. The crucible must be allowed to cool in an exsiccator, as silica is very hygroscopic. When its weight has been ascertained, the purity of the silica is tested by boiling with concentrated hydrochloric acid and filtration. After the residue has been washed and re-ignited it is again weighed.

According to Mitscherlich, the finely-divided silicate is heated in a sealed tube of Bohemian (difficultly fusible) glass with concentrated sulphuric acid (3 parts H_2SO_4, 1 part H_2O). The tube is kept at a temperature of 210° C. for two hours, opened, and the contents removed and evaporated to dryness, etc., as above. The method is especially convenient for the determination of ferrous oxide in silicates. Jannasch has developed a similar method, which consists in heating the mineral with concentrated hydrochloric acid at 200° C. in a sealed tube (*Zeitschrift für analytische Chemie*, vol. xxx. p. 336).

Silicates which are not decomposed by acids. 2. *Fusion with sodium and potassium carbonates.*[1]—The very finely powdered silicate is mixed with sodium and potassium carbonates, or with the sodium salt alone, an intimate mixture being secured by means of a glass rod or platinum wire, and the latter finely rinsed off by more of the carbonates. The whole substance should not fill more than half the crucible. A gentle heat is at first applied, which reduces the substance to the form of a coherent porous mass, from which the carbon dioxide can quietly escape. As soon as the evolution of the latter has ceased, the crucible is more strongly heated, and its contents brought into a state of fusion. The glowing crucible is then placed upon a clean thick iron plate, the sudden cooling preventing the substance from adhering to the sides of the crucible. The mixture is now removed to a beaker (if a portion still clings to the crucible, the latter is also placed in the glass), covered with water, and hydrochloric acid added. The glass must be kept covered by a large watch-glass during the operation. When the evolution of carbon dioxide has ceased, the watch-glass is rinsed with hot water (the crucible also taken out of the liquid and washed). The contents of the beaker are then heated, whereupon the residue goes more or less completely into solution. As soon as the dissolved carbon dioxide has been driven off, the liquid is poured into a porcelain or platinum dish, evaporated to dryness, and the residue treated as in 1. If a portion of the silicate has been left undecomposed (which is ascertained by rubbing the bottom of the vessel with a glass rod, see 1), the analysis should be made again. The residue can also be filtered off, and the unaffected portion determined and subtracted from the amount taken for the analysis, but this method gives less satisfactory results. The dry residue of silica must be treated several times with fuming hydrochloric acid, rewashed, ignited, and

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[1] Compare p. 257, footnote.

weighed. Furthermore, when the aluminium of the silicate is precipitated, it will always be found to contain a small quantity of silica; the aluminium oxide must be twice digested with hydrochloric acid, and the weight of the residual silica determined and added to that of the chief portion.

The following methods are employed for the determination of the alkali metals in silicates which are not decomposed by acids:

3. *Ignition with barium oxide, calcium oxide, etc.*—The decomposition of silicates by ignition with barium carbonate requires a higher temperature than can be obtained by the usual means; but with barium oxide the reaction is more easily obtained. Four parts of anhydrous barium oxide (obtained by ignition of the crystallised oxide) are taken for each one of the silicate, and the mixture placed in a crucible and covered with a layer of barium carbonate. A silver crucible should be employed if possible, as the mass then rarely fuses, but merely becomes baked. The crucible and its contents are next placed in a beaker and treated with water, hydrochloric acid is added, and the solution evaporated, etc., as in 1. Calcium oxide is employed in the same way. A method has recently been proposed in which the reaction takes place in presence of barium chloride, if barium oxide is employed, of calcium chloride if calcium oxide (or carbonate) is used. Fusion with ammonium chloride (1 part) and precipitated calcium carbonate (8 parts) has also been recommended. The addition of the chlorides serves to make the mass more readily fusible. They are converted to oxides during the operation, by the action of the oxygen of the air.

4. *With hydrofluoric acid.*—The finely-pulverised silicate is covered with hydrofluoric acid and stirred about in the dish (of platinum) with a platinum wire. The mixture is then warmed for some time on the water-bath, and sulphuric acid (1 : 1) finally added in a quantity sufficient to convert all the metals of the silicate into sulphates. It is then evaporated to dryness and heated until all the sulphuric acid has been removed. The silicon escapes as silicon fluoride, and the excess of hydrofluoric acid also volatilises during the operation. When the residue has cooled off, it is treated with concentrated hydrochloric acid, set aside for an hour or so, and eventually diluted

with water and heated. If the operations have been properly made, complete solution is hereupon effected: should a residue still remain, it must be filtered off and again treated with hydrofluoric acid in the same manner (for a second method of decomposing silicates with HF, see Examples of Gravimetric Analysis). The method can be simplified by the use of gaseous hydrofluoric acid. Fluor spar and sulphuric acid are placed in a leaden box, inside which, and about half-way up the side, is fitted a ring of the same metal for the support of the platinum dish containing the silicate and sulphuric acid. The box is then shut by a leaden lid and allowed to stand for some days in a warm spot. When the reaction is complete the platinum dish is placed inside another one, somewhat larger, and evaporated with concentrated sulphuric acid. It is then ignited in the same manner as above. The silica can also be estimated by this method, by the use of a special platinum apparatus, in which the silicon fluoride is absorbed by ammonia and the resulting solution precipitated as potassium silicofluoride (§ 133). Silicates can also be decomposed easily by ammonium fluoride (4 parts), and the method yields accurate results. The mixture is moistened with sulphuric acid and heated, first on a water-bath, subsequently over the open flame, until the sulphuric acid has nearly escaped. The further treatment necessary is described above. As a modification of this method, the silicate is sometimes treated with ammonia and hydrofluoric acid, evaporated to dryness, and the easily fusible residue heated until the ammonium fluoride has escaped. Sulphuric acid is then added, etc., as above. Jannasch and Locke have recently proposed the use of lead oxide as a decomposing agent for silicates. The details of the method are described in the *Zeitschrift f. anorgan. Chemie,* Bd. VI. S. 321. (For the use of acid potassium fluoride in the analysis of silicates, see § 55.)

Separation.—The separation of silica from other acids must be considered, as well as that from the metals. The general methods of silicate analysis — fusion with alkali carbonates, decomposition with hydrochloric or nitric acid, and the subsequent operations—effect the separation of silica from all the acids. When fluorine is present, only fusion with the alkalies can be employed, and certain modifications are necessary in the further treatment of the substance. The fused mass is boiled out with water, filtered, and the residue washed with hot water and subsequently with ammonium carbonate. The filtrate is heated with ammonium carbonate (which must be re-added from time to time), again filtered, and the precipitate washed with ammonium carbonate. The second filtrate contains all the fluorine, which is now determined as in § 133. The various precipitates obtained are treated together, and their silica determined according to § 138 1. Silicates often contain not only fluorine but also *phosphoric acid.* The silica is separated in this case, also, by means of ammonium carbonate (see above). The separation of silica from *titanic acid* is very difficult, and is sometimes only to be accomplished by the determination of the former from the difference (by treatment with hydrofluoric acid and removal of the silica as silicon fluoride). In direct determinations, when possible, the mixture is fused with acid potassium sulphate and, after cooling, the mass treated with cold water and the silica filtered off. The titanium is then precipitated from the filtrate as metatitanic acid by boiling (§ 55).

CARBON

§ 138. (*b*) **Carbonic Acid.** *Free carbon dioxide.* 1. *In a mixture of gases.*—When the mixed gases contain a sufficient quantity of carbon dioxide, the latter is estimated by absorption in potassium hydroxide. The gas is measured over mercury with the usual precautions, and its carbon dioxide absorbed either by passage through a solution of the alkali, or by a solid moistened lump of the latter, which is introduced into the gas by means of a platinum wire. The loss in volume is then measured, and equals that of the carbon dioxide.

2. *In aqueous solution.*—Carbon dioxide in aqueous solution is gravimetrically determined by precipitation as calcium or barium carbonate. A solution of barium chloride (or calcium chloride) is mixed with an excess of ammonia, heated to boiling, and filtered, without exposure to the air, from the precipitate which separates. The mixture, freshly prepared in this manner for each determination, is then precipitated by a measured volume of the carbon dioxide solution and heated on the water-bath. The barium carbonate obtained is filtered, washed, and weighed.

In carbonates.—The carbonic acid is driven from the salt and determined from the loss in weight; or absorbed by a weighed medium and directly estimated.

1. *Determination from the loss of weight. By ignition.*—In certain cases carbonic acid can be determined from the loss simply by ignition (in the carbonates of zinc, cadmium, lead, copper, magnesium, etc.); the weight lost by the crucible corresponds to that of the carbonic acid. In the analysis of salts containing water of crystallisation, the substance is ignited in a weighed bulb-tube of difficultly fusible glass, which is connected with a calcium chloride tube to absorb the water (see below). The latter is also weighed before the operation. The loss in weight of the bulb-tube after the ignition equals the weight of the carbonic acid plus that of the water; the increase in the weight of the calcium chloride tube represents the quantity of water, and the difference between the two data, the carbonic acid. This method of ignition may be modified by the addition of a non-volatile acid or, with still greater advantage, of fused borax, to the substance before ignition. A known amount of borax (about 4 parts) is added to the weighed carbonate, and the mixture weighed again and then ignited. The weight lost on ignition represents the carbonic acid.

By liberation with acids.—This method requires a special apparatus, for which very many forms have been proposed. All, however, are based on a common principle, which the description of the following modification explains. The simplest apparatus consists in an Erlenmeyer flask of not more than 100 c.c. capacity (a larger flask would be too heavy), which is closed by a doubly perforated cork. In one hole is inserted a tube reaching to the bottom of the flask, and the lower end of which is bent upward and drawn out to a narrow opening (it serves for the entrance of air, etc.) In the second perforation of the cork is fitted a calcium chloride tube (to dry the carbonic acid liberated). The apparatus is filled with dilute nitric acid (1 : 5) to one-third of its capacity. A platinum wire is wound about the neck of the flask, and its loose end fastened to a small glass tube which is sealed at one end, and forms a receptacle for the substance. The preliminary arrangement having been completed, the weight of the apparatus is ascertained, the substance (small lumps are preferable to powder) placed in the proper tube, and the apparatus reweighed. The gain equals the weight of the substance. To make the determination, the platinum wire is unwound from the neck of the flask, the cork removed, and the tube and its contents dropped in. The cork is then quickly put back, and the apparatus set aside until the carbonate has completely dissolved. The carbon dioxide which is set free must necessarily pass through the calcium chloride tube. A rubber tube is next attached to the end of the latter, and a very gentle current of air drawn (preferably by means of an aspirator) through the liquid, which is at the same time slightly heated. In its passage the air drives the carbon dioxide from both the solution and the flask. The suction is continued for five minutes, and the apparatus then weighed. The loss in weight gives the quantity of carbon dioxide.

2. *By liberation and absorption.*—This method is perhaps the most accurate. The carbon dioxide is most advantageously absorbed in a concentrated potassium hydroxide solution (1 part KOH; 2 parts H_2O), which is contained in a special apparatus called a potash bulb (Liebig's bulb, etc.; see Section III.) The potash bulb is usually fitted with a small tube containing lumps of potassium hydroxide, to keep back the small quantity of water which a rapid current of gas may take up from the alkali solution.[1] To make a carbonic acid determination, the apparatus is set up as follows. The flask in which the carbonate is to be decomposed is closed by a cork provided with two holes, through one of which passes a funnel tube (for the introduction of the acid), extending to the bottom of the flask. In the other hole is inserted a tube which is connected with a calcium chloride apparatus (to dry the carbon dioxide). The potash bulb, which has previously been filled with potassium hydroxide solution and weighed (or a U-tube containing soda-lime), is then attached to the calcium chloride tube. The apparatus having been arranged, the weighed substance is placed in the bottom of the flask (in a small tube), and water and acid added through the funnel. The liberated carbon dioxide passes through the calcium chloride tube, where it is freed from moisture, and is absorbed in the caustic potash.

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[1] Soda-lime (Mulder) is less convenient as an absorption agent for carbon dioxide. When used it is placed in a U-tube.

When the evolution of the gas has ceased (when no more bubbles can be seen to pass through the potash bulb) the absorption tube is connected with an aspirator by rubber tubing, and a current of air cautiously sucked through the apparatus, in order to drive all the carbon dioxide into the potash bulb. The increase in weight of the latter gives the quantity of carbonic acid.

Many carbonates may also be directly analysed by volumetric methods (*e.g.*, the alkali carbonates; see Alkalimetry).

HYDROGEN, OXYGEN

Water. *Determination from the loss.*—Salts lose their *water of crystallisation* under various conditions. It escapes from some on exposure to the air (efflorescence); from others on drying over sulphuric acid in a bell-jar (or in a vacuum). As a rule, however, the water of crystallisation must be driven out by heat, which in the case of some salts need be raised only to 100° C., with others, still higher – 200°, 250°, etc. If a salt contain several molecules of water, it often happens that they will escape at different temperatures. The ease with which the hygroscopic or mechanically bound water of different substances can be removed also varies; it usually escapes at 100° C., but sometimes, especially in the case of minerals, intense ignition is required. The determination is made in all cases in the following manner. The fairly-well pulverised salt is dried by pressing between two thicknesses of filter paper, or if it is not hygroscopic or efflorescent, simply by exposure to the air. A weighed portion (the weighing is most conveniently performed in one watch-glass covered by another, the two being held together by a clamp) is then placed upon a watch-glass, and at first warmed to 100° C. in a water-bath or air-bath. To ascertain whether the volatilisation of the water is complete, a still higher heat is then applied—usually 140°-150° C. If the substance withstands this heat and the weight remains unaltered, the experiment may be considered finished. The loss in weight equals the weight of the water. For the determination of hygroscopic water present in substances which resist a high temperature, ignition may be employed. The details of the operations will be explained among the Examples. A salt often loses volatile constituents, other than its water, on being heated, and to avoid this difficulty a sufficiently low temperature must in such cases be employed. If an acid may be driven off on heating, the resulting error is prevented by the addition of ignited lead oxide to the substance in which the water is to be determined. The conditions necessary for the determination of water in different compounds vary so among themselves, that a description of them all is impossible in this book.

By absorption.—The water is absorbed by calcium chloride, which has previously been either thoroughly dried or fused (anhydrous). The calcium chloride is placed, in small lumps, in a glass tube (the form varies) of thin glass, which terminates in a narrower tube. The other end is closed by a cork in which is inserted a thin glass tube. To provide against the loss which might ensue through a rapid current of air carrying away particles of calcium chloride, a small piece of cotton or glass wool is placed in each end of the apparatus (not in the narrow tube). Such an apparatus is called a calcium chloride tube. The direct determination of water is employed when the substance cannot be dried without loss or increase in weight (for instance, without giving off or absorbing carbon dioxide), or in the estimation of hydrogen (in acid salts, etc.), and the conditions involved vary in each instance. The substance is placed in a bulb-tube, one end of which is connected with a weighed calcium chloride tube, and the other with a gasometer and an apparatus for drying the air. A current of dry air is then passed through the bulb-tube, and the latter heated; the water volatilises and is collected in the calcium chloride tube. If the substance parts with an acid on being heated, the experiment is made in presence of lead carbonate; when not only the water, but also the hydrogen which the substance contains is to be determined, the latter is mixed with lead chromate or cupric oxide (when nitrogen oxides are apt to form from the decomposition, or halogens are released, metallic copper is placed behind the mixture). It is then placed in a glass tube, one end of which is sealed up and the other closed by a perforated cork, through which passes the calcium chloride tube. The glass tube is laid in a specially-constructed oven, and on its being heated (the determination can also be made in a current of dry air), the water escapes and is received in the calcium chloride tube. The increase in weight of the latter gives the amount of water present. We cannot enter into the details of the operation here; it is the same method as is employed in the analysis of organic bodies. The heat is generated in a gas or charcoal furnace, such as is used in organic combustions (see Section III.; Analysis of Organic Compounds).

As a much simpler method of determining the water in substances in which there are other volatile constituents (such as silicates containing fluorine), Jannasch and Locke recommend the following: The weighed substance is mixed with lead oxide in the bulb of a bulb-tube, the posterior arm of which contains a layer of lead oxide. A current of dry air is then passed through the tube, and the substance heated to fusion. The lead oxide over which the aqueous vapours pass retains the hydrofluoric acid, etc., and the water is collected in a calcium chloride tube and weighed. For the estimation of water in hygroscopic substances the same principle can be employed; the substance is first dried to constant weight by passing a rapid current of dry air over it, in a specially constructed apparatus. The details of both methods will be found in the *Zeitschrift für anorganische, Chemie*, Bd. VI. S. 168, 174.

OPERATIONS AND EXAMPLES

We have now become acquainted with the principal methods of quantitative determinations and separations of the various elements. The operations which they involve still require explanation, and will form the subject of this chapter; a series of examples is annexed, to give the student an opportunity for familiarising himself with both the operations and principles of gravimetric analysis.

§ 139. **Selection of the Substance.**—When a substance is to be quantitatively analysed, caution must be used in selecting a homogeneous portion, and all impurities must be removed, if the results are to really express the true composition of the material. The homogeneity of chemical compounds is most readily recognised from the crystalline form; the chance impurities being in this case removed by repeated recrystallisation. Upon the choice of a well-crystallised and homogeneous portion depends the accuracy of the results. Substances which are insoluble in water can sometimes be selected in the same manner; many of them form well-defined crystals, the conformity of which can be ascertained through the microscope. Amorphous, insoluble substances must be thoroughly washed, etc.; but their homogeneity cannot be so absolutely guaranteed. The material for the analysis of a mineral is also more difficult to prepare. It must be freed as much as possible from the rock in which it was embedded, or its matrix, and only the purest pieces selected. For this purpose a strong magnifying glass or magnet, etc., must often be used. The precaution of having good material for analysis having been observed, the analysis may be commenced immediately, if the qualitative composition of the substance is known. It must be ascertained by qualitative analysis, which of the constituents are the more prominent, and which (in minerals, etc.) exist only in small quantities or traces. This information determines to a large degree the choice of methods of analysis.

Pulverisation.—The substance used in the following analytical operations must be in the state of powder, to which it is reduced in an agate mortar. Crystallised salts can be easily pulverised (a porcelain mortar can be used in such cases), but to obtain minerals, etc., in a finely-divided state is a much more difficult task. A few large pieces are crushed in a steel mortar, or, if the latter be unavailable, wrapped in several folds of paper, and broken by striking with a hammer upon a steel anvil. The finer pieces thus obtained are then further reduced in an agate mortar. Substances which dissolve readily in water or acids do not require so fine a division, but if their solution is to be effected by fusion, etc., the greatest care must be taken in their pulverisation. The treatment in the mortar must be continued until no more grittiness is felt when a sample is rubbed between the thumb and forefinger. Sometimes, indeed, a sufficient degree of fineness can be secured only by sifting. For this purpose the mouth of a wide-necked bottle is covered by a cloth, which is pushed down into the neck so as to form a small bag. The already finely-pulverised powder is then placed in this sack, covered by a piece of bladder or rubber cloth, and the latter bound about the bottle. On the latter being shaken, the substance passes through the cloth and collects in the bottom of the bottle. The finest powder is obtained by lixiviation. The pulverised substance is rubbed up with water in the mortar, and then thrown into a glass containing a large quantity of water. After being vigorously stirred, it is allowed to subside for a few minutes, and the turbid liquid decanted from the portion of the mineral which has settled, into another beaker: the residue is again subjected to the same operation. When enough substance has been lixiviated, the second beaker is set aside until the powder has completely settled, the water decanted off, and the residue dried in the same glass. Metals and alloys which are not brittle enough to be pulverised, are beaten into thin sheets, and the latter then cut up with a pair of scissors.

Drying.—Substances almost invariably contain hygroscopic water as an impurity, and this must be removed by drying before the analysis. The methods of drying vary greatly, since the hygroscopic water of some substances can be removed only with great difficulty, and a number of other bodies, on the contrary, especially salts with water of crystallisation, part with their constitutional water very easily. Salts with water of crystallisation are dried between layers of filter paper. They are first powdered, and then pressed several times between sheets of filter paper, being transferred to the fresh layers as rapidly as possible. When this operation has been finished, the salt is placed in a glass tube, fitted with a cork, and weighed without delay. Salts which do not effloresce can be dried in the air (on a watch-glass to constant weight) or, more rarely, under a bell-jar which stands upon a ground glass plate holding a vessel of sulphuric acid (the latter serves to dry the air—loss of water of crystallisation sometimes ensues by this method). Anhydrous substances are freed from their hygroscopic water by heating in an air-bath to 100° C. The air-bath is a small copper box which is provided with a door and a shelf to hold the substance to be dried. The heat is furnished by a lamp or Bunsen's burner, and the temperature measured by a thermometer passing through the roof of the bath. Steam-baths are also sometimes employed in the laboratory. These are fitted with double walls, and heated to 100° C. by steam. When a higher temperature is necessary the air-bath must be made of plate iron. Hygroscopic salts, of which the water of crystallisation is to be determined, can be dried in a current of dry air. The operation is best performed in a special apparatus, in presence of lead oxide (§ 138).

The substance to be dried is always placed on a watch-glass, and the complete removal of the water can be assumed only when two consecutive weighings give the same results. To guard against reabsorption of moisture, the watch-glass containing the substance is covered by another (both having their edges ground, to secure a good junction) and the two held together by a copper clamp during the weighing. Certain substances, finally, must be ignited before they completely release their hygroscopic water. For this purpose a platinum crucible is employed. The above operations are also employed in determining the water in salts, etc. (§ 138).

The Balance.—As this book is intended chiefly for beginners, I shall not endeavour to give a complete description of an analytical balance, but merely indicate the points which are requisite in a good apparatus. 1. When the support is lowered, the balance must be in equilibrium, and the needle either rest in front of the zero division of the scale, or oscillate through an equal distance on each side of it. 2. The equilibrium must not be destroyed by the removal of the pans. 3. Where equal weights have been placed in both pans and equilibrium obtained, the latter must not be lost if the weights be reversed, *i.e.*, placed in the opposite pan. 4. The delicacy and accuracy of the balance must be tested by weighing some body under the most varying conditions. The weight of a substance, shown by an accurate balance at the ordinary temperature, should never vary more than 0·0002 gr.

The weights used must also be proved. Since the weight of an object is always determined from the difference of two weighings, the weights must be compared with one another, *i.e.*, the equality between the two-gram piece and two one-gram pieces tested, and, in the same way, that of a one-gram piece with the sum of the smaller weights. Milligrams are usually weighed by means of a so-called rider.

The following rules must be observed in weighing. 1. The equilibrium of the balance must be tested and secured before each operation. 2. The beam must be freed gently from its supports. 3. No substance should be laid directly upon the balance pans, but always weighed in its proper vessel. 4. No substance or apparatus should be weighed while warm. It should be allowed to remain in the same room as the balance until it has attained the same temperature, before being placed in the pan. 5. Any change in the weights or substances must be preceded by the arresting of the beam. 6. The weights must be laid on the balance pan in a systematic way; they are counted, when equilibrium has been obtained, before being removed from the pan, and the results confirmed from the empty places in the weight-case.

The Operation of Weighing.—After being freed from moisture by one of the methods explained under Drying, the substance is weighed. If destined for some operation in which a platinum crucible is employed, such as fusion or mixture with another substance and subsequent fusion, the compound to be analysed is weighed directly in the crucible, the weight of the latter having first been ascertained. If, on the contrary, as is more frequently the case, the substance weighed is to be dissolved in water or an acid, in another vessel, it is placed in the balance in a thin glass tube provided with a stopper (which may be another glass tube, sealed at one end, and slightly larger in diameter than the first). The weight of the substance plus that of the glass having been ascertained, the cork is cautiously drawn and the requisite amount of the substance shaken into the beaker or flask. The stopper is then again inserted and the tube reweighed. The difference between the first and second weighings gives the amount of substance taken for analysis. It is advantageous to know the weight of the empty tube, as the first weighing then shows how much substance the tube contains, and the eye can readily judge as to when the requisite amount has been poured out.[1] This is especially convenient if several portions of one and the same substance are to be weighed off. In the determination of water by drying at 100° C., finally, the substance is weighed, as we have already stated, between two watch-glasses which are held together by a clamp. Warm apparatus must not be weighed until its temperature has fallen to that of the balance, for which purpose it is allowed to stand for some time (at least a quarter of an hour) in the room containing the latter. To prevent the absorption of moisture whilst cooling, the apparatus is placed in a glass vessel containing sulphuric acid or some other hygroscopic substance. Such vessels are called " Exsiccators."

The quantity of substance to be used in the analysis depends upon the number of constituents to be determined, and also to some extent upon the exactness of the method to be employed, the physical properties of the compound, and the probable amount of the constituent to be estimated. If several determinations must be made in one portion of the substance, from one to two grams are taken (it sometimes happens, when only traces of the constituent to be determined are present,

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[1] If the amount to be taken need only approximate a certain weight, it may conveniently be weighed off on a rough balance first, and then in the analytical balance.

that five or ten grams must be employed). When only one or two determinations are to be made, however, 0·5-1·0 gr. are entirely sufficient, and if the methods are accurate, less than 0·5 gr. are all that are necessary. The larger the amount weighed off, the greater becomes the accuracy obtained (since the sources of error involved in filtration, etc., decrease with the increase in quantity), but operations with a large amount of substance are far slower than when a small quantity is employed. Substances which are obtained during the analysis as gelatinous compounds (such as ferric, chromic, and aluminium oxides) can be most easily determined when only 0·2-0·5 gr. are employed. For the benefit of the beginner it may again be remarked that the substance weighed off must be perfectly homogeneous. If a salt with water of crystallisation, for instance, is to be analysed, it must either be first made anhydrous (the portion used for the water determination can usually be here employed), or weighed in the crystalline state: in the latter case it must be ascertained that no water of crystallisation has been lost by efflorescence or the like, and the material should be freshly crystallised if possible.

§ **140. Solution.**—In the greater number of instances, quantitative determinations involve the precipitation of the constituent from solution as one of its insoluble compounds. The vessel in which the substance is to be dissolved in water or acids, therefore, should be suitable for the subsequent precipitation. If the solution is to be hastened by warming, it is advisable to use a water-bath: an open flame or a sand-bath can sometimes be employed, but in such cases the liquid must not be permitted to boil, as a loss may be incurred through its spirting. If the passage of the substance into solution is accompanied by evolution of a gas (as in the action of acids upon carbonates), the operation should be slowly performed, the acid being added little by little, and the vessel covered by a watch-glass: the latter must be rinsed off when the reaction is complete. Solution of the substance in nitric acid, *aqua regia*, or the like, must be effected in a flask standing obliquely, or which, if upright, is covered by a watch-glass. If access of air to the liquid must be prevented (as in the treatment of ferrous compounds, etc.), a current of carbon dioxide or some other indifferent gas should be led into the vessel. There are two more preliminary operations which must be explained before we pass on to the further analytical processes; evaporation and fusion.

Evaporation.—If the volume of the solution must for any reason be reduced, before the precipitation, this is effected by evaporation, preferable in a platinum (for the use of platinum vessels, comp. Fusion) or porcelain dish. The use of glass vessels is to be avoided, as water and solutions attack glass to a very noticeable extent on prolonged heating. The heat is most advantageously supplied by a water-bath, or, in general, by steam. Fluids may also be concentrated, especially if their volume be sufficiently great, over the gas burner; a small flame must be employed, and allowed to bear directly upon the dish (the bottom of the latter must not be more than two-thirds of an inch above the top of the burner). The liquid, however, must never be allowed to boil (see Solution). Care must also be taken that no dust falls into the solution during the evaporation, as the filtration and washing thus entailed would increase the volume of the liquid again. Solutions in which precipitates are suspended must without exception be placed upon the water-bath, since, when an open flame is employed, bumping can never be avoided in such cases, especially if the precipitate be crystalline. Solutions which are to be evaporated to dryness are also heated on the water-bath. If the residue is to be weighed, the solution is first reduced to a small volume in a porcelain dish, and then transferred, with the aid of a glass rod (see Filtration) to a weighed platinum dish, in which the weight of the residue is finally to be ascertained. The evaporation of the liquid, to which has been added the rinse water of the porcelain vessel, is then continued, and the residue treated as required. To wash the porcelain dish, it is rinsed three times with fresh water, as small a quantity as possible being used each time, in order to avoid diluting the liquid more than necessary (if the dish be very small, only a few drops need be added at a time). The thoroughness of the rinsing is controlled by evaporation of a drop or two upon platinum foil. Before the residue can be weighed, it must be dried at 100° C., or a higher temperature if necessary. The determination of the alkalies, in presence of ammonium salts, by evaporation and ignition (a very frequently occurring case), is explained among the examples. If a difficultly volatile liquid is to be evaporated from a slight precipitate in a platinum crucible, the latter is placed in an oblique position and the flame directed against its upper half; if heated from below, the liquid can only with the greatest difficulty be prevented from spirting. This operation can be very conveniently performed in a muffle, the bottom of which is perforated near the back, for the introduction of the mouth of the burner, the apparatus itself resting on the triangle of the latter. The crucible fits into a hole made in the front part of the muffle's bottom. The use of a small, cup-shaped, air-bath is also advantageous for this purpose.

Fusion.—Substances which are insoluble in water or acids are brought into solution by complicated operations, such as ignition with a proper flux, *e.g.*, alkali carbonates, sodium carbonate and potassium nitrate, acid potassium sulphate, or the like; or by heating with concentrated sulphuric acid, hydrofluoric acid, etc. All of these operations must be performed in a crucible, generally of platinum. Platinum cannot be used when an alkali or barium oxide is employed as the flux, however (it is attacked by these compounds), and in such cases a silver crucible is taken. If the fusion causes the reduction of metals with low melting points, the latter form easily fusible alloys with the platinum, and the crucible may thus be attacked. Compounds of silver, lead, tin, bismuth, antimony, and arsenic, therefore, must be ignited in a porcelain, and not a platinum crucible. Lastly, operations in which chlorine, bromine, or iodine are set free (as in fusion with potassium chlorate under certain conditions) must never be conducted in platinum vessels.

These precautions must also be observed in the evaporation of liquids in platinum dishes, and the latter never be employed in operations with caustic alkali solutions, or those which evolve chlorine.

The reactions procured by fusion vary in each instance, and they are too many to be described in detail in this paragraph.

Precipitation.—This is the most frequent, and consequently the most important, operation in analysis. Special attention must be paid to securing the necessary conditions (*e.g.*, concentration of the solution, time, and other requisites for complete precipitation). These conditions have been pointed out in the description of the various gravimetric methods. The precipitation cannot be considered thorough, until it has been ascertained by a confirmatory test that enough of the reagent has been added to ensure a complete reaction. If the precipitation is to be assisted by heat, the operation should be performed in a beaker, or in a porcelain or platinum dish.

§ 141. **Filtration.**—This operation effects the separation of the precipitate from the liquid in which it was formed. For this purpose the solution is usually passed through a filter made of so-called filter paper; thin glass tubes, which are drawn out at one end, and in which the precipitate is caught by a layer of asbestos, may also be employed, though rarely resorted to.

The filters are made of rough, so-called Swedish paper, and cut in various sizes, either directly, after round patterns, or having first been twice folded, the second time in a direction at right angles to that of the first; in the latter case the pattern is in the shape of a quadrant (Mohr's patterns). The size to be used depends upon the bulk of the precipitate. The latter should fill about half, never more than two-thirds, of the filter. The weight of ash which a filter of each size leaves on combustion must be ascertained (the method will be described in the paragraph on Ignition of the Precipitate). When acid solutions are to be filtered, it is preferable to use filters which have been treated with hydrochloric acid, washed with water, and dried. Filters can be procured in the market which have been extracted with hydrofluoric acid, and the ash of which is already determined. These are almost always employed in quantitative work.

The funnel must be perfectly smooth and have an angle of 60°. The filter is chosen according to the size of the funnel; its edge must be at least a third of an inch below the rim of the latter. To insert the filter, it is folded twice in opposite directions, and then opened in such a way that three layers of paper form one side, and one the other. It is then placed in the funnel, moistened, and pressed smoothly against the sides of the funnel, with the forefinger, until no space is left for air bubbles (the precipitate cannot be completely washed otherwise). A filter folded in this manner will fit the funnel only when the latter has an angle of 60°. If this is not the case, the filter must be folded to a slightly obtuse angle, and then opened in the requisite way. In this manner a greater or lesser diameter may be obtained, and the filter consequently fit a funnel with an angle of either more or less than 60°. The water used to moisten the filter must be allowed to run through the funnel, and not be poured out. In the operation of filtration, the funnel is held by a special support (it is never advisable to insert it into the neck of the glass). The proper vessel—flask, beaker, or dish—is placed below it, in such a manner that the end of the funnel touches its side, and the liquid runs down the latter; the filtrate should never be allowed to drop from the end of the stem.

Filtration.—The operation of filtration must be commenced only after the precipitate has completely subsided and the supernatant liquid become clear (the precipitate, especially if it be crystalline, will otherwise pass through the filter). This may often be hastened by heating the liquid on the water-bath, or stirring it during the addition of the reagent; as complete precipitation usually requires some time, however, the precipitate will, as a rule, have subsided by the time it is finished. The filtration is performed as follows. The liquid is poured from the vessel along a glass rod, which is held against the rim or lip of the vessel, and extends to the side of the filter. When the funnel is full, the rod is placed in the beaker, care being taken in its removal, lest a drop of the liquid be thrown off and lost. It is advisable to grease the outside of the rim of the vessel before the operation is commenced. Both the beaker and the funnel should be covered by watch-glasses during the filtration, to prevent dust from falling into the solution. The supernatant liquid must first be filtered, the operator being careful not to stir up the subsided precipitate, and also not to add more than the filter itself will hold. The precipitate is transferred to the filter afterwards, the last traces being rinsed from the vessel with a little water. If small portions of the precipitate adhere obstinately to the sides of the vessel, they can be released by means of a large feather, cut away in such a manner as to leave only a small fan at the end of the quill; or with a glass rod, over one end of which is slipped a piece of rubber tubing. The particles clinging to the feather or rod are finally rinsed into the filter with the rest. After a little practice, also, the precipitate can be removed by a steady stream of water from the water bottle, the vessel being almost inverted over the filter. (It may sometimes, though very rarely, happen that the last portion of the precipitate must be redissolved in the beaker and again precipitated.) Solutions should be filtered while hot, if possible, as the operation is then much more rapid than when performed in the cold.

Washing.—The precipitate may be directly collected on the filter and then washed, or the operation may be preceded by decantation, as will be explained below.

Washing on the filter.—The liquid employed is usually water (sometimes alcohol, acids, ammonia, or the like). It is delivered from a wash-bottle, the tube from which the liquid flows being bound by rubber tubing to a glass tube with a fine outlet, so that the finger can direct the stream against any section of the filter. Hot water should be used whenever possible. The washing must not be commenced until all the original liquid has passed through the filter; the stream is then directed against the upper part of the filter, to which the precipitate must not extend. The filter is filled each time, and one portion of water allowed to run through completely, before another is added. It must not be forgotten to wash the upper edge of the filter, and, toward the end of the operation, to drive all the precipitate into the bottom of the cone. The precipitate cannot be considered washed until a satisfactory confirmatory test has been made (by evaporating a drop of the wash-water on platinum foil, adding a proper reagent, or the like). If the conditions are such that no confirmatory test can be made, the thoroughness of the washing must be judged from the quantity of water used. When the above rules are carefully observed, the precipitate need be washed, as a rule, only about five times. The operation must be finished in one day. Unwashed precipitates should never be allowed to stand over night on the filter and washed the next day. If the time is insufficient for the whole operation, the precipitate must not be transferred to the filter, but allowed to stand under water in the vessel in which it was formed.

The time required for washing precipitates may be materially shortened by using a flask, in the stopper of which the funnel fits air-tight, and sucking out the air by means of a water-pump, or, in case the latter is unavailable, by an aspirator. The method is inapplicable for gelatinous precipitates.

Decantation (see p. 35) alone is rarely employed, but when accompanied by filtration, is one of the most frequent analytical operations. It consists in pouring only the solution through the filter. The precipitate is treated with water (hot if possible) in a beaker, thoroughly stirred with a glass rod, allowed to settle, and the clear solution then filtered off. After this operation has been repeated several times, the precipitate is itself collected on the filter, and its washing there completed. This method ensures more perfect (and often more rapid) washing. If the precipitate is to be redissolved after its washing and again thrown out (double precipitation), it need not be brought on the filter at all, but, after thorough decantation, is redissolved in the beaker; the filter through which the solution was decanted must in this case be also washed with the solvent.

§ 142. Determination of the Weight of the Precipitate. I. *By ignition. Drying the precipitate.*—The precipitate having been washed, the next process is its drying; this is done without removing it from the filter or taking the latter from the funnel. The funnel is covered with a piece of paper, and the operator holds it in his left hand, while with his right he folds the edges of paper under, below the rim, in such a manner as to form a well-fitting and secure cover (beakers, containing solutions which must be protected from the dust, can be secured in the same way). The funnel is then placed in an air-bath and dried at 100° C.

Ignition.—Since the ignition of a precipitate involves the burning of the filter, it is necessary to know the weight of ash which the latter yields on combustion. Either a porcelain or platinum crucible can be used for the ignition, the choice depending upon the character of the precipitate, and platinum being given the preference whenever possible. The crucible must first be ignited and weighed alone. It is then placed upon a sheet of black glazed paper, the filter taken out of the funnel, and the dry precipitate cautiously transferred to the crucible. Its removal from the filter must be as perfect as possible, and can be accomplished most readily by gentle pressure of the latter with the fingers. The filter is next folded, wound about with a platinum wire, and set aside until the small pieces of the precipitate which have fallen upon the glazed paper have been swept into the crucible, by means of a feather fan. The next step is the burning of the filter. For this purpose the crucible is again placed upon the glazed paper, and the filter, enveloped in the platinum spiral, is held directly over it and lighted by the flame of a gas-burner, the latter being removed as soon as the filter is on fire. This preliminary burning affords a more perfect and rapid combustion. When the filter has ceased to burn or glow, the residual carbon is held in the apex of a low flame (still over the crucible) until all the residue has become white (*i.e.*, until the combustion of the carbon is complete). The wire is then either unwound or pulled straight, in such a manner that the ash will fall into the crucible beneath. The dust caught on the glazed paper having again been added to the contents of the crucible, the latter are ready for ignition. The degree of heat applied varies between wide limits. Subjection to the flame of an ordinary burner for fifteen minutes usually suffices, but a blow-pipe must at times be employed. When the operation has been finished, the crucible is allowed to cool in an exsiccator, and finally weighed. The increase in weight (over that of the empty crucible) gives the quantity of the precipitate plus that of filter ash.

The filter may sometimes, though very seldom, be ignited with the precipitate (only when the latter is finally divided, and therefore apt to be carried away on ignition, especially if a gas be evolved). In such cases the dry precipitate is rolled up in the filter, placed in the crucible, and the latter covered and very gently ignited, to secure the preliminary charring of the filter. When this has been attained, the cover is removed, the crucible placed in an oblique position, and a stronger heat applied until the carbon has completely burned away and the residue become white (the addition of ammonium nitrate is advantageous, when possible).

Remark 1. *The determination of the ash in a filter* is made in the manner described above. Ten filters are folded together, bound by a platinum spiral, and ignited with the same precautions. The ash is collected in a crucible which has previously been ignited and weighed. The weight of the ash obtained from the ten filters, divided by ten, gives that of each one, and this value must be subtracted from the weight of the ignited precipitate. The ash yielded by each size of filters must of course be determined.

Remark 2. *The platinum crucible.*—Operations with a platinum crucible involve several precautions, which, though in themselves slight, will in the end be found very valuable. The crucible employed must be perfectly clean and lustrous, both inside and out, and after each operation must be cleaned, dried, and polished. It may be cleaned by boiling with dilute hydrochloric acid, or, if this is insufficient, by fusing acid potassium sulphate in it, and rinsing the sides with the molten salt. It is polished by rubbing a little moist talc or fine sand over it with the finger, washing with distilled water, and igniting. For ignition, the crucible is placed on a triangle made of platinum wire, or, which is cheaper, of iron wire wound with platinum foil. Iron triangles protected by pipe-clay have recently been used with advantage, but the latter are unfitted for operations which involve protracted ignition, as in such cases they are apt to injure the platinum. Much caution is required in using the gas-burner for the ignition of platinum crucibles. Only the upper, non-luminous cone must be allowed to come in contact with the crucible; if a luminous flame, or, still worse, the inner cone, be employed (which at the same time produces less heat), it may lead to the formation of platinum carbide, which is very brittle, and completely destroy the crucible. The various substances for the ignition of which platinum crucibles cannot be used, have already been mentioned (see Fusion).

II. *Determination on a weighed filter* is employed when the ignition of the substance is impossible or involves complications in the analysis. The method is much more apt to give rise to errors than ignition. The filter to be used for the collection and drying of the precipitate must first be dried and weighed, the same temperature being employed as that intended for the precipitate (usually 100°-110° C.) The latter precaution is necessitated by the fact that the weight lost by the paper depends upon the temperature to which it is heated. The filter is weighed either between two watch-glasses, held together by a clamp, or in a light, wide weighing glass (or a glass tube, over which passes another of slightly larger diameter; see § 139, Weighing). As filter paper is extremely hygroscopic, it must be placed in an exsiccator to cool before being weighed. It is advantageous to weigh the whole apparatus without paying attention to the weight of the filter alone. The drying cannot be considered finished until two consecutive weighings give the same results. The precipitate is next collected upon the prepared filter, washed, and dried in the funnel, with the same precautions. The filter is finally taken from the funnel, folded about the precipitate, and placed between the watch-glasses or in the weighing glass previously used. It is then dried to a constant weight, at the same temperature as was employed to dry the filter in the first place. The increase in weight is equal to the weight of the precipitate. When acid solutions are to be filtered, greater accuracy is secured by washing the filter, first with dilute hydrochloric acid and then with water, before it is dried and weighed.

The determination having been finished, the quantity of the element is calculated from that of its compound. The calculation of results and their checks have already been explained (§ 114).

EXAMPLES

§ **143.** Laboratory practice in quantitative analysis has for its purpose the completion of the student's chemical training, by making him familiar with exact work. The time to be spent in fulfilling this object, and the proper period for beginning, depend entirely upon the progress of the student. As it is both impossible and unnecessary to go through all the quantitative operations, the work must be so conducted as to render the student capable of carrying out any analysis, the description of which has been given him, and to familiarise him with the principal methods. He must also learn how single reactions can be combined in quantitative separations, and when this has been attained, he must become able to compare them critically, so that he can exercise good judgment in choosing the methods which he thinks the best or most expedient in a given analysis. The point also, at which the student can give up quantitative analysis, depends only upon himself. It should at least be continued until he not only has complete confidence in his results, but can demonstrate their correctness. It is impossible to specify for all when this point is reached. One passes on rapidly, another more slowly; but it is always advisable to present the work in regular graduations, such as are seen in the following examples. In the references which these contain, paragraphs are denoted by §, the different analyses by No.

I

Practice is begun with simple determinations, for which the most accurate methods have been developed. If several determinations are to be made from the same salt, separate portions of the latter should be taken for each. These analyses should be made with pure compounds, in order to ensure the student a check on his results. If, for instance, the salt contains water, it should be freshly crystallised (repeated crystallisation is sometimes necessitated in obtaining the salt in a pure state), and the student must convince himself, furthermore, that no water of crystallisation has been lost, or, in general, that the composition of the compound taken for analysis is well defined. Compounds, the composition of which cannot be relied upon, should first be converted to the anhydrous state. A check on the analysis is found in the agreement or non-agreement of its results with the values required by theory.

1. **Barium Chloride,** $BaCl_2 + 2H_2O$.—How much water, barium, and chlorine does crystallised barium chloride contain? The pure salt (recrystallised if necessary) is pulverised, dried between two layers of filter paper, and immediately weighed off for the water determination.

Determination of water.—Weigh two watch-glasses, together with a clamp, and then place in one of them about 1·5 gr. of the salt. Clamp the two glasses together and weigh again; the difference is the weight of the salt taken. Dry in an air-bath, at a temperature of 125° C. (§ 138), separating the glasses during the operation, but shutting them together with the clamp again before weighing the dry substance. The salt cannot be considered perfectly anhydrous until the weight remains constant, *i.e.*, is the same in two consecutive weighings made at an interval of an hour. The loss in weight equals the amount of water of crystallisation. Calculate the result to percentage, and compare the value obtained with that required by theory (§ 114). Now transfer the anhydrous salt to a glass tube, and pour two portions of it from the latter into separate weighing glasses. One portion is for the determination of the barium (as sulphate), the other for that of the chlorine (as silver chloride).

Determination of barium, § 118.—Weigh off 0·7 gr.; dissolve it in water with application of gentle heat, and add a few cubic centimeters of hydrochloric acid. Then heat the solution to incipient boiling, and precipitate with dilute sulphuric acid (making a confirmatory test for complete precipitation). Keep the solution hot for some time, until the precipitate has thoroughly settled, and then filter (§ 141), washing the precipitate with hot water, first by decantation, and then on the filter (§ 141). The washing must be continued until the sulphuric acid is removed, *i.e.*, until the filtrate shows no precipitate on the addition of barium chloride. Dry the precipitate (§ 142), remove it from the filter to a weighed platinum crucible, and ignite the filter in a platinum spiral, letting the ash fall into the crucible (§ 142). Ignite the latter, containing both the precipitate and ash, for twenty minutes, and finally weigh. Calculate the barium found to percentage of barium chloride, and check the result by comparison with the percentage of barium in the anhydrous salt according to the formula, $BaCl_2$ (§ 114).

Determination of chlorine.—Weigh off about 0·5 gr. Dissolve this in water, and acidify with nitric acid. Precipitate with silver nitrate, heating the liquid to 70° C., and making a confirmatory test for the completeness of the precipitation; put the liquid aside for twelve hours. The subsequent operations are as in the determination of silver (§ 127). The quantity of chlorine is calculated from the silver chloride, and the results checked by comparison with the percentage of chlorine corresponding to the formula $BaCl_2$ (§ 114).

2. **Determination of Iron.**—How much pure iron is there in a piece of iron wire? Weigh off 0·15-0·2 gr. of piano wire (which must be clean and free from rust) on a watch-glass, and dissolve it, in a beaker, in hydrochloric acid of medium concentration, with occasional addition of nitric acid to aid the oxidation. The beaker should be protected by a watch-glass, and the liquid gently warmed (§ 124). Rinse the watch-glass off with water, heat the solution to incipient boiling, and precipitate the ferric hydroxide with ammonia, as in § 121

(make a confirmatory test, to see whether the precipitation is complete). Filter the supernatant liquid, wash by decantation and then on the filter, using hot water. To ascertain whether the washing has been thorough (ammonium chloride is especially detrimental), test the filtrate with silver nitrate, after the addition of nitric acid; it must cause neither a precipitate nor turbidity. Dry the precipitate, separate it from the filter, and ignite in a platinum crucible, adding the ash of the filter, which must be burned by itself (§ 142). After weighing the ferric oxide obtained, ascertain its purity by solution in concentrated hydrochloric acid. If a white residue remains (it is silica), it must be filtered off, washed, ignited, and weighed, and its weight subtracted from that of the ferric oxide. To answer the question as to how much iron the wire contains, calculate the oxide, Fe_2O_3, to the metal, and find the percentage (§ 114).

3. **Alum,** $KAl(SO_4)_2 + 12H_2O$. *Determination of the aluminium* (according to § 121 *a*).—The estimation of the water is somewhat complicated (it is made in the manner described in No. 4 or No. 5). The alum taken must be freshly crystallised, powdered, and dried between sheets of filter paper. Weigh off 1·5-2·0 gr. Dissolve in water in a beaker, and after heating almost to boiling, add ammonium chloride; precipitate with a slight excess of ammonia, and then boil the solution for a few minutes. Filter, and wash with hot water, first by decantation, finally on the filter. Dry the precipitate very thoroughly, ignite it (the filter must always be burned alone) at first very carefully (in a closed crucible), and subsequently before the blow-pipe. Calculate the weight of aluminium oxide to percentage.

4. **Copper Sulphate,** $CuSO_4 + 5H_2O$.—Determine the water as in No. 1, at first at 120°-140° C., until the weight is constant, then at 250°-260° C. (in an iron air-bath, or as in No. 5). Make the determination with 2·0 gr., and heat as in No. 1, until a constant weight has been obtained.

Determination of copper, as oxide, according to § 127 *c*.—Weigh off 1·0 gr. It is preferable to make the estimation with the hydrated, recently crystallised salt. If, during the filtration of the cupric hydroxide, the last particles of the precipitate adhere obstinately to the sides of the beaker, they may be dissolved in a few drops of nitric acid and the solution (evaporated to a smaller bulk if necessary) poured into the crucible containing the rest of the precipitate. The contents of the crucible are then evaporated to dryness on the water-bath and finally ignited.

Determination of sulphuric acid.—Weigh off 1·0 gr. (of the hydrated salt). Precipitate the hot solution with barium chloride in presence of a few cubic centimeters of hydrochloric acid, and then proceed as in the determination of barium in No. 1. Make a confirmatory test of the thoroughness of the washing, by testing a portion of the filtrate with sulphuric acid.

5. **Sodium Acid Phosphate,** $Na_2HPO_4 + 12H_2O$.—Place the portion designed for the water determination in a platinum crucible, taking about 1·0 gr. Heat the crucible to 100° C., then to 150°, and finally place it directly over the burner, but a few inches above it, to prevent the crucible becoming red-hot. Twelve molecules of water will thus be driven off; on ignition, the salt parts with still more water, and sodium pyrophosphate is formed. The water may be considered expelled as soon as the weight remains constant.

Determination of phosphoric acid.—Weigh off 1 gr. of the hydrated salt (freshly crystallised and dried between sheets of filter paper). Dissolve in water, add ammonium chloride, and precipitate the solution with magnesia mixture, according to § 136. The crystallised salt must be taken for this determination, because the transition of the ignited salt (the pyrophosphate) to the orthophosphate is very slow.

In closing this first series of analyses, we remark that the determinations which it contains are, so to speak, in many instances twofold. For example, sulphuric acid is determined in almost exactly the same manner as barium, chlorine as silver, etc.

II

SEPARATIONS

In the following analyses, two or more determinations are made with one portion of the substance. Well-defined salts are at first employed, in order to obtain a check on the analysis. A definite quantity of each salt is weighed off, the respective samples mixed together, and the determinations made with the mixture. Double salts may also be taken. The calculation of the theoretical quantities is obvious, when the weight of each of the salts is known.

6. **Separation of Iron from Manganese.**—Weigh off 0·1-0·2 gr. piano wire, and about 0·3 gr. of pure mangano-manganic oxide (prepared as in the determination of manganese; see below). Dissolve in hydrochloric acid, in a flask or beaker covered by a watch-glass, and add a little nitric acid from time to time during the operation (comp. No. 2).

Separation of the iron.—Remove the iron from solution by precipitation with sodium acetate, as in § 122 *a.*

Determination of the manganese.—Throw down the manganese from the filtrate with sodium carbonate, according to § 123, and weigh it as Mn_3O_4; to secure accurate results the conditions given must be closely observed.

7. **Analysis of Marble** (or preferably of Iceland spar).—Weigh off 1·0 gr., and

Determine the carbonic acid from the loss, by means of the apparatus described in § 138 *b.* The apparatus should be prepared by the student himself.

Determination of calcium.—Weigh off 0·5 gr. and dissolve it in hydrochloric acid in a beaker. The acid must be added gradually, and the beaker covered by a watch-glass during the process of solution. When the substance has entirely dissolved, heat the solution, to drive out the carbon dioxide, rinse off the watch-glass, and finally precipitate the calcium with ammonium oxalate, according to § 118. Be careful to pour only the liquid upon the filter during decantation, without stirring up the precipitate, and, while completing the washing on the filter, not to add hot water until all the last portion has filtered through. If these precautions are not observed, the precipitate will run through the filter. Weigh as calcium oxide, according to § 118.

8. **Potassium Sodium Carbonate,** $NaKCO_3$ (determination and separation of the alkalies).—The double salt of the above formula is obtained by ignition of potassium sodium tartrate. It must be strongly ignited before the weighing.

Weigh off 1·0 gr., dissolve it in water, and add dilute hydrochloric acid, covering the beaker with a watch-glass. Evaporate the solution to dryness, and ignite the residue very gently in a weighed platinum dish, as directed in § 116. Weigh the chlorides obtained, and then determine their chlorine as in No. 1 (indirect determination of the alkalies; calculation, § 117). If you wish to make the separation by a direct method, dissolve the salt in hydrochloric acid and remove the potassium with platinic chloride, according to §§ 116 and 117. The sum of the chlorides being already known, the amount of sodium is determined by the difference.

III

We now pass to the analysis of alloys. An accurate qualitative examination must first be made, and the course of procedure be governed by the results obtained. As regards the sample of the substance to be taken, consult § 139.

9. **Silver Coin.**—Weigh off 0·7-1·0 gr., and dissolve it in 8-10 c.c. of nitric acid (sp. gr. 1·2), in a beaker. If gold is present, it remains undissolved; filter it off, ignite, and weigh. Determine the *silver* by precipitation with hydrochloric acid according to § 127, and the *copper* as in No. 4 (after concentrating the silver chloride filtrate, if necessary, by evaporation).

10. **Brass** (often contains small quantities of tin, lead, or iron).—Weigh off 2 gr., and dissolve in nitric acid (§ 140). If tin be present, the solution must be evaporated to dryness on the water-bath, and the residue treated with nitric acid and water. Heat the solution, filter off the stannic acid (which is determined according to § 129), add about 20 c.c. of dilute sulphuric acid to the filtrate, and evaporate to dryness on the water-bath. Treat the dry residue with water, and filter off the lead sulphate (on a weighed filter; determination, § 127). The filtrate contains copper and zinc.

Determination of the copper.—The solution must not contain a large excess of sulphuric acid. Add an aqueous solution of sulphurous acid, and precipitate with a slight excess of potassium sulphocyanate. Allow the precipitate to settle, filter, dry, and ignite it with sulphur in a current of hydrogen, as in Rose's method (§ 127 *c*; § 123). Weigh as cuprous sulphide, Cu_2S. The sulphur must be tested before being used; 5 gr. must leave no residue on combustion.

Determination of the zinc.—Concentrate the filtrate from the cuprous sulphocyanate by evaporation, and precipitate the zinc with sodium carbonate, carefully following the directions given in § 123. Determine it as the oxide. If iron was present in the brass, it will be precipitated together with the zinc carbonate.

11. **Solder** (lead and tin).—Treat the finely-divided alloy with nitric acid, evaporate to dryness, and extract the residue with water and nitric acid, as in No. 10 and § 129 (test the purity of the stannic oxide by fusion with sodium carbonate and sulphur; § 130). Evaporate the filtrate to dryness with dilute sulphuric acid (in a porcelain casserole), filter off the lead sulphate, and determine the lead according to § 127. If the alloy contained any other constituents, they will be found in the filtrate from the lead sulphate (test with ammonium sulphide).

12 *a*. **Bronze** (tin and copper).—Weigh off 1·0 gr. of the alloy, treat it with nitric acid, and when the oxidation is complete, evaporate the solution almost to dryness. Moisten the residue with hydrochloric acid, let it stand for some time, and then add water (this brings the metastannic acid into solution; § 75). Precipitate the tin from the resulting solution by means of sodium sulphate or ammonium nitrate, consulting § 129 upon the operation and subsequent determination. Determine the copper in the filtrate as in No. 4.

12 *b*. **German Silver** (copper, nickel, zinc—usually together with traces of tin, lead, iron, cobalt, and manganese).—Weigh off 1·0-1·5 gr.; treat it with nitric acid, evaporate to dryness, and separate the stannic oxide as in No. 10. Evaporate the filtrate, adding 20-30 drops of sulphuric acid toward the end, and filter off the lead sulphate (No. 11). Add 2 c.c. of concentrated hydrochloric acid to the filtrate, and then precipitate the copper with hydrogen sulphide. Weigh as cuprous sulphide, as in No. 10. Evaporate the copper sulphide filtrate to dryness, to remove the hydrochloric acid, and dissolve the residue in water; transfer it to an Erlenmeyer flask, exactly neutralise with potassium hydroxide, and after adding a little sodium acetate, treat with hydrogen sul-

phide. When the solution has become saturated with the gas, close the flask with a good cork, and put it aside for several hours. Determine the zinc as zinc sulphide (§ 123). Free the filtrate from hydrogen sulphide by boiling, oxidise the ferrous iron with bromine, and then precipitate ferric hydroxide with ammonia. Filter off the precipitate, ignite, and weigh. The filtrate contains nickel; it is best determined by the electrolysis of its solution in ammonium oxalate (VII).

IV

13. **Bone Ash** (calcium carbonate and phosphate, with a small quantity of magnesium phosphate).—The analysis is made with thoroughly ignited bone. The substance should be previously dried at 100° C.

Determination of the carbonic acid from the loss, as in § 138 *b*; use 1·0 gr. for the estimation. To determine the other constituents, weigh off 1·0 gr., dissolve in the least possible quantity of dilute hydrochloric acid (in a beaker covered by a watch-glass), neutralise with sodium carbonate, and add sodium acetate and acetic acid. Precipitate the calcium from the acetic acid solution with ammonium oxalate, according to No. 7 (a double precipitation is necessary; § 120, II., and § 141). Concentrate the filtrate by evaporation on the water-bath, allow it to cool, and then precipitate with ammonia. Filter off the precipitate of ammonium magnesium phosphate, and weigh it (No. 5). This precipitate contains all the magnesium and a portion of the phosphoric acid. Concentrate the filtrate if necessary, and determine the remainder of the phosphoric acid by precipitation with magnesia mixture (as in No. 5). By this method all the phosphoric acid is found in two determinations.

14. **Carnallite,** $KCl, MgCl_2 + 6H_2O$.—The mineral usually contains sodium chloride, calcium sulphate, and ferric oxide as impurities. The water can be determined most accurately by the use of lead oxide. Pour 3-4 gr. of the latter into a weighed crucible, ignite, being careful not to fuse the oxide, and find the exact weight of the latter. Now add the substance, weigh again, and heat the mixture at a temperature

of 150° C. until all the water has escaped. The loss in weight represents the water.

Weigh off a second portion for the determination of the other constituents; dissolve in water, filtering off and weighing the insoluble ferric oxide. If calcium is present, separate it as in No. 13. Evaporate the filtrate on the water-bath, dry the residue, and, without transferring it to another dish, drive off the ammonium salts by ignition. The following method is still more satisfactory: transfer the dry residue to another dish, with the aid of a platinum spatula, and let it stand under an exsiccator while you rinse the first dish out with water; pour the wash-water into a small platinum vessel, and evaporate it to dryness. Ignite this portion first, then add the chief portion of the residue, ignite again, and finally add the rinse water of the second dish and ignite a third time.

Separation of the magnesium from the alkalies.—Dissolve the final residue in water and hydrochloric acid, transfer the solution to a platinum crucible, separate the magnesium with mercuric oxide, and determine it as the oxide, MgO, according to § 120. The alkalies can be determined as chlorides, by evaporating the liquid to dryness and carefully igniting the residue. After the determination has been made, dissolve the chlorides in the least possible quantity of water, filter, and weigh the trace of magnesium oxide which they contain.

V

Silicates.—The description of analyses of individual silicates would require more space than can be assigned to the subject in this book, but the principal operations required are illustrated in the following examples.

Special attention must be paid to the pulverising of the mineral (§ 139). The majority of silicates contain, together with their silica, the elements: iron (ferrous and ferric), aluminium, manganese (almost always, but usually in small quantities), magnesium, calcium, and the alkalies. The quantities in which they are present vary greatly in different silicates, and must be approximately estimated in the preliminary qualitative examination, in order that the analyst may select the best quantitative methods for their determination.

The analysis must be preceded by ignition of the mineral and determination of the resulting loss.[1]

15. **Silicates which are decomposed by Acids.**—Weigh off 2·0 gr., or less, according to the number of constituents to be estimated. Determine the silica according to the directions given in § 138 *a*, and test its purity by treating it with concentrated hydrochloric acid (§ 138; it usually contains traces of aluminium). Determine the metals in the filtrate from the silica.

Determination of iron and aluminium. a. In presence of manganese.—1. Remove most of the free hydrochloric acid by evaporation, neutralise with sodium carbonate, and precipitate with sodium acetate as in No. 7 (ammonium salts must be substituted for those of sodium in case the alkalies are to be determined). Filter off the precipitate and determine the iron and aluminium which it contains, according to § 122 *c*. Test the purity of the ignited precipitate by solution in an acid. Fuming hydrochloric acid can be used if the two metals are not to be separated; if they are, the test may be combined with the subsequent operations. The simplest course is to fuse the oxides with acid potassium sulphate and dissolve the resulting sulphates in water, or to simply dissolve them in sulphuric acid (8 parts H_2SO_4, 3 parts H_2O). The oxides are placed in a covered beaker, and solution assisted by applying a slight heat and crushing the substance with a glass rod. If silica is present it remains undissolved (the confirmatory test); filter it off, and determine it, adding its weight to that of the chief portion. Treat the solution with zinc, in a current of carbon dioxide, and titrate the iron with potassium permanganate (Volumetric Analysis, § 150). 2. Neutralise the solution as before, and precipitate with barium carbonate. (This method is, of course, inapplicable when the mineral contains barium.) Dissolve the washed precipitate in hydrochloric acid, in a covered beaker (look for silica), remove the excess of barium with sulphuric acid; and precipitate the iron and aluminium from the hot solution with ammonia. Estimate them as in No. 2 and No. 3, or separate them as above.

b. When manganese is absent, heat the solution to in-

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[1] The loss by ignition is often of great importance in determining the composition of a mineral.

cipient boiling, and add ammonium chloride and ammonia (the latter must be freshly prepared and contain no carbonate; it must give no precipitate with barium chloride). Boil the solution until the ammonia has been driven off, and proceed as above. (The presence of silica can be decided only when a platinum dish is employed.) A simpler method consists in precipitating with ammonia, decantating the supernatant liquid through a filter, redissolving the hydroxides in hydrochloric acid, and again precipitating them with ammonia. After having weighed the oxides, dissolve them in fuming hydrochloric acid, and filter off and determine the silica if present.

Separation of manganese.—Evaporate the filtrate from the iron and aluminium hydroxides, if necessary; treat with bromine water, and precipitate with ammonia. Be sure that all the manganese is thrown down. Filter, dissolve the precipitate in hydrochloric acid, and determine the manganese as oxide (§ 123 *a*). The method is not absolutely exact, as the precipitate almost always contains calcium and magnesium oxides and the alkalies. If only traces of manganese are present, oxidise the solution with bromine, and precipitate the manganese together with the aluminium and ferric hydroxides. The separation from Groups I. and II. is more accurately accomplished by means of ammonium sulphide (§ 123 *b*).

Separation of calcium, magnesium, and the alkalies.—Precipitate the calcium with ammonium oxalate as in No. 13. (Double precipitation is necessary.) Separate the magnesium from the alkalies as in No. 14, or, if but little magnesium is present, by direct precipitation with ammonium sodium phosphate, as in No. 5 (§ 120).

16. **Silicates which are not decomposed by Acids. Feldspar.**—The mineral must be very finely pulverised, and the loss by ignition determined.

Determination of the silica.—Fuse the substance with the alkali carbonate mixture[1] and estimate the silica according to § 138. (Test its purity by extraction with fuming hydrochloric acid.) Determine the aluminium and iron by precipitation with ammonia, as in the foregoing example, and

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[1] If a silicate containing manganese be fused with alkali carbonates, the manganese imparts to the product a bluish, or, if present in quantity, a green-blue colour.

afterwards dissolve the weighed oxides in fuming hydrochloric acid and estimate the silica which they contain. Precipitate barium, if it be present, with sulphuric acid (No. 1), and the calcium with ammonium oxalate (No. 8).

Determination of the alkalies.—Weigh off 1·0 gr. of the mineral and decompose it with gaseous, or, still better, with liquid, hydrofluoric acid (§ 138). A very good method is to treat 1·0 gr. of the mineral with 40 c.c. water, 7 c.c. concentrated hydrochloric acid, and about 4 c.c. hydrofluoric acid. Heat this mixture almost to boiling in a platinum dish, and when the reaction is complete (it requires only a few minutes), add 4 c.c. concentrated sulphuric acid and drive off the hydrofluoric acid by evaporation. The operation must be very carefully performed, in the open air if possible, as hydrofluoric acid is very dangerous. Dissolve the residual paste in water, acidify with hydrochloric acid, precipitate the sulphuric acid with a slight excess of barium chloride, and, without filtering, add ammonium carbonate and ammonia (to throw down the iron, aluminium, barium, and calcium). Now filter, and separate the alkalies from the magnesium in the filtrate as in No. 14. Separate and determine the alkalies according to No. 8. As was explained in § 117, the alkalies cannot always be determined by indirect methods.

VI

17. **Pyrites** (iron and copper pyrites).—Weigh off about 1·0 gr.

Determination of sulphur.—Pour the finely-divided mineral into a porcelain dish which is covered by an inverted funnel, add nitric acid (sp. gr. 1·37), heat on the water-bath, and add potassium chlorate from time to time.[1] If there is a residue of silica, determine it by the usual method. Precipitate the solution with barium chloride and weigh the barium sulphate, as in § 134 *b*. The purity of the precipitate must also be tested. Separate the iron and copper in the filtrate by the usual methods (precipitation of the copper with hydrogen sulphide, § 128 *b*).

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[1] Finely-pulverised pyrites can also be completely decomposed by fuming nitric acid in the same way.

18. **Gray Copper** (Cu, Fe, Zn, Bi, Ag, Hg), Sb, S, As (§§ 124 and 134).—Weigh off about 2·0 gr. of the finely-pulverised mineral, in a bulb-tube (preferably one with two bulbs) of difficultly fusible glass, one end of which is bent into a right angle. Connect this end with a receiver (a Wolf's bottle), adjusting it in such a manner that the tube will almost reach the water (or, in presence of antimony, the sulphuric and tartaric acids) which the receiver contains. Connect the other end of the tube with a chlorine generator and drying apparatus, and lead the gas over the mineral (all of which must be in the bulb nearest the generator). The chlorine at first attacks the substance in the cold, and the apparatus becomes heated of itself: as soon as the action ceases, warm the bulb containing the mineral, at the same time diminishing the flow of chlorine, and when the section between the two bulbs has again become transparent, allow the apparatus to cool and then break the tube off at this point. Put a glass cap, moistened with water, over the end of the portion which remains attached to the receiver, and let the apparatus stand for twenty-four hours, so that the sublimed chlorides can take up moisture from the air. Finally, moisten the contents of the tube with hydrochloric acid and rinse it out, adding the wash water to the solution in the receiver. If the latter contains free sulphur, it must be filtered through a weighed filter and the sulphur estimated.

1. *Analysis of the non-volatile residue.*—Let the bulb which contains the residue stand for some time in dilute hydrochloric acid, filter, and determine the precipitated silver chloride (§ 127). Throw down copper from the filtrate with hydrogen sulphide (determination; § 127 *c*). Next remove the iron by precipitation as its basic succinate (§ 122 *c*), and, after filtering it off, add sodium carbonate to the filtrate to throw out the zinc (§ 123).

2. *Analysis of the solution in the receiver.*—Heat the solution to 60° C., pass hydrogen sulphide through it, and when saturated with the gas place it aside for about twelve hours. Collect the precipitate (HgS, As_2S_3, Sb_2S_3) on a weighed filter, and wash with hydrogen sulphide water. Transfer the sulphides as fully as possible to a flask, and treat them with warm potassium sulphide (twice if necessary; § 130). Bring the insoluble mercuric sulphide on the same

filter, and wash with ammonium sulphide water. Complete the washing with water alone, and determine the weight of the precipitate as in § 127 *b*. Precipitate the thio-salts from their solution by hydrochloric acid, adding the latter a few drops at a time. Dissolve the sulphides obtained in boiling hydrochloric acid, assisting solution with potassium chlorate, add tartaric acid, and precipitate the arsenic acid as ammonium magnesium arsenate (§ 129). Precipitate the antimony as its trisulphide, as directed in § 129. The solution filtered from the hydrogen sulphide precipitate contains iron. Add ammonium sulphide, wash the precipitate, transfer it, with the filter, to a beaker, and dissolve in hydrochloric acid. Oxidise with potassium chlorate, and precipitate ferric hydroxide with ammonia. Determine the iron as oxide (No. 2).

Determination of the sulphur.—Determine the sulphur in a separate portion, using either the wet method (No. 17) or fusing the finely-powdered mineral with 3 parts of potassium nitrate and 3 parts of sodium carbonate, in a platinum crucible. The bottom of the crucible should be covered by a layer of sodium carbonate before the mixture is added. Ignite very gently at first, finally with a powerful flame. Extract the fusion product with water, acidify with hydrochloric acid, and precipitate the sulphuric acid with barium chloride. The purity of the barium sulphate must be tested (§ 134). Hempel recommends the oxidation of sulphur by means of sodium peroxide, the violent action of which is reduced by the addition of two parts of sodium carbonate. The operations are similar to those already described.

VII

Determinations by Electrolysis.—A general idea of these methods, the application of which has recently been extended to the determination of a large number of metals, can be gained from the following brief examples. The electrolysis is effected either with thermo-piles or with batteries which produce a constant current. Of the latter, the Meidinger or Bunsen elements are to be especially recommended. The conducting wires are made of thin copper wire, and fastened to the zinc or copper cylinders of the battery. All metal work on the battery must be carefully shellacked. The strength of current employed (three or four elements) varies in different analyses. When necessary, it is measured by a voltameter, or by the quantity of copper precipitated in a given time from a solution of cupric sulphate of given concentration. Electrolytic precipitations are conducted in several different ways. If a platinum dish be employed, it, itself, is made to form one of the poles, while for the other either a cylinder or cone of platinum foil is used, this being connected with the wire leading to the negative pole of the battery. The positive pole of the battery is connected with the platinum dish by means of the copper or brass standard which supports the latter. If a beaker is used instead of a platinum dish, the positive pole is made of a coil of platinum wire which rests on the bottom of the glass: the negative pole in this case is again a platinum cone or cylinder connected with the battery by means of a wire of the same metal.

19. **Brass.**—Dissolve a weighed quantity in nitric acid in a flask, transfer the solution to a casserole, and evaporate to dryness on the water-bath. Dissolve the residue in water and dilute sulphuric acid, and pour it into a beaker. The solution, including the wash-water, should contain about 1 gr. of brass to 50 c.c. of water, and the beaker should be of a corresponding size. The platinum spiral, which is to form the positive pole, is then inserted, and the cone, which has previously been weighed, is so adjusted that its lower rim will be separated by about an eighth of an inch from the spiral, and the upper portion extend above the liquid. The apparatus is now ready for the current. For the precipitation of copper, the current should be of such a strength that the voltameter shows the evolution of 2-2·5 c.c. of gas in the minute. The copper begins to separate as soon as the current is turned on, and is completely deposited within two or three hours. The thoroughness of the precipitation is tested by sinking the cone further into the solution; if the part which was previously above the surface receives no perceptible deposit, the time already allowed has been sufficient. The acid liquid must be removed from the beaker before the current is broken, as a small quantity of copper would otherwise pass into solution. This is accomplished by syphoning the liquid into a dish and pouring water

into the beaker. The acid can be considered removed when gas bubbles cease to appear at the positive pole. The current can now be turned off, and the platinum cone, with its deposit of copper, is taken out. It is then rinsed with absolute alcohol, and dried in an air-bath at 100° C., until the weight remains constant. The increase in weight gives the quantity of copper contained in the brass.[1]

To determine the *zinc*, the acid solution and wash-water are again evaporated to about 50 c.c. bulk, treated with sodium hydroxide until the zinc begins to separate out, and the precipitate then dissolved in potassium cyanide. The remaining operations are conducted the same as before. The electrolysis is effected in a beaker, the electrodes adjusted, and the current turned on, etc. The liquid heats up rapidly during the operation, however, and the beaker should therefore be placed in a porcelain dish which is filled with cold water. The current generated by four Bunsen elements deposits about 0·1 gr. zinc in an hour. When the separation of the zinc is deemed complete, the cone is taken from the liquid, rinsed with water, alcohol, and finally with ether, and dried over sulphuric acid in an exsiccator. To determine whether the deposition was complete, the cone, after being weighed, is freed from zinc by hydrochloric acid, washed, dried, reweighed, and again inserted in the liquid and the stream turned on. No more zinc must be deposited.

20. **German Silver.**—Dissolve the alloy in the same manner as brass, and determine the copper as before. Concentrate the residual acid solution, and separate the zinc from nickel as zinc sulphide (No. 12 *b*). Free the solution from hydrogen sulphide by evaporation, neutralise with ammonia, add 3-4 gr. of ammonium oxalate, and submit the solution to electrolysis. The nickel which deposits upon the cone is treated exactly as above.

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[1] To clean the platinum cone after it has been weighed, dissolve the copper in nitric acid, and rinse the cone with water. If the alloy contained lead, the latter will be found deposited on the *positive* pole in the form of its peroxide, and can be weighed.

SECTION II

VOLUMETRIC ANALYSIS

§ **144.** VOLUMETRIC analysis is the second chief division of quantitative analysis. Determinations by its means are effected by measuring the volume of a solution whose strength (*i.e.*, the weight of substance dissolved in a unit of volume) is known, and which has been used to complete a definite chemical reaction. Solutions of known strength are said to be standardised. If the volume of the standardised solution used be known, the weight of substance required for the reaction is also known, and it is then possible to calculate the equivalent quantity of the other factor in the reaction—the element to be determined.

A volumetric method can be based upon any chemical reaction which complies with certain requisites, the nature of which we will explain later. The reactions employed differ greatly among themselves, but can be classed together in a few simple groups—methods of volumetric analysis.

1. *Alkalimetry and acidimetry.*—Determination of bases and acids. This method is based upon the saturation of a base by an acid or *vice versâ.*

Oxidation and reduction methods serve for the determination of compounds which can unite with oxygen, and pass into a higher state of oxidation (oxidimetry), or *vice versâ*, be reduced from higher to lower degrees of oxidation. This division includes, beside oxidimetry, the methods of chlorimetry and iodometry.

3. *Precipitation methods.*—These require the formation of an insoluble substance from two soluble ones: they include the most varied determinations.

The unit used for measuring volume in volumetric analysis is the *cubic centimeter.* The weight of one cubic centimeter of water at 4° C. equals one *gram*, and 1000 cubic centimeters equal one *liter.*

The first requisite in a reaction which can be employed in volumetric analysis, is this: under the conditions under which the experiment is made, the reaction must be complete—*i.e.*, the relative weights of the substances which cause it must be definite, and capable of expression by a formula. To illustrate this rule, let us take an example from each of the methods:

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O.$$

In this reaction exactly 98 parts (grams, centigrams, etc.) of sulphuric acid act upon 80 (2 × 40) parts of sodium hydroxide; and 142 parts of sodium sulphate, and 36 parts of water result. Whatever quantity of sulphuric acid, a, was used, indicates a quantity of sodium hydroxide, x, which stands in the same relation to a, as 98 does to 80, *i.e.*,

$$a : x = 98 : 80. \qquad x = \frac{a \cdot 80}{98}.$$

As an example of oxidimetry let us take the reaction:

$$2FeO + O = Fe_2O_3\,;$$

16 parts of oxygen combine with 144 parts of ferrous oxide, to form ferric oxide. The oxygen used, a, indicates the quantity of ferrous oxide, x, according to the equation:

$$a : x = 16 : 144. \qquad x = \frac{a \cdot 144}{16}.$$

In precipitation methods we find the following example:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

The quantity of sodium chloride, x, is found from that of the silver nitrate, a, which was necessary to complete the reaction:

$$a : x = 170 : 58{\cdot}5. \qquad x = \frac{a : 58{\cdot}5}{170}.$$

We thus see that it is possible to find the weight of an unknown quantity of a substance, from the definite relation which exists between its molecular weight and that of the reagent. The second requisite, which is, in fact, as important as the first, is the exact determination of the value denoted by "*a*" in the above examples—*i.e.*, of the quantity of the reagent employed in the reaction. This determination is dependent upon two conditions: the strength of the solution used as the reagent, and the clearness with which the "final point" of the reaction—*i.e.*, the moment when it becomes complete—is indicated.

Volumetric analyses are carried out, as we have already remarked, by means of standard solutions, or solutions the unit of volume of which contains a known weight of substance. The "strength" of such a solution is the weight of substance which is dissolved in one cubic centimeter of the solution. Solutions which contain per liter a number of grams corresponding to their molecular weight, are called *Normal*. A liter of normal sulphuric acid, for instance, contains 98 gr. of the acid. A decinormal solution contains one-tenth as much substance as a normal solution—*e.g.*, 9·8 gr. sulphuric acid. The system of normal solutions is used chiefly with the view of simplifying calculation, and becomes extremely advantageous when many determinations of the same character are to be made.

As we shall see later, the standard solutions are prepared in several different ways: the methods of standardisation, or of determining their strength, also vary more or less in different instances. They can be more clearly explained by a few illustrations of standardisation. If the substance be solid and can be obtained in a perfectly pure state, the solution is prepared and its strength determined simultaneously, by weighing off the substance and dissolving it in a definite volume of water. If, for instance, one gram of oxalic acid be dissolved in two hundred and fifty cubic centimeters of water, the strength of the solution will be $\frac{1000}{250}$ mg., or 4 mg.; each cubic centimeter of water contains 4 mg. of oxalic acid. If, on the contrary, the substance cannot be obtained pure, or some other cause prevents its being weighed off, the solution is first made to approximate the concentration which we desire, and its strength is determined in a special operation. Sulphuric acid, for example, is never at hand as the pure compound H_2SO_4, since it always contains more or less water. To determine the actual strength of a roughly prepared solution of sulphuric acid, we find its relation to a weighed quantity of sodium carbonate. According to the equation:

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2;$$

106 gr. of sodium carbonate correspond to 98 gr. of sulphuric acid. Let us assume that we have weighed off 1·0 gr. of sodium carbonate, and found that it is exactly neutralised by 100 c.c. of the sulphuric acid solution. From the proportion:

$$106 : 98 = 1 : x.$$

we obtain the quantity of sulphuric acid in 100 c.c. of the solution:

$$x = \frac{98}{106} = 0{\cdot}924 \text{ gr.}$$

The strength of the solution, *i.e.*, the quantity of sulphuric acid in 1·0 c.c., will be 0·924÷100 = 9·24 mgr. This is but one of many means of determining the strength of a solution. The various methods differ widely in detail, but all are based upon similar principles and experiments.

The second requisite in volumetric analysis, the determination of the *final point of the reaction*, is just as important as the determination of the solution's strength. To be able to apply the relations between molecular weights to analysis, the moment of the cessation of reaction, *i.e.*, the moment when the weights of the substances in interaction are in proportion to their molecular weights, must be very sharply defined. For this purpose we use either reagents which dissolve to coloured solutions (such as potassium permanganate), when the moment in which the colour appears or vanishes defines the final point in the reaction; or we employ *indicators*. Indicators are substances which have no influence upon the chief reaction, but which give with the one or the other of the reacting substances a characteristic colour. The phenomenon which tells us that the final point has been reached is obviously in this case also the appearance, or disappearance, of a certain colour. The indicator, for example, used in the analysis of iodine solutions is starch-paste, which turns blue in the presence of free iodine. The theory of titration with iodine is based upon the conversion of the free halogen to hydriodic acid, which has no effect upon starch-paste. If, therefore, a standard solution of iodine be added to the substance under analysis, say arsenious acid, we know, at the moment when the previously colourless solution assumes a blue tint, that the reaction is complete (that the arsenious acid is converted to arsenic acid, the free iodine to hydriodic acid). The final point of a reaction is also at times, though much more rarely, determined by the formation of a precipitate, or the cessation of precipitation.

§ 145. The Form and Use of Apparatus for Measuring Liquids.—The measuring apparatus employed in volumetric analysis consists of flasks, cylinders, pipettes, and burettes. The first two are distinguished from pipettes and burettes in holding a definite quantity of a liquid; the latter two, on the other hand, being used to deliver a measured quantity of liquid. The various vessels are graduated by means of water at 17·5° C. (see below).

Measuring Flasks are of the ordinary shape, with the exception that they are provided with long narrow necks and ground glass stoppers. The point to which the flask must be filled, in order to hold its proper volume of liquid, is marked by a scratch upon its neck. The flasks in ordinary use contain 1 liter (1000 c.c.), ½-liter (500 c.c.), and 250, 200, 100 c.c. To measure a liquid by means of such a flask, the vessel is filled almost to the scratch on its neck, and the quantity still wanting then added, drop by drop (if necessary, after the liquid has been warmed or cooled to the proper temperature). To ascertain when the surface of the liquid is at an exact level with the scratch, the flask should be raised until the mark is in a direct line with the eye (so that it appears straight). In the measurements made in ordinary analyses, a slight variation from the temperature at which the flask was graduated has little influence upon the results, as the same error is repeated in all measurements. The final measurement, however, must be made some time after the liquid has been poured into the flask, in order to allow it to flow down from the sides of the neck.

To determine (or test) the capacity of a liter-flask, the vessel is placed upon one pan of a balance (which is accurate for 0·1 gr.) together with a 1000 gr. weight. A similar flask is then placed on the other pan, and shot added until the balance is in equilibrium. The weight is now removed, and water poured into the flask in question until equilibrium is restored. The temperature is then determined: if it be normal (17·5° C.), a mark encircling the neck is made at the level of the water. Should the temperature be higher or lower than 17·5° C., however, both flask and liquid must be cooled or warmed, as the case may be, to the proper temperature, before the mark is made. Flasks of less capacity are graduated in the same manner. To test the capacity of a flask already graduated, it is placed on a balance together with 1000 gr., tared, the weight removed, and the flask filled to the mark with water at 17·5° C. It is then again placed on the balance; if it brings the latter into equilibrium, the graduation was correct.[1]

The use of measuring-flasks.—Flasks of large capacity (1000-500 gr.) are employed in the preparation of standard solutions. For this purpose a weighed quantity of the solid or liquid is dissolved in 1000 c.c. or 500 c.c. water. The substance is placed in the flask, water is added in a quantity somewhat less than that called for by the capacity of the flask, the glass stopper inserted, and the liquid vigorously shaken. As soon as solution has taken place, the one or two cubic centimeters of water still wanting are added, and the level brought up to the mark according to the directions above. It is obvious that if the temperature fell or rose during the process of solution, the final measurement must not be made until the liquid has been brought back to the normal tempera-

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[1] Mohr's suggestion to prepare liter-flasks in this manner has now been universally adopted. Such flasks, nevertheless, holds about 2 cubic centimeters more than the true liter, which should contain 1000 c.c. water at 4° C. This difference has no influence on an analysis, however, as any desired unit may be employed, provided that flasks, pipettes, and other measuring vessels correspond to each other. To prepare a correct liter-flask, a certain weight must be subtracted from 1000 gr. It varies with the temperature, and can be seen (expressed in grams) in the following table; *t* is the temperature, *x* the weight to be subtracted.

t° C.	10	11	12	13	14	15	16	17	18	19
x (gr.)	1·34	1·43	1·52	1·63	1·76	1·89	2·04	2·20	2·37	2·55
t° C.	20	21	22	23	24	25	26	27	28	29
x (gr.)	2·74	2·95	3·17	3·39	3·63	3·88	4·13	4·39	4·67	4·94

If the flask is to be graduated with water at 17·5° C., the true liter can be obtained by putting 997·7 gr., upon the balance pan, instead of 1000 gr.

ture. Measuring-flasks of 500 c.c. and 100 c.c. capacity are used both in the determination of a solution's strength and in the analyses themselves. They are to be handled in the same manner as those of larger content.

Measuring cylinders also have a varying capacity (1000 c.c., 500 c.c., etc.) They differ from flasks in being divided into divisions of 1 c.c., 10 c.c., etc., and thus permitting not only the maximum volume, but any fraction of it, to be measured off in one and the same vessel. They are handled in the same way as flasks; but are most frequently employed in diluting liquids to a definite volume, for instance, to dilute a liquid measuring 380 c.c. up to 400 c.c. They are very often used in the preparation of normal and decinormal solutions (which involves dilution with water): more rarely in operations with solutions of arbitrary concentration, the use of which we will consider later. To measure volume by means of a cylinder, the level of the liquid is brought into a line with the eye, and its height read off on the scale which is engraved on the vessel. The latter is then turned around and the level of the liquid observed from the other side. It may be well to remark that cylinders of any great width afford by no means as much accuracy as the measuring-flasks.

Pipettes, as we have already noticed, are graduated in such a manner as to allow the *delivery* of a definite volume of liquid. They vary in capacity, the volume ranging from 1·0 c.c. (with its subdivisions) to 100 c.c. Small pipettes, holding from one to ten cubic centimeters, are tubes which simply taper off at each end. Those of greater capacity are also made of tubing, but are somewhat widened in the middle, either into a bulb, or a tube of larger diameter. A mark on the neck of the pipette denotes the height to which it should be filled in order to deliver the proper volume of liquid.

The pipette is employed to take a definite volume of liquid from a vessel. For this purpose it is inserted into the liquid, and the latter then sucked up slowly until it passes the mark. The suction must be cautiously applied, to prevent foaming. The upper end is then quickly covered by the finger, and the pipette raised out of the vessel. Pipettes, the upper ends of which are slightly narrowed, can be much more securely closed by the finger than those of the other form. The mark is next brought to a level with the eye, and the liquid allowed to flow out drop by drop, until it stands exactly at the mark. The correct volume having been secured, the finger is pressed down again, and the mouth of the pipette inserted in the glass or flask into which the liquid is to be delivered. In emptying a pipette, one general and universal method must be adopted. If the vessel already contains a liquid, the end of the pipette should pass below its surface: if the vessel is empty, the end should be dipped in the first few drops which flow out. The pipette is held quietly in the same position until empty, and then carefully removed. We emphasise again that this rule must be observed: the liquid must neither be allowed to flow from the pipette while the end of the latter is suspended in the air, nor forced out by blowing into the other end.

§ **146. Burettes** are employed to measure an arbitrary volume of liquid. Their form varies, but, as a general thing, only two varieties are employed. In the first of these, the outlet is a separate piece of glass which is attached by rubber tubing to the burette itself. This instrument is used in titrating with liquids which have no action on rubber. The second variety is resorted to only when liquids which attack rubber are being employed; they are described in the Examples (titration with potassium permanganate), and only the first and more common form will be here explained.

This burette is a cylindrical glass tube, of varying diameter, upon which is engraved a scale (with the zero at the top), showing the successive cubic centimeters and their subdivisions ($\frac{1}{10}$, $\frac{2}{10}$, $\frac{1}{2}$, c.c., etc.) The burette terminates at its lower extremity in a narrow glass tube, which is connected, by a good piece of rubber tubing, to a short glass tube tapering off to a point at its lower end. The intervening portion of the rubber tubing is surrounded by a brass clip, which closes the burette, and controls the outflow of the liquid. The instrument is supported in a vertical position by a standard (which usually holds two or even more burettes), or some other means.

There are various forms of clips, but that suggested by Mohr is without doubt the simplest, as it can be opened simply by pressure with the thumb and forefinger upon two copper buttons. Some force is required in overcoming the elasticity of the brass wire; but if the operator is familiar with his clip, he can judge of the rapidity of the outflow merely from the pressure which he exerts, without keeping his eye on the clip (this becomes of great advantage when the attention must be fixed on the scale and not on the escaping liquid). The outlet of the tip should be of such size as to allow a flow of about 20-25 drops to the cubic centimeter. The tubing should of course be tested occasionally, and replaced by a new piece as soon as it begins to leak.

Filling the burette.—To fill an empty burette, the lower extremity is dipped into the solution, the clip opened, and the liquid drawn up by gentle suction until it has passed beyond the rubber tubing. The clip is then closed, a small funnel, the stem of which has been cut off obliquely, is inserted in the upper end of the burette, and the latter filled to a point above the zero of the scale. The clip is now pressed slightly open, and the solution allowed to flow slowly out until its level is exactly at the zero-point (the manner in which its height is read off will be described later). If the burette already contains some of the liquid, and merely requires filling, the funnel alone is needed.[1]

It quite frequently happens that the burette must be repeatedly filled, for which purpose the following apparatus is very convenient. The standard solution is kept in a reservoir, resting on a sufficiently high support, and consisting of a bottle with a fairly wide neck, in which a trebly perforated cork is inserted. Through one of the perforations passes a tube which reaches to the bottom of the bottle, and is bent into the form of a syphon; this serves as a passage for the liquid, from the bottle to the burette. The second perforation contains a small tube bent at right angles, and employed to allow the air displaced in filling the burettes to pass into the bottle. In the third hole is inserted a bulb-tube, which connects the contents of the bottle with the outer air. The burette itself is modified as follows. The rubber tubing at its lower extremity connects it with a glass tube, from the middle of which, and at right angles to it, projects an arm. The latter is connected by rubber tubing to the syphon of the reservoir (this tubing is closed by a clip during the titration). The lower end of the straight section is connected with the burette tip, and the latter provided with a stop-cock as usual.

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[1] To avoid waiting until burettes and pipettes have dried after being washed, it is convenient to rinse them a few times with the solution to be used; they can then be filled without delay.

The upper end of the burette is closed by a cork holding a tube which is connected with the second tube of the reservoir. It is convenient to have the reservoir and burette supported by the same standard. To fill the burette by means of this apparatus, the clip closing the syphon is simply opened, and the solution flows into the burette. As soon as it has passed beyond the zero-point, the clasp is again closed, and the level of the solution brought to the zero-point in the usual manner. In setting up this apparatus, it is advisable to use as little rubber tubing as possible.

Reading off the Burette.—A correct reading can be made only when the following conditions are observed.

1. A sufficient interval must be allowed between the escape of the solution and the reading, to permit the level to become constant.
2. The eye must be in line with the surface of the liquid.
3. One and the same portion of the meniscus of the liquid must be used in all readings.

The last rule requires explanation. It is well known that the surface of water or aqueous solutions contained in tubes is not horizontal, but convex. If the convex meniscus of a liquid in a burette be viewed against a bright background, it will be seen to contain a dark, more or less curved arc, and above the arc, a bright segment which is bound by a horizontal line. This dark arc is employed in reading off the burette, either its under or upper surface being brought against the scale. To secure a bright background, Mohr suggests the use of a square slip of white paper, over the lower half of which is pasted a black piece. When such a paper is attached to the burette, or held behind it in the hand, in such a manner that the dividing line between the two colours will be two or three millimeters below the level of the solution, a portion of the meniscus appears as a sharp black segment (due to reflection); a very exact reading can be made from either the upper or lower surface of this segment. Lastly, the height of the solution can be accurately read off by means of a so-called Erdmann's float; the comparison is here made, not between the level of the liquid and the scale, but of the latter with a mark engraved upon the float.

Testing the Apparatus.—An explanation has already been given (§ 145) of the manner of preparing a liter-flask. The same operation is performed in testing vessels which are already graduated. To test the accuracy of a pipette or burette, a small flask (to receive the water from the burette or pipette) is placed upon a balance-pan, together with the appropriate weight (for 10 c.c. water at 17·5° C., 10 gr.), and the balance is brought into equilibrium by a similar flask and some shot. The weight is then removed, and the requisite amount of water allowed to flow into the flask from the instrument to be tested. The entire scale of a burette can be tested, or "calibrated," in this manner; ten cubic centimeters being allowed to escape at a time. To be available, a burette or pipette must not possess an error of more than 0·002 gr. in any ten cubic centimeters of its contents. Small errors which apply to all the pieces of apparatus are without influence upon the results. Volumetric analysis does not depend upon the cubic centimeter as the unit of volume: the latter can be chosen at will, without causing inaccuracy in the analysis, provided that all the apparatus corresponds to the same. The measuring instruments need therefore merely be ascertained to agree with one another—flasks with the burettes, pipettes with the cylinders. Assume, for the purpose of illustration, that a liter-flask to be used holds only 998 grams of water, and the pipette of 50 c.c. has an actual capacity of only 49·9 c.c. The relation between the two is correct, because

$$1000 : 50 = 998 : 49{\cdot}9.$$

Standard Solutions.—A thorough understanding of operations involved in volumetric analysis requires some preliminary explanation of the solutions which are used. When the same solution is to be employed in several consecutive analyses, the calculation of the results is much simplified if its concentration stands in a simple ratio to the number of grams corresponding to the molecular weight of the substance dissolved. Normal solutions are those which contain in each liter the same number of grams as there are units in the molecular weight of the substance; for instance, 98 gr. sulphuric acid, 126 gr. oxalic acid ($C_2H_2O_4 + 2H_2O$), 40 gr. sodium hydroxide, etc. Decinormal solutions contain one-tenth as many grams as the normal. The preparation of normal solutions, however, requires a great deal of time, and the receipts for the solutions to be used in the following analysis have therefore been arbitrarily chosen; though in such a manner that the deviation in their strength will have no influence upon the exactness of the results. Solutions of arbitrary concentration can be made normal in the following way. Assume that a decinormal solution of sulphuric acid, one, therefore, which contains 9·8 gr. H_2SO_4 in 1000 c.c., is to be made up, and that the arbitrary solution already prepared contains 10 gr. in 1000 c.c. To make the latter decinormal, it must be diluted with water, according to the proportion :

$$9{\cdot}8 : 1000 = 10 : x$$
$$x = 1020{\cdot}3$$

That is, 20·3 c.c. water must be added to each liter of the solution. It is obvious that the strength of the modified solution should also be determined by experiment.

Calculation of Results.—If the chemical equation, according to which the analysis is made, and the weight of substance (volume of solution) necessary for the reaction are known, the equivalent of this weight, or the weight of the substance to be determined, is found by a simple proportion, under the conditions explained in § 139. The method of calculation is explained under each class of examples. The substance to be analysed must of course be previously weighed.

I

ALKALIMETRY AND ACIDIMETRY

§ **147. Alkalimetry.**—For the volumetric determination of the alkalies, we use reactions in which neutral salts are formed by the saturation of the hydroxides or carbonates with acids, as in the equations :

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O,$$
$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2.$$

The determinations are made with a standard solution of sulphuric acid. The various operations described below follow the order in which they are performed in analysis.

1. *Preparation of the sulphuric acid solution.*—It is advantageous to make the analyses with an approximately decinormal solution of sulphuric acid. About 10 gr. of the English acid are weighed off, diluted, in a liter-flask, and the solution made up to 1000 c.c. (for the operation see § 145). Before describing the determination of the solution's strength (by means of a weighed quantity of sodium carbonate), the conditions which influence the accuracy of alkalimetric analyses must be explained.

The final point in the reaction between sulphuric acid and sodium carbonate is found by means of litmus tincture. If sulphuric acid be allowed to run into an alkaline solution which has been coloured blue by litmus, the colour remains unchanged until the exact quantity of acid necessary to form a neutral salt has been added; the slightest excess over this amount of acid changes the blue solution to red. The point at which this change occurs is the final point of the reaction. In the titration of sodium carbonate the liberation of carbonic acid prevents the change of colour occurring instantly, and the point of neutralisation is found, in this case, by supersaturating with the acid, and determining the excess added. This method requires an additional solution of sodium hydroxide, the volumetric relation of which to the standard sulphuric acid must be known.

2. *Preparation of the sodium hydroxide solution.*—9 gr. of sodium oxide are dissolved in water, and the solution boiled with lime-milk, in an iron dish, until all the carbonic acid has been removed. To ascertain whether this has been effected, a sample of the perfectly clear alkaline solution is treated with lime-water, and diluted if necessary; if it becomes turbid carbonic acid is still present. As soon as it has been freed from the last traces and grown cold, the solution is poured into a flask and diluted with water (to make its strength approximate that of the sulphuric acid, the final volume should be about one liter). The flask is then closed by a cork through which passes a tube filled with sodium oxide, to prevent absorption of carbonic acid from the air, and is allowed to stand until the solution has become perfectly clear. The latter is finally syphoned off into the reservoir or vessel in which it is to be preserved. The vessel and, while in use,

the burette, must be closed by corks provided with soda-lime tubes.

3. *Preparation of litmus tincture.*—Commercial litmus is allowed to stand for some time under water, the extract poured off (this preliminary digestion may be still more advantageously effected with alcohol), and the operation repeated. Six parts of water should be employed for the second digestion, and the liquid set aside for twenty-four hours to clarify. The bases dissolved in the solution having finally been neutralised by a few drops of very dilute acetic acid, the tincture is ready for use. It must be preserved in an *open* vessel (the dust is kept out by a paper cover), and some salicylic acid added, to prevent the formation of mildew. To obtain success in the experiments which will be described below, extreme importance must be attached to the tone of colour which the litmus solution is given through the action of alkalies or acids. It is advisable for the beginner to have at hand a sample of the neutral litmus; a second which is slightly acid; and a third alkaline. To prepare the samples, a definite quantity of litmus (3-4 c.c.), which must correspond as closely as possible with that used in the analysis, is diluted with water (about 50 c.c.), and an intensity of colour thus obtained which agrees very nearly with that imparted to the solution to be analysed. One and the same quantity of litmus tincture must obviously be used in every experiment, to obtain the same tint. The amount to be added depends more or less upon the ease with which the operator can distinguish between different shades of colour: 2-3 c.c. of a not too-highly concentrated solution are usually employed.

4. *The volumetric relation between the sulphuric acid solution and that of sodium hydroxide* must be accurately determined. The burettes having been filled with the two liquids (§ 146), 10 c.c. of the sulphuric acid are run into a sufficiently-capacious flask, and coloured with litmus. The glass is then taken in the hand, a piece of white paper placed on the stand beneath it (the operation can be performed in a white porcelain dish), and the operator, constantly stirring the liquid, lets the sodium hydroxide flow into the glass, rapidly at first, then drop by drop, until the final point is reached, *i.e.*, until another drop of the alkali turns the solution blue. The amount of

alkali used is then read off on the burette. The first neutralisation is usually not made exact, but simply performed in order to learn the approximate relation, and the absolute relation ascertained in a second test. The beaker is rinsed out, another 10 c.c. of sulphuric acid run into it, and the operation repeated in the same manner. For the sake of convenience in reading off the results, the level of the sodium hydroxide solution should be lowered to the next cubic centimeter mark on the scale, and its height noted. As the approximate volume necessary is already known, this amount is added at once, and the rest run in drop by drop, with constant stirring, until the change from red to blue in the solution is caused by a single additional drop. The results are checked by the addition of another 10 c.c. sulphuric acid to the contents of the beaker, and repetition of the operation. If the quantities used in the two experiments are in approximate agreement (the difference must not be more than $\frac{1}{10}$, or at highest, $\frac{2}{10}$ c.c.), their average is taken as the correct result (attention must be paid to the precautions necessary in reading off the volume; § 146). The relation between the two solutions is now ascertained. It is well to have it a simple one, as 1 : 1 or 1 : 1·5, if possible. If the ratio be more complicated, a factor is calculated, by multiplying with which the number of cubic centimeters of alkali used can be expressed in cubic centimeters of the acid. We can now proceed with the standardisation of the acid.

5. *Determination of the strength of the sulphuric acid* (and simultaneously that of the sodium hydroxide).—For this purpose a separate experiment is necessary; the strength of the acid being determined by means of a weighed quantity of sodium carbonate. A quantity of sodium bicarbonate is washed with cold water, dried, and converted to the carbonate by gentle ignition in a platinum crucible. It is then permitted to cool in an exsiccator, placed in a weighing tube (§ 139), and about 0·7 gr. exactly weighed off and dissolved in a flask (of about 200 c.c. capacity) in 200 c.c. of water at 17·5° C. (§ 145). The salt must be transferred directly from the weighing glass to the flask, and the former then closed and weighed back, the difference between the two results equaling the sodium carbonate taken. When the salt has passed

into solution, and the contents of the flask been well mixed, 50 c.c. (*i.e.*, one-fourth of the sodium carbonate) are transferred, in a pipette, to a sufficiently capacious flask (§ 145), and about the same amount of litmus tincture added as was employed in the previous tests. The level of the sulphuric acid in the burette is then adjusted, the figures taken down, and the acid slowly added to the alkali until the blue solution has become violet. The flask is next heated until the liquid begins to boil, whereupon the carbon dioxide escapes and the blue colour reappears. Acid is again added until the solution becomes red, and the latter again boiled: this is repeated until the red colour has become permanent, whereupon the level of the acid in the burette is read off, and the solution retitrated with sodium hydroxide until a drop of the latter restores the blue colour. The volume of sodium hydroxide used is calculated to cubic centimeters of sulphuric acid, and subtracted from that of the latter. The determination is repeated twice or three times (in the same flask), 50 c.c. of the solution being taken each time, and the average of the three, or of the last two, results taken, if they agree closely (again within $\frac{2}{10}$-$\frac{1}{10}$ c.c.) This average is then multiplied by 4 (to obtain the number of cubic centimeters corresponding to the whole of the sodium carbonate), and the strength of the sulphuric acid deduced from the proportion,

$$106 : 98 = a : x;$$

106 is the molecular weight of sodium carbonate, 98 that of sulphuric acid, a the quantity of sodium carbonate neutralised, and x the quantity of sulphuric acid employed in neutralising it. The strength of the acid is found by dividing the weight of that which was used, by the number of cubic centimeters run out.

As the relation between the sulphuric acid and the sodium hydroxide is known, the strength of the latter can be calculated from the results of the one experiment. Assuming that the relation is 1 : 1 (if this is not true, a slight additional calculation is involved), and that the strength of the sulphuric acid has already been determined to be a, the strength of the alkali is deduced from the proportion:

$$98 : 80 = a : x.$$

REMARK.—Mohr determines the strength of sulphuric acid by means of crystallised oxalic acid, $C_2H_2O_4 + 2H_2O$. About 12·6 gr. of the latter are weighed off and dissolved in one liter of water, and the strength of the solution found by dividing the number of grams taken by the number of centimeters in which they were dissolved. With this solution the sodium hydroxide is standardised; the latter can then be employed to determine the strength of sulphuric, nitric, or any other acid required. Oxalic acid often contains the acid potassium oxalate, and must be freed from this impurity by repeated crystallisation, each yield of crystals being only partially dissolved, and the solution thus obtained again evaporated. The purity of the oxalic acid must in every case be tested by the combustion of 2-3 gr. in a platinum crucible, the acid being rejected if a residue is left. Solutions of oxalic acid are partially decomposed by light. The standard sodium hydroxide can also be prepared by weighing off a piece of clean, lustrous metallic sodium (in two test-tubes, one of which passes over the other), and dissolving it in a small quantity of alcohol. The alcoholic solution is then diluted to the mark with water. The strength is found by calculation.

§ 148. Examples of Alkalimetric Determinations.—Alkalimetric determinations are made with standard solutions of sulphuric acid and sodium hydroxide, the latter being used for retitrating the excess of acid. The analysis is made in the same way as the solutions are standardised. The material for analysis is weighed off (whether fluid or solid), dissolved in 200 c.c. of water, filtered if necessary, and three portions, of 50 c.c. each, titrated (either with the acid or alkaline solution). The average of the two last determinations is multiplied by 4, which gives the number of cubic centimeters of the standard solution necessary to neutralise the whole substance. This value is multiplied by the strength of the acid, the result being the weight of the acid or alkali used. The weight of alkali (or acid) in the substance analysed is found by the substitution of this number in the proportion given above, and the weight found is calculated to percentage as in gravimetric analysis (§ 114; analyses of compounds of known composition should be checked by calculation). A brief explanation of a few frequently occurring determinations follows.

1. *Alkalies* are determined in the manner described. The cold solution is titrated with sulphuric acid until the litmus has a very faint red tint.

2. *Carbonates of the alkali metals* (pearl ash, soda).—The titration is made with the boiling solution, an excess of acid

run in, and the residual quantity titrated with sodium hydroxide.

3. The determination of carbonates in presence of alkaline hydroxides necessitates two experiments. 1. The sum of the hydroxides and carbonates is determined by titrating the boiling solution. 2. The alkalies are titrated alone, with phenolphtalein, which is not altered by carbonates, as the indicator (for its preparation, see Acidimetry). The final point is determined by the disappearance of the violet-red colour. This method can be employed only in presence of small quantities of carbonates. If more be present, the solution must be precipitated with barium chloride, filtered, and the filtrate and wash-water collected in a 250 c.c. flask. An aliquot portion of this solution is then titrated as usual. The carbonates are found from the difference between the results of the two determinations.

4. *Ammonia.*—The titration must be performed in the cold, and with litmus tincture as the indicator. Ammonium carbonate is determined in the same way.

5. *Ammonium salts.*—A weighed quantity is dissolved in water, and a known volume of standard sodium hydroxide added. The latter must exceed the ammonia present. The solution is then boiled until the ammonia has been entirely driven out, and the excess of sodium hydroxide determined. The quantity lost corresponds to the ammonium salt.

Ammonium salts which dissolve in alcohol can be very easily titrated in alcoholic solution by a standard solution of sodium hydroxide, in the same medium, in presence of phenolphtalein; the alkali is added until the violet-red colour appears. The method depends upon the fact that in alcoholic solution sodium hydroxide displaces ammonia in ammonium salts in equivalent quantities at the ordinary temperature, and that in this case phenolphtalein forms no compound with ammonia.

6. *Alkalies in presence of ammonia* can, as is obvious from the above, be determined by direct titration with standard sulphuric acid and phenolphtalein in alcoholic solution. The acid is added until the violet-red colour has disappeared (Menschutkin, *Ber. d. deutschen chemischen Gesellschaft,* 1882).

The hydroxides of barium, strontium, and calcium can be determined in the same way as the alkalies. A standard solution of hydrochloric or nitric acid is employed, the strength of which has been determined by titration with standard sodium hydroxide. Phenolphtalein is the best indicator.

Further applications of alkalimetric determinations can be only mentioned. Many metallic salts (those for instance of Mg, Cu, Ag, Fe, Hg) can be analysed by the addition of standard sodium hydroxide in excess and titration of the superfluous quantity of the latter. The difference between the alkali added and found is equivalent to the quantity of the metallic salt. For the analysis of the neutral salts of the metals Ba, Sr, Au, Al, Zn, Bi, Ni, Co, Pb, etc., a standard solution of sodium carbonate is employed. The decinormal solution is prepared by dissolving a weighed quantity of anhydrous sodium carbonate in the necessary volume of water.

§ **149. Acidimetry.**—The reagent used is a standard solution of sodium hydroxide; all acids, the neutral salts of which show a neutral reaction and have no effect upon the indicator, can be volumetrically estimated by its means. A great number of indicators have been proposed during the last few years, but space will permit the mention of merely a few in the examples of acidimetry which follow.

Examples of Analysis by Acidimetry.—The substance containing the acid to be determined is weighed off and dissolved in 200 c.c. water, and three portions of this solution, each containing 50 c.c., are then titrated with sodium hydroxide. The quantity of the latter used is equivalent to that of the acid present.

1. *Strong acids*, the neutral salts of which yield perfectly neutral solutions, can be estimated, as we have said, with sodium hydroxide, with phenolphtalein as the indicator. The final point is indicated by the appearance of a violet-red colour.

For use as an indicator, the phenolphtalein of commerce must be dissolved in sodium hydroxide, precipitated by acetic acid, thoroughly washed with water, and dissolved in alcohol. Of this alcoholic solution, two or more drops, depending upon its concentration, are used in each estimation. It must be remembered, in using this indicator, that the alkali compounds of phenolphtalein are decomposed by carbonic acid, and that traces of colour may in consequence be destroyed. Accurate analyses should be made with water from which the carbonic acid has been expelled by boiling. When this precaution has been taken, the delicacy of the indicator is very great.

Hydrochloric, nitric, sulphuric, oxalic, tartaric, citric, and formic acid can be determined by the above method.

2. *Organic acids* are, as a rule, to be determined by titration with baryta-water, since, when soluble in water, their barium salts are neutral, their alkali salts, on the contrary, alkaline. Organic acids in alcoholic solution can be very exactly titrated with standard alcoholic sodium hydroxide.

To prepare the standard baryta solution, crystallised barium hydroxide is dissolved, in a closed flask, in enough water to make the solution approximately decinormal. After some days, when the precipitate of barium carbonate has completely subsided and the supernatant liquid become clear, the latter is syphoned off into the bottle in which it is to be preserved. The air in the bottle must previously be freed from carbonic acid by passage through a soda-lime tube, and after being filled with the solution, the bottle must be closed by a cork in which is inserted another tube of the same description. The strength of the baryta water is found by the addition of a few drops of sulphuric acid to about 20 c.c. of the solution in a platinum crucible, and evaporation to dryness in a muffle (heated by a Bunsen-flame). The residual barium sulphate is finally ignited and weighed. The best indicator with which to determine organic acids is phenolphtalein; its use must be subject to the precaution necessitated by its behaviour toward carbonic acid (see above).

The final point, as shown by different indicators, varies with different acids, both organic and inorganic. The reader will find the account of thorough investigations on this point in the articles by Thomson (*Zeits. für anal. Chemie*, 1885, p. 222) and Engel (*Comptes rendus*, vol. cii.)

3. *Carbonic acid.*—The determination of this acid may be required either in a mixture of gases (in the air) or in aqueous solution. To estimate its percentage in the atmosphere a current of air is passed for about ten minutes, by means of a bellows, into a large flask (of about 10 liters capacity) which can be closed by a tightly-fitting cork. A known volume of baryta water is then run in, the cork inserted, and the flask

thoroughly shaken and set aside until the barium carbonate has settled. An aliquot portion of the solution is then taken out, and the residual barium hydroxide which it contains titrated with oxalic acid. A standard solution of the latter is prepared by dissolving 2·8636 gr. in 1000 c.c. water. The final point of the reaction is determined by turmeric paper, the acid being added until the paper ceases to turn brown. The carbonic acid is found from the quantity of barium hydroxide with which it has united.

The further generalisation of acidimetric methods is exactly analogous to that which we have observed in alkalimetry.

II. OXIDATION AND REDUCTION METHODS

OXIDIMETRY

§ 150. The oxidising agent usually employed in volumetric analysis is potassium permanganate; more rarely, potassium dichromate. Both salts are applied in acid solution (their acids being the oxidising mediums).

Determination of Iron (Marguerite's method).—The volumetric estimation of iron is based upon its conversion from the ferrous to the ferric state. As free permanganic acid is too unstable to be used, a solution of potassium permanganate is employed, and its acid liberated by sulphuric acid during the determination. In surrendering its oxygen to the ferrous salt, the permanganic acid becomes reduced to a manganous salt:

$$10FeSO_4 + 8H_2SO_4 + 2KMnO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Permanganic acid and its salts dissolve in water to a dark carmine-red colour, which is so intense that even a thin layer of the concentrated solution is opaque, and one drop colours 250 c.c. water a fine rose-red. Manganous and ferrous solutions are colourless, and the dilute solution of a ferric salt is only slightly yellow. As long as ferrous salts are present, the carmine colour caused by the addition of potassium permanganate vanishes almost instantly, and the point at which the reaction is complete is indicated by the appearance of a red tint, which lasts for several minutes.

We shall explain the practical operations involved in this method in the order in which they are performed in the analysis. The burette used also requires a short description: the ordinary burette is unsuitable, owing to the action of potassium permanganate upon rubber.

Gay Lussac's and Mohr's burettes.—Titrations with potassium permanganate are performed with a Gay Lussac's burette, or one of its many modifications (*e.g.*, Geissler's burette). This instrument consists in a wide, graduated tube, at the bottom of which is joined a second, of small diameter; the latter runs up the side of the burette proper, and at its upper end is bent over, to form a good outlet. The outlet must be higher than the zero-point of the scale. The liquid can be poured out in drops by inclining the burette, but a more convenient method consists in closing the instrument, which should be fastened to a support, with a cork fitted with a glass tube, and regulating the outflow by blowing air through the latter. The following modification, proposed by Mohr, is to be still more highly recommended. The burette is made of a narrow graduated cylinder, provided with a wooden foot, and closed by a double perforated cork. Through one of the perforations the delivery tube passes, reaching to the bottom of the cylinder; its outside end is not drawn out, but bent over to an angle of slightly less than 90°. The cork holds in the other perforation a tube for the introduction of air. In making an analysis, the operator takes the burette in his right hand, and in his left the beaker containing the solution to be titrated. Finally, ordinary burettes in which the rubber tubing and clamp are replaced by a glass stopcock are sometimes used. The difficulty with which the outflow is controlled, and the tendency of the passage to become clogged by sediment, however, give these burettes little advantage over others.

1. *The potassium permanganate solution* is made up to an arbitrary strength, *e.g.*, so that one cubic centimeter will correspond to 0·010 gr. iron. The solution is made by dissolving up the crystallised salt, and preserved in a flask similar to a wash-bottle, from which it can be transferred directly to the burette. The deep colour of the solution prevents the meniscus

in the burette from being seen, and for this reason the reading must be made from the upper line of the liquid, by reflected light (a light is placed at the side or in front of the burette, and a piece of white paper held behind it). The solution of the crystallised salt rarely changes in strength, but it is still advisable to standardise it anew from time to time.

2. *Determination of the strength of potassium permanganate.*—The most accurate method is by means of metallic iron; about 0·2 gr. of iron piano-wire (free from rust) are weighed off and dissolved in about 20 c.c. dilute sulphuric acid, the process of solution being assisted by warmth. The operation should be performed in a wide-mouthed flask, which is placed in an oblique position, and closed by a stopper holding two tubes: through one of the latter is led a current of carbon dioxide, not only during the process of solution, but also while the liquid is cooling. When perfectly cold the solution is transferred to a beaker, the flask rinsed out several times with water, and the whole brought up to about 200 c.c. The beaker is then placed on a piece of white paper (the experiment may be equally well made in a porcelain dish), and constantly stirred while the potassium permanganate is being added. As long as the colour disappears instantly, the permanganate may be rapidly run in, but it must be gradually checked as the colour becomes more permanent, and is finally added drop by drop. The final point has been reached when the solution assumes a faint rose-red tint which can be seen for several minutes. Time must be allowed for the permanganate to flow down the sides of the burette and assume its true level, before the reading is made. The accuracy of the results must be confirmed by a repetition of the experiment. The strength of the potassium permanganate solution should be expressed in its equivalent of iron; this is found by dividing the weight of the wire taken by the number of cubic centimeters of permanganate used. As the iron in piano-wire is slightly impure, the calculation should be based on the assumption that it contains 99·70 per cent of pure iron.

In dissolving metallic iron in sulphuric acid, whether for analysis or in standardising the potassium permanganate solution, the above apparatus may be replaced by that proposed by Bunsen. This consists of an ordinary flask in which is inserted a tube provided with a valve. The valve is made of a piece of rubber tubing in which a short smooth slit, about a centimeter in length, has been cut by a sharp knife. The tubing must fit tightly over the glass tube, and be closed at its free end by a piece of glass rod. Before using the apparatus, the operator must test the efficiency of the valve by blowing strongly into the flask, and observing whether the air escapes freely. When the iron has passed into solution the flask is placed in cold water to cool, and the cork then withdrawn. If a slight vacuum has been created by the cooling, it is an indication that the contents of the vessel were correctly and hermetically shut off from the outer air.

3. *Performance of the analysis.*—A quantity of the ferrous compound, corresponding to about 0·2 gr. iron, is dissolved in a flask in water or an acid, and a stream of hydrogen or carbon dioxide led into the flask, both during the process of solution and while the liquid is cooling. The solution is then made up to 200 c.c. As the titration with potassium permanganate is to be made in acid solution (see the equation which expresses the reaction) aqueous ferrous solutions must be acidified with sulphuric acid. The analysis is repeated three times, each time with 50 c.c. of the solution, and in the same beaker or dish, the liquid used in the preceding experiment not being thrown out. The second and third titrations usually give the same results. The directions given above must be carefully followed. The quantity of ferrous iron present is found by multiplying the number of cubic centimeters used, by the strength of the permanganate.

Examples of Oxidimetric Determinations.—1. *The estimation of iron in ferric compounds* requires their previous reduction. For this purpose the solution is heated with zinc (iron-free) and sulphuric acid, in an atmosphere of carbon dioxide or hydrogen, until it has become perfectly colourless. The heat must be very cautiously applied: the remaining operations are the same as above.

If hydrochloric acid has been used as the solvent (as in the analysis of iron ores), the solution must be strongly diluted before being titrated, and, to secure accurate results, the potassium permanganate must first be standardised against a solution of approximately the same concentration, and containing an equal quantity of hydrochloric acid. The rest of the analysis is performed in the same manner as before. The action of hydrochloric acid on potassium permanganate is so detrimental to good results, however, that its use should be dispensed with as much as possible.

Fresenius has made a number of experiments which go to prove that, under certain conditions, potassium permanganate which has been standardised against sulphuric acid can be used in titrating hydrochloric acid solutions. The concentrated solution of the ferrous compound in hydrochloric acid is made up to 250 c.c. with pure water, and then to 1000 c.c. with water which has been strongly acidified with sulphuric acid. Different portions, of 50 c.c. each, are then titrated, as before: the second and third results should be the same (the first is usually high). The constant results are calculated to the entire volume of the ferrous solution, and the quantity of iron deduced from the value obtained. Zimmermann recommends the titration of hydrochloric ferrous solutions, in presence of 25 c.c. of a manganous sulphate solution which contains 200 gr. $MnSO_4$ in 1000 c.c. water.

REMARK.—In titrating with potassium permanganate, the presence of easily oxidisable substances, such as nitric acid which contains nitrous acid, and of organic compounds, must of course be avoided.

2. *Separation of ferrous from ferric iron.*—(Example; oxidised ferrous sulphate). For this purpose two operations are necessary: (1) a direct titration to determine the quantity of iron present in the ferrous condition; (2) an estimation of all the iron, after reduction of the ferric salt. The difference between the results of the two determinations gives the quantity of ferric iron reduced, and this value is calculated to the sesquioxide. Each determination is made in a separate portion of the salt; the quantity to be weighed off depending upon that of metallic iron employed in standardising the potassium permanganate.

56 Iron (Fe) = 72 Ferrous oxide (FeO) = 80 Ferric oxide $\left(\frac{Fe_2O_3}{2}\right)$.

3. *Separation of aluminium and iron.*—The sum of the aluminium and ferric oxides is first determined, by one of the gravimetric methods, and a weighed quantity of the mixture then brought into solution, either by fusion with acid potassium sulphate and extraction with water and sulphuric acid, or by heating with sulphuric acid alone (§ 143; Example No. 15).

The iron is then reduced by zinc (as in the estimation of ferric salts), and titrated with potassium permanganate. The quantity of ferrous iron found is calculated to ferric oxide, and subtracted from the weight of the original mixture, the difference being the aluminium oxide. Hydrochloric acid solutions are less suitable for the titration (see above).

4. *Determination of nitric acid. By oxidation of a ferrous salt.*—1. Method of Pelouze and Fresenius. The superfluous ferrous salt is estimated with potassium permanganate, and the amount oxidised by the nitric acid calculated to the latter: $3Fe = HNO_3$, according to the equation:

$$3FeCl_2 + KNO_3 + 4HCl = NO + 3FeCl_3 + KCl + 2H_2O.$$

One gram of piano-wire is treated with 30-40 c.c. fuming hydrochloric acid, in a tubulated retort (of about 200 c.c. capacity), into which is led a current of hydrogen or carbon dioxide, the retort being placed on the water-bath. As soon as complete solution has been effected and the liquid cooled off (the current of gas still flowing), the cork is taken out, a small glass tube containing the substance (a quantity representing 0·2 gr. HNO_3) introduced, and the cork then hastily reinserted. The retort is again heated on the water-bath (for half an hour), and its contents are finally boiled until all the nitrous oxide has been expelled. The liquid is then allowed to cool in a current of carbon dioxide, diluted with water, and the residual ferrous chloride titrated with potassium permanganate. The calculation of the results is obvious. The permanganate must be standardised against a solution of the same concentration, and containing the same quantity of hydrochloric acid as that used in the estimation of the nitric acid. The quantity of ferric oxide formed can also be determined directly, by titration with stannous chloride (see Iodometry).

5. *Determination of tin.*—The tin must either be in the metallic form or as stannous chloride. The method is based upon the reduction of ferric to ferrous iron by tin in either of these forms. A definite volume of a standardised ferric chloride solution (prepared by dissolving piano-wire in hydrochloric acid and adding potassium chlorate) is treated with stannous chloride, or heated with finely-divided tin. The reduction results in the formation of a certain quantity of ferrous chloride, which can be determined by titration with potassium permanganate. As

the titration is made against a hydrochloric solution, the proper precautions must be taken, as explained above. The quantity of tin is calculated by means of the formulae:

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2,$$
$$Sn + 4FeCl_3 = SnCl_4 + 4FeCl_2.$$

6. Oxidimetry is extended to the analysis (1) of many easily oxidised substances, *e.g.*, organic bodies, such as oxalic acid, oxalates, etc., by titration with potassium permanganate; and (2) of all substances which oxidise ferrous salts (chromic acid, etc.) The latter class are analysed in the same way as nitric acid.

IODOMETRY

§ **151.** Iodometry has as its basis the determination of iodine by titration with sodium thiosulphate. The equation involved is as follows:

$$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

The necessary operations will be described in the order which they assume in an analysis. The first is the determination of the iodine, upon which all the methods are based. The operations can be performed with ordinary burettes.

Determination of Iodine.—The titration is made with sodium thiosulphate, the latter being added in excess, and the final point found with the iodine solution. Starch-paste is used as the indicator, and the final point made the appearance of a blue tint.

1. *Preparation of the solutions.*—10 gr. of sodium thiosulphate are dissolved in 1000 c.c. water. The solution must be standardised by experiment, as the commercial salt always contains impurities.

The iodine solution is prepared by dissolving 5 gr. of sublimed iodine in a concentrated aqueous solution of 8 gr. potassium iodide, which must be perfectly free from iodate.[1] The solution is then made up to 1000 c.c. The volumetric relation between the iodine and thiosulphate solutions must

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[1] The purity of the potassium iodide is tested by adding some starch-paste, and then hydrochloric acid, to its solution. If the solution becomes blue, iodic acid is present. To purify the iodine, 6 parts of the halogen are mixed with 1 part potassium iodide and sublimed between two well-fitting porcelain dishes. The sublimate (and iodine solutions in general) must be preserved in glass stoppered bottles, as iodine eats into ordinary cork.

be ascertained by experiment. The solutions change on standing, especially under exposure to the light, and must therefore be compared and restandardised from time to time.

To prepare the starch-paste, perfectly pure starch is digested with 100 parts of water, and the latter gradually heated to incipient boiling. The mixture must be stirred without cessation, throughout the operation. The emulsion obtained is then allowed to cool and settle, and the supernatant liquid decanted from the undissolved portion. Starch-paste is unstable, and must therefore be made anew for each series of determinations. About 3·0 c.c. of the solution are added in each titration.

2. *Relation between the solutions* of iodine and sodium thiosulphate. 20 c.c. of the sodium thiosulphate solution are run into a beaker from the burette, starch-paste added, and the sample titrated with the iodine, to incipient blueness. There must be a short wait before the reading is made (§ 146). The relation between the two solutions can be accurately determined only by taking the average of several titrations. If it is found to be very complicated, a factor is calculated for expressing a given volume of iodine solution in its equivalent of thiosulphate (§ 147).

3. *The sodium thiosulphate is standardised* by titration against a weighed quantity of pure sublimed iodine. About 0·15 gr. of the latter are weighed off between two watch-glasses (it is well to first subject it to sublimation in the same way). The watch-glasses are then placed in a beaker holding a solution of potassium iodide (1 : 10). When the iodine has passed into solution, sodium thiosulphate is run in from the burette until the brown colour has completely disappeared, and the volume used is then read off. Starch-paste is next added, and the excess of sodium thiosulphate titrated with the iodine solution. The numbers of cubic centimeters of iodine solution used having been calculated to cubic centimeters of thiosulphate, the result is subtracted from the volume of the latter originally employed, and the strength of the thiosulphate is found by dividing the weight of the iodine by this value. The strength is expressed in milligrams of iodine. It should be deduced from the average results of several concordant experiments.

When the sodium thiosulphate has been standardised, the known relation which it bears to the iodine solution used in titrating the excess of thiosulphate of course determines the strength of the iodine, without a second titration being involved. It is therefore unnecessary to describe the standardising of the iodine.

§ **152. I. Examples of Iodometric Methods.**—1. *The determination of iodine* with standard sodium thiosulphate is made in the manner just described, and therefore requires no further explanation. Example: commercial iodine.

The iodine solution having once been standardised, several substances which convert iodine to hydriodic acid can be estimated by its means. A few examples involving this method follow.

2. *Determination of hydrogen sulphide* in aqueous solution. The iodometric determination of hydrogen sulphide is based upon the equation:

$$H_2S + I_2 = 2HI + S.$$

It becomes inaccurate when more than 0·04 per cent of hydrogen sulphide is present. The titration is carried out until the blue colour appears.

3. *Determination of sulphurous acid.*—The equation expressing the reaction is as follows:

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI.$$

Bunsen used this method only for solutions which contained no more than 0·05 per cent SO_2. Volhard has shown that it also gives exact results with more concentrated solutions, if sulphurous acid be added to an excess of standard iodine solution, and the superfluous iodine then determined with sodium thiosulphate.

4. *Determination of arsenious acid.*—About 1 gr. of arsenious acid or an arsenite is dissolved in a concentrated solution of sodium bicarbonate, starch-paste added, and the solution titrated with standard iodine. The reaction is represented by the equation:

$$As_2O_3 + 4NaOH + 4I = As_2O_5 + 4NaI + 2H_2O.$$

5. *Determination of stannous tin.*—Metallic tin or the

stannous salt is dissolved in hydrochloric acid, in a current of carbon dioxide, and a piece of platinum added while the reaction is proceeding. After the addition of some sodium potassium tartrate (Rochelle salt), and an excess of sodium bicarbonate, a few cubic centimeters of starch-paste are added, and the solution titrated with standard iodine. Two atoms of iodine (254) correspond to one atom of tin (118).

A standard solution of stannous chloride can also be prepared in this manner, and substances which are reduced by stannous chloride determined by its aid. The following is an example of this method.

6. *Determination of ferric oxide* with stannous chloride. The volumetric determination of ferric oxide is based upon the reduction of ferric chloride to the ferrous state by stannous chloride:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

To standardise the stannous chloride solution, a weighed piece of piano-wire is dissolved in hydrochloric acid in presence of potassium chlorate, and the resulting liquid titrated with the stannous chloride solution, the strength of which is to be found. The final point of the reaction is indicated by the complete decolorisation of the previously yellow solution. To ascertain whether too much stannous chloride has been added, the solution must be cooled off, starch-paste added, and any excess titrated with a solution of iodine in potassium iodide, the relation of which to the stannous chloride is known. The iodine is added until the solution begins to turn blue. If stannous chloride was present in excess, the superfluous amount is deduced from the volume of iodine solution run in. Ferric compounds can be determined with a solution of stannous chloride in the same manner.

II. **Chlorimetry.**—The second group of iodometric methods comprises the estimation of free chlorine and bromine. For this purpose the equivalent quantity of iodine liberated by the one or the other is titrated.

7. *Determination of bromine* in bromine water. Ten cubic centimeters of bromine water are delivered from a pipette into a beaker containing a solution of potassium iodide. The pipette used should be joined, by rubber tubing, to a tube con-

taining pieces of lime which have been soaked in a concentrated solution of sodium sulphate, with which to hold back the bromine fumes: the rubber tubing is encircled by a pinchcock. The brown colour produced by the liberation of iodine from the potassium iodide is next destroyed by sodium thiosulphate, and the excess of the latter titrated with starch-paste and standard iodine solution, as described above. 127 I = 80 Br.

8. *Analysis of bleaching powder* (chloride of lime).—10 gr. are mixed to a paste with water in a mortar, rinsed into a liter-flask, and diluted to the mark. After being thoroughly shaken, an aliquot portion of the solution and precipitate is taken out, and treated with potassium iodide and hydrochloric acid. The iodine which separates is determined as usual. Each atom of iodine (127) corresponds to one of chlorine (35·5).

III. *Analysis of compounds which generate chlorine when heated with hydrochloric acid:* peroxides, certain oxides, chromic acid, etc.

The gaseous chlorine is led into a solution of potassium iodide, and the liberated iodine determined. The oxygen compounds undergo reduction; $2I = 2Cl = O$.

9. *Potassium dichromate.*—A weighed quantity of the salt (about 0·3 gr.) is introduced, together with fuming hydrochloric acid, into a long necked flask. The latter is placed in a slightly oblique position, and closed by a black caoutchouc cork, holding a tube which is in connection with a receiver containing potassium iodide. The receiver is supplied in a common retort, which is fastened in an inverted position, the bulb thus being above the neck. The lower half of the retort must be placed in a porcelain dish containing cold water, as the reaction would otherwise generate too much heat. The quantity of potassium iodide solution (5 gr. KI) to be placed in the retort is governed by the capacity of the latter; it must be small enough to secure against its ejection from the retort by a rapid generation of the gas. A piece of magnesite (magnesium carbonate) should also be placed in the flask, and a continuous stream of carbon dioxide thus generated, to prevent recession of the potassium iodide. The apparatus having been set up and filled with the respective solutions, the con-

tents of the flask are gently heated, and finally boiled for about ten minutes. Close attention must be paid to this operation, and when the lamp has once been placed below the apparatus, it must not be removed, even while the apparatus is being taken apart. When the reaction has ceased, the cork is taken out of the flask, and the retort turned over and allowed to cool. Its contents are then poured into a beaker, the retort rinsed out several times, and the wash-water added to the solution. Sodium thiosulphate having been run in until the solution has lost its colour and the volume used having been noted, its excess is determined with standard iodine solution, as above. The results are calculated to chromium trioxide or potassium dichromate. The equation and equivalent quantities follow:

$$K_2Cr_2O_7 + 14HCl = 6Cl + 2CrCl_3 + 2KCl + 7H_2O.$$

381 parts iodine $(3I) = 106{\cdot}5$ parts chlorine $(3Cl) = 100$ parts chromium trioxide (CrO_3).

762 parts iodine $(6I) = 213$ parts chlorine $(6Cl) = 294$ parts potassium dichromate $(K_2Cr_2O_7)$.

Manganese dioxide and chloric and iodic acids are analysed in exactly the same manner, and with the same apparatus.

$$MnO_2 + 4HCl = 2Cl + MnCl_2 + 2H_2O,$$
$$KClO_3 + 6KI + 6HCl = 6I + 7KCl + 3H_2O.$$

IV. *The analysis of substances in a lower degree of oxidation,* but which pass into higher oxides in presence of chlorine, is merely an extension of this method.

If we know the quantity of chlorine employed (it is found by acting with hydrochloric acid on a weighed amount of potassium dichromate, and calculating the chlorine), and determine the quantity unconsumed in the reaction (again by liberation and determination of iodine), the difference corresponds to the quantity of the substance oxidised.

10. *Arsenic trioxide.*—About 0·3 gr. of potassium dichromate and a like quantity of arsenic trioxide are weighed off, and the amount of chlorine which the former can release is calculated. The analysis is made in the same manner as that of potassium dichromate (9). The iodine liberated

having been determined, the corresponding quantity of chlorine is calculated, and this value subtracted from the entire quantity set free by the potassium dichromate; the difference represents the chlorine which has been consumed in oxidising the arsenic trioxide. This quantity stands in the following proportion to the arsenic trioxide:

142 parts chlorine (4Cl) = 198 parts arsenic trioxide (As_2O_3).

11. *Ferrous and ferric oxides.* Bunsen's method.—The determination of ferrous and ferric oxides is made in the same manner. Fuming hydrochloric acid and a piece of marble are introduced into the flask, and after the air has been completely displaced by carbon dioxide, the cork is removed for an instant, and weighed quantities of the substance and potassium dichromate dropped in. The remaining processes are the same as above. The loss in chlorine corresponds to the quantity of ferrous oxide.

35·5 parts chlorine (Cl) = 72 parts ferrous oxide (FeO).

III

PRECIPITATION METHODS

§ **153.** The precipitation methods are based upon the formation of an insoluble, from two soluble bodies. The final point of the reaction may be indicated by the cessation, or, more rarely, the commencement, of precipitation; but in the majority of cases is shown by a fitting indicator. Although its principle would permit this method to be widely extended, the difficulties presented in finding the final point limit its application to a few determinations.

1. **Estimation of Chlorine in Soluble Chlorides.**—In this method the chlorine of the chloride is precipitated by a standard solution of silver nitrate. To find the final point, a concentrated solution of potassium monochromate is used; the reaction is complete when the precipitate assumes a permanent reddish-brown colouration. The silver solution is made by dissolving about 17 gr. of fused silver nitrate in 1000 c.c. water (if less than this quantity of solution be needed, a corresponding reduction is made in the weight of

the salt; *e.g.*, for 500 c.c., 8·5 gr.) This solution must be standardised by experiment.

The strength of the solution is determined with sodium chloride. Pure sodium chloride (obtained by precipitating a saturated solution of the salt with concentrated hydrochloric acid) is cautiously ignited, at a temperature somewhat below its melting point. It is pulverised while still warm, and placed in a weighing-glass and weighed off, in two or three portions of 0·1-0·2 gr. each, which are then dissolved in beakers or casseroles, in 20-30 c.c. of water each. After the addition of three drops of a solution of potassium monochromate, the chloride is titrated with the silver solution, under constant stirring. The final point is reached when the precipitate attains a brownish-red tint. This tint should be as nearly as possible the same in every experiment. If the results of the last two titrations agree, this is all that is necessary, and the values can be immediately calculated; the strength of the solution should be expressed in the equivalent of either silver or chlorine. The proportion is as follows:

58·5 parts sodium chloride = 35·5 parts chlorine =
108 parts metallic silver = 170 parts silver nitrate.

REMARK.—If too much of the silver solution has accidentally been added (and the colouration is consequently very dark), the excess can be titrated with sodium chloride. For this purpose a decinormal solution, *i.e.*, one which contains 5·85 gr. sodium chloride in the liter, is used. The pure salt is weighed off (see above) and dissolved in 1000 c.c. water, and the strength calculated.

The analysis.—The chlorine in chlorides can be determined by this method only when in *neutral* solution. About 0·5 gr. substance are weighed off, dissolved in water, and the solution made up to 200 c.c. (first neutralised, when necessary, by nitric acid or sodium carbonate). Three portions of this solution, each containing 50 c.c., are then coloured by three drops each of a saturated solution of potassium monochromate, and titrated as above. The results are calculated, as usual, from the number of cubic centimeters of the silver solution used.

Examples: sodium chloride; potassium chloride; ammonium chloride.

2. **Hydrocyanic Acid, Potassium Cyanide.**—The volumetric determination is made with a standard solution of silver nitrate: the final point is indicated by incipient turbidity.

The *silver solution* is prepared by dissolving a weighed quantity of pure silver nitrate in a known volume of water, and calculating the strength. A decinormal solution is much to be preferred.

Potassium cyanide.—About 0·3 gr. of the salt are weighed off and dissolved in 100 c.c. of water: 25 c.c. of this solution are taken up with a pipette for each analysis.

Hydrocyanic acid.—To determine hydrocyanic acid in a concentrated solution, from 2-3 gr. of the latter are weighed off, saturated with potassium hydroxide, and diluted to 150 c.c.: 20 or 30 c.c. of this solution serve for each titration.

In the analysis of both potassium cyanide and the free acid, the silver solution is added until the solution assumes a slight turbidity which does not disappear on stirring. The reaction is as follows:—

$$2KCN + AgNO_3 = AgK(CN)_2 + KNO_3$$

170 parts silver nitrate = 130·2 parts potassium cyanide = 54 parts hydrocyanic acid.

3. **The determination of silver** can be accomplished in acid solution by Volhard's method. Ammonium sulphocyanate precipitates silver salts, from their nitric acid solution, as silver sulphocyanate. Ferric sulphate, upon which ammonium sulphocyanate has no action until the silver has all been precipitated, serves as the indicator. The final point is told by the appearance of the red colour of the ferric compound.

a. Ammonium sulphocyanate solution.—The solution is prepared by dissolving about 8·0 gr. of the salt in a liter of water: it must be empirically standardised, as the pure salt is unattainable. For this purpose, about 2·0 gr. of silver nitrate are weighed off and dissolved in one liter of water, previously acidified by nitric acid, and the strength of the solution calculated. From 200 c.c. to 300 c.c. of this solution are then removed to a beaker; 5 c.c. of a solution of ferric sulphate which contains about 50 gr. of the salt in 1000 c.c. are added; and the ammonium sulphocyanate solution slowly run in from the burette until the silver solution assumes a reddish tint which does not disappear on stirring. Several consecutive experiments must agree before the results may be used to calculate the strength of the ammonium sulphocyanate. It is most convenient to express the strength in milligrams of silver.

b. The analysis.—About 0·5 gr. of metallic silver or of a silver coin are dissolved in nitric acid, and the solution made up to 500 c.c. It is then titrated as above. The presence of copper is no objection, even though it constitutes 70 per cent of the alloy.

4. *Determination of the halogens.*—When in a solution slightly acidified by nitric acid, the halogens also can be determined by Volhard's method, in the manner just given. Standard silver-solution is first added in excess, and the residual quantity determined by titration with ammonium sulphocyanate. The difference between the silver added and found equals that which has combined with the halogens.

5. *Determination of silver* by Gay Lussac's method.—The theory of this method is very simple. A solution of silver nitrate is precipitated by sodium chloride, with formation of sodium nitrate and silver chloride:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

A definite quantity of sodium chloride (estimated by weighing the salt or measuring the solution) represents an equivalent quantity of silver chloride, or, in general, of metallic silver. The theoretical simplicity of this reaction, however, is lost in analysis. When a certain point has been reached, toward the end of the precipitation, equilibrium is established between the sodium chloride added, and the sodium nitrate and silver nitrate in solution. In this state the solution is precipitated by silver nitrate as well as by sodium chloride, though on the addition of either reagent the equilibrium is destroyed. This phenomenon prevents the standardising of a sodium chloride solution, to be used for determining silver, merely from a weighed quantity of the salt; and its strength must accordingly be empirically established by titration with a standard silver-solution. The final point of the reaction, on the other hand, can be denoted by one of several phenomena: (1) by the precipitate ceasing to form on the addition of sodium chloride;

(2) by a precipitate being caused on the addition of silver nitrate. If, after the final point, as denoted by the first method, has been reached, a standard (preferably quite dilute) solution of silver nitrate be added, drop by drop, until this ceases to give a precipitate, the solution is again in condition to be precipitated by sodium chloride. Let us suppose that for this exactly twenty drops of silver nitrate were necessary. Sodium chloride is now run in until it, too, ceases to give a precipitate. If we assume that the solutions of silver nitrate and sodium chloride correspond in strength (are decinormal, for instance), it will be found that the number of drops of sodium chloride used exactly equals that of the silver nitrate, viz., twenty. A certain point, conveniently called the "neutralisation point," at which the precipitate produced by either solution would be equally dense, would be reached on the addition of ten drops of one or the other solution. This point can also be taken as the final reaction. (3) Finally, an excess of sodium chloride can be added, and silver nitrate then run in until it ceases to cause a precipitate. The sodium chloride having once been determined, the analysis can be made with equal accuracy by employing any one of the three final points, if the one chosen was also used in standardising the solution. The first, *i.e.*, the point at which sodium chloride ceases to cause a precipitate, is the most convenient, and is generally employed.

Standardisation of the sodium chloride solution.—5·4145 gr. fused sodium chloride are dissolved in one liter of water (at 16° C.) Each cubic centimeter of the solution corresponds in theory to 0·01 gr. silver, 100 c.c. to 1 gr. silver, but its strength must also be empirically found. For this purpose, 1·001 gr. metallic silver are dissolved in 5 c.c. of nitric acid (1 : 3), in a so-called test-bottle. The latter should have a capacity of about 200 c.c., and be closed by a cork which tapers to a point below. During the experiment the bottle must be kept in a case of black paper or cloth, provided with a cover. Solution is assisted by placing the flask in a slanting position and gently heating on a water-bath. When the silver has dissolved and the solution has cooled down to 16° C., 100 c.c. of the likewise freshly prepared sodium chloride solution are run into the bottle from a pipette, and the bottle closed and thoroughly shaken until the silver chloride has settled.

This precipitated solution is used to standardise the sodium chloride. The experiment must be made with decinormal solutions, which are prepared as follows. A decinormal solution of sodium chloride is made up simply by diluting 50 c.c. of the concentrated solution, obtained as above, to 500 c.c. at 16° C.: 1 c.c. of this solution corresponds to 0·001 gr. silver. 0·5 gr. metallic silver are next dissolved in nitric acid (2-3 c.c. of 1·2 sp. gr.), and the solution made up to 500 c.c. (at 16° C.) This solution contains 0·001 gr. silver in each cubic centimeter. The decinormal silver solution is for use in case an excess of sodium chloride be accidentally added in the titration. We will now proceed with the operations. The precipitation of the silver in the test-bottle is completed with the decinormal sodium chloride, the latter being added in half cubic centimeters at first, finally two drops at a time, and the bottle shaken after each addition until the liquid clears. The final point is reached when the last two drops produced no precipitate. It is readily distinguishable, but for the sake of security it is advisable to add 2-3 c.c. of the decinormal silver solution and find the point again. The number of cubic centimeters taken of the decinormal sodium chloride solution are then calculated to the normal (divided by 10), and added to the 100 c.c. of the latter which were first used: the result expresses the strength of the normal solution (1 gr. of metallic silver usually represents, in fact, 100·1 c.c., or slightly more, instead of 100 c.c., of the normal sodium chloride). The empirical strength is employed in calculating the results of silver determinations.

The analysis.—Enough of the sample for analysis (silver or alloy) is weighed off, to represent somewhat more than one gram of silver (*e.g.*, 1·002-1·003 gr.) This is dissolved in nitric acid (just as that used in standardising the solution); 100 c.c. of the normal (concentrated) sodium chloride are added; and the titration finished with the decinormal solution. The final point must be the same as that taken in the standardising operations. The result is calculated according to the empirical strength of the sodium chloride. As it is necessary to take for the analysis an amount of the silver or alloy which represents one gram of pure silver, the approximate amount of silver which the sample contains must first be ascertained. For this purpose a rough test is made in the same manner as the above, but without resort to the decinormal solutions. This volumetric method of determining silver is remarkably exact, having even served Stas in his determination of the atomic weights of several elements. The details which he observed in its use, however, cannot be described in this book. This method is employed in the laboratory only when many successive silver determinations are to be made. A single analysis can be much more rapidly performed by gravimetric means.

6. *Pisani's method.*—This is very convenient when but small quantities (up to 0·02 gr.) of silver are to be estimated. It is based upon the fact that a blue, aqueous solution of iodised starch is decolorised by silver nitrate, with separation of silver iodide. The moment when the last trace of colour disappears is the final point, and can easily be discerned. Two grams of iodine are rubbed together with fifteen grams of starch, and a few drops of water added to the mixture. The paste is then heated upon the water-bath, in a closed flask, until the violet colour changes to grayish blue; the transition requires about an hour. Water is then added, and the solution standardised with silver nitrate (containing 1 gr. Ag in 1000 c.c.) The concentration should be such that 50-60 c.c. correspond to 10 c.c. of normal silver solution. The methods both of standardising the solution and of the analysis itself are obvious. Pisani's method may be coupled with the foregoing one with great convenience, the decinormal sodium chloride solution used in the last stage of the titration giving place to the iodised starch.

SECTION III

ORGANIC ANALYSIS

CARBON possesses the property of entering into numberless and most diverse compounds with other elements. These carbon compounds possess a far more complicated and peculiar character than those of other elements, and (with the exception of a few simple forms) are given a separate place in the study of chemistry. This branch of the science is called "Organic Chemistry," the "chemistry of organic or of carbon compounds."

Organic compounds usually contain, besides their carbon, the elements hydrogen and oxygen; comparatively few contain, in addition to these three, nitrogen; and sulphur and phosphorus are still more rarely met with. These are the principal elements found in organic compounds, although the presence of any of the others is possible.

In analysis, the elements which constitute the compounds are determined by conversion to the respective stable forms which we have described in the foregoing pages. The carbon is changed to carbonic acid, hydrogen to water, phosphorus to phosphoric acid, etc. The methods for the direct determination of oxygen are alone unsatisfactory, and in spite of the fact that this object has been the point of many investigations, oxygen is still determined from the difference. We are already acquainted with the forms in which the various elements are estimated. The problem of organic analysis is therefore only to convert the elements of the compound into these stable forms, and to weigh them as such. The peculiar nature of organic bodies has necessitated for this purpose the invention of equally distinct methods of analysis.

DETERMINATION OF CARBON AND HYDROGEN

§ **154.** Organic compounds possess characteristic properties which sharply distinguish them from compounds of the other elements. On being heated in the air the majority of organic compounds burn: those which are volatile leave no residue on combustion (unless they contain a metal): solid substances, when ignited on platinum foil, as a rule first become carbonised, and the residual carbon finally burns away. When the substance contains a metal, it leaves an *ash* on combustion. These properties, alone, usually suffice for the detection of carbon, and a special test is necessary only in isolated cases. When such a test is required, the substance is mixed with cupric oxide, and the mixture introduced into a tube of difficultly fusible glass, which is sealed at one end, and connected at the other with a tube leading into baryta water. The mixture is then ignited, whereupon the carbon becomes oxidised by the cupric oxide, and the carbonic acid produces a white precipitate of barium carbonate in the baryta water.

As we have already said, carbon is quantitatively estimated by conversion to carbonic acid; hydrogen by conversion to water. The oxidation of the substance for this purpose is effected by a special process, in which the carbon is burned to carbonic acid, the hydrogen to water. The operation is therefore known as a " Combustion." The oxidising agent must be some substance which readily parts with its oxygen—cupric oxide, lead chromate. The combustion is made in a tube of glass or other suitable material, and the carbonic acid and water which form are received in appropriate apparatus. Before taking up the operations of analysis it will be well to explain the preparation and use of the oxidising agent, and the apparatus used for the combustion.

The Oxidising Agent. I. *Cupric oxide.*—This reagent is used in three forms; either as a light, flocculent powder, in scales, or in coarse grains. The powder is used chiefly in the combustion of solid organic substances, where an intimate mixture can be secured. The granular preparation and that in scales are more generally employed in the analysis of liquids, but also, in connection with the powder, in the analysis of solid substances.

Preparation of the cupric oxide.—Pulverulent cupric oxide is obtained by dissolving metallic copper in hot nitric acid and evaporating to dryness in a porcelain dish. If copper scales are employed, they are mixed to a paste with nitric acid, and, after the effervescence has ceased, the mixture cautiously evaporated to dryness. In either case, the dry residue is next placed in a Hessian crucible, and the latter heated in a furnace fire until the cupric nitrate has completely decomposed. The form in which the oxide is obtained depends upon the degree of heat at which it has been prepared: if the temperature was not too high, it is left in a light flocculent state, and is easily reduced to powder; if the heat was very great, on the contrary, the residue will be a hard, caked mass. The latter preparation is broken up and passed through a sieve,[1] and granular cupric oxide thus obtained. It is prepared in the flocculent state by the ignition of copper (copper filings) in a muffle, and subsequently in a glass tube in a stream of oxygen.

It is to be remarked that cupric oxide, especially its powder, is exceedingly hygroscopic, and requires extreme caution in drying. The method will be described in connection with the analysis itself.

As the combustion of the carbon and hydrogen takes place at the expense of the cupric oxide, the latter becomes reduced to metallic copper. When the analysis is finished, a current of oxygen may be led through the tube, and the metallic copper again oxidised. The regenerated oxide can thus be used directly for the next determination. If ignition in oxygen is not employed, the reduced copper must be moistened with nitric acid and ignited in a crucible. The first method is obviously much the better.

2. *Lead chromate* is used in the same manner as cupric oxide. It is less hygroscopic, and can therefore be employed with advantage when the hydrogen in an organic substance must be determined with great accuracy. Cupric oxide cannot be used in the combustion of sulphur compounds, or of such

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[1] The sieves are made of metallic boxes, the bottoms of which are filled with holes, the diameters of which vary in the several sieves. Several of these boxes are placed one above the other, in the order of the size of their perforations, and the top one covered by a metallic plate. The cupric oxide is gradually sifted from one box to another, and finally obtained in different grades of coarseness, from a fine powder to large granules. Such sieves are used in preparing granules of equal size of cupric oxide, calcium chloride, pumice, etc.

salts of organic acids as contain alkali or alkaline earth metals (see below); these substances, therefore, are always analysed by means of lead chromate. As lead chromate fuses during the operation, a much more perfect combustion is obtained by its means than with cupric oxide (without oxygen).

Preparation of the lead chromate.—A lead acetate solution is precipitated by potassium dichromate, and the precipitate at first washed by decantation; it is then collected upon a linen strainer and the washing completed. After being thoroughly dried, it is placed, in small portions, in a Hessian crucible and fused.[1] The molten salt is poured out upon an iron or stone plate; when cold it assumes a steel-gray colour. It is next broken up and powdered in a mortar (the powder is reddish-yellow or reddish-brown). Analyses are quite frequently made with lead chromate which has first been fused with one-tenth its weight of potassium dichromate; the mixture fuses more readily than the pure salt.

Commercial lead chromate usually contains impurities which render it unfit for analysis, and it must not be used until its purity has been tested. Riethausen and N. Ljubawin have both found that, even though properly prepared, lead chromate gives off carbon dioxide when heated. The latter chemist recommends igniting the salt in a current of oxygen before each experiment.

The carbon and hydrogen of an organic substance undergo combustion at the expense of the oxygen of the chromic acid. The same portion of lead chromate can be used for two or three analyses. Old lead chromate is converted to a state suitable for analysis by fusion with one-tenth its weight of potassium dichromate (if the latter has not already been added). It is still better to pulverise the salt and moisten it with nitric acid before igniting.

§ 155. **Combustion Tubes.**—The combustion is performed in tubes of difficultly fusible (Bohemian) glass, which have a diameter of from $\frac{2}{5}$ to $\frac{3}{5}$ of an inch. The length depends upon the nature of the analysis; it should be at least

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[1] Perrot's gas furnace is very convenient for this purpose, the fusion being quickly brought about by its use. If the Hessian crucible be new a portion of the molten chromate is apt to pass through its sides. The crucible can be prevented from cracking by allowing it to remain in the furnace while cooling; and, on being used a second time, will be impervious.

twenty inches. A piece of thoroughly dry and clean tubing is slightly rounded at one end, to permit the ready insertion of a cork, and the other extremity drawn out into a long, narrow tail; this narrow portion is then twice bent into a right angle and the tip sealed up. The first bend is made at the point where the contraction begins; the second about one or one and a half inches farther along. The whole tube now has a form somewhat similar to a bayonet. The glass at the bent end must be thin, so that it can readily be broken at the close of the combustion, in order to allow the passage of a current of oxygen. Instead of this bayonet-shaped tube, one is sometimes employed, the end of which is pulled straight out. The tube must be carefully dried by drawing air through it while hot before each analysis: it is then ready to be filled with the combustion agent.

The Combustion Furnace.—The combustion furnace consists of a long narrow gutter, which serves to support the tube in which the combustion is performed, and which can be heated along its entire length by gas-burners. The gutter is made either of iron (with a lining of calcined magnesia) or of clay. Two rows of tiles, which extend the whole length of the furnace, and on both sides of the tube, serve to reflect the heat and thus bring the upper part of the tube to a high temperature. Each burner is fitted with a movable ring, to reduce the supply of air when a small flame is employed. They are all joined to a single cylindrical tube, which is attached at both ends to the gas-pipe.[1] In making an analysis, a block is placed under the posterior end of the furnace, so that the latter inclines slightly toward the absorption apparatus. The furnaces which are now most used are those of Erlenmeyer and Glaser. The latter furnishes more heat than the former.

Liebig's charcoal furnace is a long narrow box of sheet iron. The combustion tube is supported by small bridges, which rest on the bottom of the box, and between which are openings which supply the air. In the anterior side of the box is a round hole, through which the end of the tube in connection with the absorption apparatus passes. The tube is heated by red-hot charcoal. The combustion must be commenced at the open end of the tube, and to secure this object and heat the different

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[1] As a great quantity of gas is consumed in combustions, the cock through which it is supplied must be of a larger calibre than suffices for an ordinary burner.

portions of the tube in succession, the latter is provided by iron screens which can be shifted from one part to another. The charcoal is put in gradually, and care must be taken during the operation, lest the perforations for the air supply become choked by ashes. The charcoal is heated in a small iron box fitted with a grate, and the sides of which are filled with holes: the draught is increased by means of a conical iron cover.

§ 156. When the combustion is over, oxygen is passed through the still red-hot tube, in order to drive any carbon dioxide which remains into the absorption apparatus, and also to oxidise the small particles of carbon which may otherwise escape combustion; if the combustion was made with cupric oxide, the metallic copper which has formed will be reoxidised at the same time.

The oxygen is generated from potassium chlorate, previously fused and pulverised, and which is sometimes mixed with one-twentieth its weight of pure manganese dioxide.[1] The salt is placed in a retort of difficultly fusible glass, and a piece of rubber tubing passed over the neck of the latter: the free end of the tubing is inserted in a gasometer which is filled with water. The retort is then heated by a naked flame, whereupon the salt fuses quickly, and oxygen escapes into the gasometer. 100 gr. of potassium chlorate can generate as much as 27 liters of oxygen. The gas must be carefully freed from moisture and impurities (especially carbon dioxide) before being used.

Apparatus for purifying and drying the oxygen.—The oxygen is purified and dried by passage through tubes which are filled with appropriate substances. So-called U-tubes, fastened to a permanent support, are the most convenient in form. The oxygen, on leaving the gasometer, is passed through a potash bulb (or some other appropriate bulb-apparatus) which is filled with concentrated sulphuric acid; and then through a tube containing either pumice soaked in sulphuric acid, or broken glass and phosphoric anhydride. The gas is now free from moisture; its carbonic acid is

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[1] The manganese dioxide to be used in preparing oxygen must be as pure as possible. It often contains carbon, and also antimony sulphide; and if these substances are present, an explosion will inevitably occur. The potassium chlorate must also be tested before being used, as it often gives off chlorine on ignition. If this be found the case with the salt at hand, the oxygen must be passed through milk of lime before its collection in a gasometer.

removed by passage through a U-tube, one stem of which is filled with solid potassium hydroxide, the other with soda-lime. From the latter, it is led directly into the combustion tube.

The drying apparatus is prepared as follows. Into the curve of a U-tube is placed a copper spiral, to prevent the drying medium from choking up the tube, and thus blocking the passage of the gas. A plug of asbestos (the threads must be fairly long) is then placed lightly over each end of the spiral, packing being avoided, and each arm of the tube filled with the substance, to within an inch and a half of the top. The substance is then covered by layers of asbestos, and the tube closed by corks, which are fitted with bent tubes for the introduction and escape of the gas. A large U-tube, one and a half feet long and from three-fifths to four-fifths of an inch in diameter, will last for a long time (for at least twenty analyses), if the sulphuric acid in the bulbs be renewed before each experiment. The pumice is broken into small pieces, the dust sifted out, and the lumps remaining soaked in sulphuric acid and ignited in a Hessian crucible. They are then soaked in the acid again and placed in the tube, or else put in in the dry state and saturated with the necessary quantity of acid afterward. The sides of the tube must be well wiped before the corks are inserted. The soda-lime is employed in the form of small lumps; its preparation is described under the determination of Nitrogen, § 167. The potassium hydroxide is used in sticks.[1]

If a current of air is to be led through the combustion tube during the analysis (as in Marchand's method, and in combustions with lead chromate), it is dried and purified with the same apparatus.

§ 157. Apparatus for absorbing the Water and Carbon Dioxide. *The calcium chloride tube.*—The water formed by the combustion of the organic substance is absorbed by calcium chloride. The apparatus in which the latter is placed has been given various forms, all of which, however, are alike in one respect: they must be made of thin glass, to avoid as

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[1] A drying apparatus of very convenient form, and also a new combustion furnace, have recently been described by Glaser (*Annal. der. chemie und Pharm.* Suppl. VII. 213).

much unnecessary weight as possible. The *straight* calcium chloride tube is of fairly large diameter, and blown at one end into a large bulb; to the latter is fused a smaller tube, also widened to a bulb at a point near the joint. The water formed in the combustion collects in this smaller tube, the main portion of the apparatus serving merely to retain the vapour which escapes condensation. The arrangement enables the tube to be repeatedly used, without renewal of the calcium chloride. Another form is the so-called U-tube. The small tube with the bulb is fused into one of the arms, near its mouth. U-tubes, connected by a cork with the bulb-tube in which the water condenses, are also employed. Such a form is convenient in this respect, that it permits one to employ as long a tube as he wishes; the further the bulb is removed from the furnace, the more complete is the condensation of the water; and, consequently, the greater the durability of the calcium chloride. In apparatus of the first form, on the other hand, the tube attached to the bulb must necessarily be short, with the result that the bulb is very near the furnace. When an analysis is finished, and the tube and water have been weighed, the condensed water is removed by holding the tube vertically and gently shaking it out.

The calcium chloride used in filling the tube is prepared by evaporating the solution obtained by the action of hydrochloric acid upon marble (residue from the carbon dioxide generator). This solution is purified by adding calcium oxide until the reaction becomes slightly alkaline, filtering, acidifying the filtrate with hydrochloric acid, and evaporating to dryness. The evaporation must be performed over an open flame, and the liquid constantly stirred during its progress. The dry, white residue is then broken up, run through a sieve (§ 155, footnote), and all the pieces of one size reserved. To fill a straight calcium chloride tube, a ball of wool is first placed over the mouth of the passage between the two bulbs, and the calcium chloride then shaken in: the salt is then covered by a second plug of wool, and the tube closed by a cork through which passes a straight tube for connection with the potash bulbs. To fill a U-tube, a copper spiral is placed in the curve, covered at each end by a plug of wool, and the tube then filled with the calcium chloride; more wool is finally inserted, and the arm into which the bulb-tube fits closed by a cork. The cork must be sealed with sealing-wax or glue. A gentle suction is then applied to the filled tube, to ascertain whether the air can find a ready and free passage through it. To convert to the carbonate the calcium oxide which forms on evaporation of the chloride, a current of well-dried carbon dioxide is passed through the tube for two or three hours, and the apparatus weighed from time to time. The conversion may be considered complete when two consecutive weighings show no change. Air must be carefully drawn through the tube, before each weighing, until the carbon dioxide which it contains has been removed. The tube is now ready for use. To prevent absorption of moisture from the air, the ends of the small arms are covered by rubber caps, made from pieces of rubber tubing in which are inserted bits of glass rod. To make the weighing easier, a piece of wire (of pure silver if possible) is attached to the tube, and the latter suspended by a loop in the wire to the hook above the balance pan. The weighing must be made without the rubber caps.

Potash bulb.—The carbon dioxide is absorbed in a concentrated solution of potassium hydroxide. The necessary apparatus is now given one of two forms: that of Liebig's potash bulb, or that of Geissler's: the latter is a modification of the first.

The Liebig's potash bulb and its use.—The apparatus consists of five bulbs, which lie in the same vertical plane, and are connected together by narrow tubes. From the two upper bulbs, of which one is considerably larger than the other, extend tubes by which to attach the apparatus to the calcium chloride tube and a potash tube respectively. When the apparatus has been filled with potassium hydroxide solution and adjusted in a slightly oblique position (by placing a cork under one of the three lower bulbs), four of the bulbs and the connecting tubes must contain the alkali. A large absorption area for the carbon dioxide is thus obtained, with a comparatively small quantity of potassium hydroxide, and the weight of the complete apparatus being also slight. The exit tube of the apparatus is connected with a small bulb-tube which tapers off at one end, and the straight section of which contains pieces of potassium hydroxide between asbestos plugs. This tube is joined to the main apparatus by a cork which is thoroughly sealed in with sealing wax. The tube serves to retain the aqueous vapours which a rapid current of gas might otherwise carry away from the apparatus. The same end is sometimes obtained by using as the potash tube a U-tube (or some other form), which is directly connected with the bulb (weighed with it also). The potash bulb, when not in use, must be kept closed by rubber caps, which are removed, however, during the process of weighing.

The potash bulb is filled with a concentrated solution of potassium hydroxide (1 part solid KOH, 2 parts water). The solution is introduced by dipping one end of the apparatus below its surface and gently sucking it up by means of a rubber tube which is passed over the other end. The three lower bulbs must be completely filled, and when the apparatus is held obliquely (as in an analysis), and a current of air blown through it, the air must pass through the three lower bulbs, and also the last one, in separate bubbles. The last bulb, *i.e.*, the smaller of the two upper ones, must not be more than half filled by the solution while a current of air is passing through the apparatus. After being filled, the apparatus must be carefully wiped off on the outside, and the inside of the tube through which the solution was drawn up must also be dried, by means of a twisted slip of filter paper. For convenience in weighing, it is provided, like the calcium chloride tube, with a looped platinum wire. If the potash bulb is small, it should be filled anew before each operation: a large apparatus may be used without changing the solution, until about one gram of carbon dioxide has been absorbed.

The Geissler's bulb is only a modification of Liebig's apparatus, likewise consisting of five bulbs which are connected together by thin tubes. The apparatus rests upon its three lower bulbs. It is also provided with a potash tube. The apparatus is filled and used in the same manner as the Liebig's bulb.

Mulder has proposed the absorption of carbon dioxide in a tube filled with soda-lime. The apparatus is prepared as directed in § 156.

§ 158. Weighing of the Substance.—The directions given in § 139, respecting the selection of the sample for analysis, also pertain to organic substances. The results of the analysis cannot be considered reliable unless it has been ascertained that the sample taken was perfectly homogeneous. The purity of solid compounds is best examined through their crystalline form and the definiteness in their melting-points; that of liquids, through the constancy which they exhibit in specific gravity and boiling-point. The numerous cases in which the homogeneity of the substance must be tested by exceptional methods cannot be here considered.

Solid substances should be weighed in thin glass tubes, which are supplied with stoppers. As we have explained in § 139, it is advantageous to know the weight of the tube, so as to be able to judge by the eye the quantity of substance to be poured out. The weight of the substance taken for analysis is learned from two weighings; that of the tube when filled, and that when the substance has been taken out. The length of the weighing tube depends upon the manner in which the substance is to be mixed with the combustion agent (§ 160). When the substance is to be introduced directly into the combustion tube, it should have a length of from twenty to thirty centimeters, in order to allow its insertion as far as possible into the latter.

Liquids are weighed off in thin glass bulbs, which are blown from a thin tube, and drawn out to a long neck. They must be small enough to slip down the combustion tube with ease. The bulb is first weighed while empty, then filled with the liquid and weighed again; the difference between the two weighings representing the substance taken for analysis. The substance is introduced into the bulb as follows: the empty bulb is heated over a gas-burner, while the end of its neck is inserted in the liquid. The air within the bulb expands and is partially forced out; as soon, therefore, as the flame has been taken away and the bulb become cool, the liquid will be drawn up into it. If the bulb has been insufficiently filled in the first attempt, it should be heated again very cautiously and again cooled off. When enough of the liquid has been drawn up, the portion which remains in the neck of the bulb is driven into the bulb itself by carefully heating the neck. The latter is then fused and drawn apart, thus closing the bulb. It must not be forgotten, in weighing the filled bulb, to also place the detached piece of the neck on the balance pan. The next steps will be described in the paragraphs on the analysis itself. This manner of weighing liquids is applicable in almost all instances, *i.e.*, for all liquids which boil between 30°-200° C. For substances which are decomposed by heat, or boil at less than 30° C., a similar apparatus, but which has two bulbs instead of one, is employed. The neck having been dipped into the liquid and the upper bulb slightly heated, the liquid is drawn up into the lower one, which has remained cold. Such an apparatus is especially convenient in weighing very volatile bodies, since the temperature of the upper bulb can be very greatly lowered by moistening it with ice or ether, and the volatilisation of the liquid thus be prevented. Small quantities of cupric oxide or lead chromate are sometimes placed in the bulb. When filled with a highly volatile liquid, the bulb must be sealed by a small piece of wax instead of by fusion. For extremely volatile substances (which boil at 0°-15° C.) a special method is employed, which will be included in the description of the analysis. Liquids with a boiling-point higher than 250° C., or which are non-volatile, are weighed in a small tube sealed at one end.

If the analysis is to be made in a combustion tube which is open at both ends (Marchand's method), the substance is weighed in a small platinum boat, which is afterwards pushed into the combustion tube. The cases in which this method becomes convenient will be mentioned below.

The quantity to be weighed off.—The analysis of organic compounds, in its present state of elaboration, contains some of the most accurate of all analytical methods. The combustion of an organic substance can, with very few exceptions, be completely effected; and the determination of the products of combustion, the water and carbon dioxide, by absorption, is remarkably exact. The error of experiment in combustions with cupric oxide is about − 0·2 per cent for carbon; for water (owing to the hygroscopicity of the cupric oxide) it is about + 0·2 per cent. In combustions with lead chromate, the error is the same for carbon and somewhat less, about + 0·1 per cent, for hydrogen. The exactness of the methods therefore permits the use of a small weight of the substance. This quantity, with substances which contain the average amount of carbon

(30-40 per cent), should be about 0·3 gr.: if they contain more than the average amount, only 0·25 gr. need be taken. The analysis of bodies which are poor in carbon (*e.g.*, which contain many other elements—chlorine, nitrogen, etc.), and also of the salts of organic acids, requires about 0·4 gr., in certain cases 0·5 gr.

Calculation of Analyses.—The carbon of the organic substance is weighed as carbonic acid; the hydrogen, as water. Carbon dioxide contains, in 44 parts by weight, 12 parts by weight of carbon, and 2 parts of hydrogen are contained in 18 parts of water. Let it be assumed that *a* gr. of the organic compound were employed in the analysis, and decomposed to *b* gr. water, and *c* gr. carbon dioxide:

The quantity c of carbon dioxide contains $c \times \frac{3}{11}$ carbon.

„ b of water „ $\frac{b}{9}$ hydrogen.

or expressed in percentage:

$$\text{Carbon} = \frac{3{\cdot}c}{11} \times \frac{100}{a}.$$

$$\text{Hydrogen} = \frac{b}{9} \times \frac{100}{a}.$$

The formula of the compound is calculated, and a check obtained on the results, in the manner indicated in § 114. In illustration of the method, let us assume that an analysis has been made with the following results; the values are expressed in percentage, those for oxygen being found from the difference, (*i.e.*, by subtracting the sum of the weights of the remaining elements from 100). Opposite the percentage weights found, are written the corresponding equivalent quantities of the respective elements (§ 114).

Found.			
Carbon	5·62	per cent	$\frac{5{\cdot}62}{12} = 0{\cdot}47 = 2C$
Hydrogen	0·30	„	$= 0{\cdot}30 = 1H$
Iodine	60·22	„	$\frac{60{\cdot}22}{127} = 0{\cdot}47 = 2I$
Silver	25·57	„	$\frac{25{\cdot}57}{108} = 0{\cdot}23 = 1Ag$
Oxygen	8·09	„	$\frac{8{\cdot}09}{16} = 0{\cdot}50 = 2O$
	100·00		

The compound consequently has the empirical formula $C_2HI_2AgO_2$, which is that of di-iodacetate of silver. The formula having once been calculated, a check on the analysis is obtained by comparison of the theoretical quantities with those obtained:

	Calculated.		Found.
C_2	24	5·73	5·62
H	1	0·23	0·30
I_2	254	60·52	60·22
Ag	108	25·78	25·57
O_2	32	7·74	...
		100·00	

It should be stated that analysis yields only the simplest empirical formula of an organic compound, and, owing to the numberless cases of polymerism which occur in organic chemistry, such a formula can denote any one of many compounds. The molecular formula can seldom be determined from the analytical results, but usually requires special and independent methods.

THE ANALYSIS

COMBUSTION WITH CUPRIC OXIDE IN A TUBE SEALED AT ONE END

This method of analysis is applicable only to bodies which consist simply of carbon, hydrogen, and oxygen (phosphorus). If the substance contains chlorine, bromine, iodine, or nitrogen, the method must be subjected to a modification, which will be described later. For sulphur compounds, and also for the organic salts of the alkali or alkaline earth metals, it is inapplicable. Other salts, such as those which leave on ignition a metallic oxide or metal, but not a carbonate, can be analysed by this method.

In the following paragraphs the various operations are described in the order in which they are performed in an analysis.[1]

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[1] In passing to the description of the analytical processes it may be remarked that, while following the same general plan, each analyst introduces slight individual changes in the minor details of the operations; on the other hand, the habit of holding too closely to these details results in his often overlooking certain simple conveniences. Although we use these methods ourselves, we cannot guarantee that they are to be preferred above all others.

A tube of about twenty inches in length is prepared according to the directions in § 155 ; a piece of rubber tubing is then slipped over the (unsealed) bayonet point, and the tube gently heated, while a current of air is being drawn through it. When perfectly dry, the bayonet point is sealed up by fusion, and a calcium chloride tube attached to the other end until it is ready for the analysis.

§ **159. Drying of the Cupric Oxide.**—Owing to the hygroscopic nature of cupric oxide, the reagent must be freshly ignited before each analysis.

The best, and, at the same time the simplest and most convenient manner of drying the cupric oxide consists in igniting the preparation, in a specially constructed tube, in the combustion furnace itself. One end of a difficultly fusible tube is gently drawn out to a slight taper, to permit its insertion into the combustion tube later, and the other end narrowed out to a long, thin tail: during the ignition the latter is connected with a drying apparatus, which is in turn attached to a gasometer, and a current of air led through the tube. The tail of the tube is next loosely closed by a plug of asbestos, and the cupric oxide introduced: a passage for the steam and gases must be made, by tapping gently upon the tube while it is held in a horizontal position. The tube is then placed in the combustion furnace, connected with the gasometer, and brought gradually to a dark-red heat, proceeding from the posterior (nearest the drying apparatus) to the anterior end. After the whole tube has been kept at this heat for fifteen minutes, its free end is pushed slightly outside the furnace, and, as soon as it has grown cold, is closed by a well-fitting cork, and the heat turned off. While the tube is cooling its contents must be exposed only to the dry air from the gasometer. When cold enough to bear handling, it is taken from the furnace and its tail sealed up. The cupric oxide should be mixed with the organic substance while still warm.[1] This method is especially convenient when two combustion furnaces are available.[2]

[1] What is not needed for the mixture must be allowed to remain in the tube.

[2] When only one furnace is at hand the method is less convenient, as the time required for the furnace to cool after the ignition of the cupric oxide is greater than that consumed in the other preparation for the combustion: the combustion tube cannot well be laid in the furnace while the latter is still hot, since this prevents a test as to the tightness of the apparatus.

If this method cannot be employed, it is expedient to ignite the cupric oxide in a covered Hessian crucible, either in a stove or portable furnace. The crucible is brought to a dark-red heat, and the oxide transferred to the filling flask or tube while still hot. The filling tube should be wide, sealed up at one end, and tapered at the other, to allow its passage into the combustion tube. A flask provided with a long neck is sometimes used instead of a tube, the mouth being likewise somewhat narrowed out for insertion in the combustion tube. The oxide is poured from the crucible directly into the filling tube, the latter being held in the left hand (which should be protected by a towel), and the crucible taken up with a good pair of tongs by the right. As soon as the mouth of the tube has grown somewhat cool, it must be closed by a well-fitting cork.

Cupric oxide can also be ignited in an ordinary crucible (of platinum, copper, or porcelain), over a gas flame; a specially constructed furnace, however, must be used, in order to sufficiently heat the preparation.

The operations to be performed during the ignition of the cupric oxide.—As much time is required for the ignition and cooling of the cupric oxide, the following operations may be performed in the meantime. Before the drying of the cupric oxide is undertaken, the cork[1] by which the calcium chloride tube is to be connected to the combustion tube is placed in an air-bath and heated to 100° C. The cork must be carefully selected, and must have no cracks, especially those running lengthwise; it must also surround the calcium chloride tube tightly, and some force must be required to push it into the mouth of the combustion tube. The weighing tube, or bulb, and substance, and also the potash bulb and calcium chloride tube, can next be weighed. The rubber caps must be slipped over the ends of the calcium chloride tube again after the weighing. The cupric oxide will by this time be cool enough to be mixed with the substance.

§ 160. Mixing the substance with the Cupric Oxide. Solid substances.—Solid substances are mixed with the

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[1] Excellent corks, selected especially for analyses, can now be obtained from the dealers. Black rubber corks are also recommended, but as I have had no occasion to use them myself I cannot pronounce judgment respecting their suitability.

cupric oxide either in a mortar or in the combustion tube itself, in the latter case by means of a wire. The former method effects a more intimate mixture, and is especially advantageous in the analysis of difficultly combustible bodies; it is open to the objection, however, that during the necessarily long operation the cupric oxide attracts moisture from the air and the water-determination consequently becomes more inaccurate. The mixture is more quickly effected in the tube itself, by means of a wire, but here, at the same time, it is less perfect. The choice of the method to be employed, therefore, must be governed by the circumstances of the analysis.

In the mortar.—The mixture is effected in a glazed porcelain mortar which has previously been slightly warmed. The dry combustion tube is first rinsed out with cupric oxide, and then filled for two or three inches at its posterior end with fresh oxide. It is then fastened to a support in an upright position, and a small copper filter, through which the mixture is to be introduced, inserted in its mouth. The mortar is likewise rinsed out with cupric oxide, a layer of the latter placed in the bottom, and the substance shaken out of the weighing tube upon this layer (the removal of the substance from the glass must be carefully effected, as the latter must be reweighed to find the quantity used). The two are then quickly stirred together with a pestle, and the mixture poured through the funnel into the tube. Another portion of cupric oxide is then shaken into the mortar, stirred, and added to the first portion. This operation is repeated two or three times, as much haste as possible being used throughout.[1] The funnel is now taken out of the tube, and the latter charged with cupric oxide directly from the filling tube, a space of about two inches being left at the end. A layer of freshly-ignited asbestos having been placed over the cupric oxide, the dry cork is taken from the air-bath, and the calcium chloride tube passed through it and connected with the combustion tube (its other end still being protected by a rubber cap). The small quantity of cupric oxide in the bayonet is then gently shaken

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[1] The quantity of cupric oxide used, including that employed to rinse the mortar, should ordinarily fill from four to five inches of the combustion tube. Much more is taken, on the other hand, if the substance undergoing analysis is explosive, in order to distribute the body, and thus avoid, as much as possible, the chance of a mishap.

down into the tube itself, and a passage secured for the gases and vapours over the contents of the tube, by gently tapping the apparatus while it is held in a horizontal position. The tube is then placed in the combustion furnace. The free end of the calcium chloride tube is next attached to the potash bulb by a piece of rubber tubing, in such a manner that their ends are in contact. All the joints having been bound with silk thread, the remaining cap of the potash bulb is removed and the tightness of the apparatus tested. For this purpose either the large upper bulb (which lies next to the combustion tube) is slightly heated by a gas flame or a piece of coal, a few bubbles of air being thus driven out from the apparatus, or else the air is slowly sucked out through a piece of rubber tubing attached to the potash bulb. If a Liebig's bulb is being used, it should rest on all three of its lower bulbs (or on the middle one) during the test. After the displacement of the air the liquid must assume a higher level in the larger bulb than in the smaller. If the difference in the two levels remains constant for some time, the apparatus may be considered air-tight, and the combustion commenced.

Mixture with a wire.—The mixing wire is made from sufficiently strong copper or German silver wire (it should be about one-eighth of an inch in thickness), and at one end is twisted into a long tapering spiral. The combustion tube having been rinsed out with cupric oxide, the mixture is effected as follows: a layer of cupric oxide about four inches long is first poured into the tube. The weighing tube is then cautiously thrust as far down into the tube as possible, and its contents shaken out upon the cupric oxide (it must be remembered that the weighing tube is to be reweighed, and that this operation must therefore be carefully performed). Another portion of the oxide, somewhat greater, is then introduced, and while it is being added the tube is twisted around, to detach any particles of the substance which may have adhered to its sides. The wire is next inserted and turned around in the direction of its spiral, until driven well into the contents of the tube. It is then screwed about in each direction, and at the same time moved in and out, until the substance ceases to be distinguishable, an indication that it is well distributed. The mixture having been secured, the wire is cautiously withdrawn and run through a further layer of cupric oxide, to remove any substance which may have adhered to it. The wire is then laid aside, the rest of the tube filled with cupric oxide, the calcium chloride tube attached, etc., as in the foregoing case. If the substance has been mixed with pulverulent cupric oxide, the rest of the tube can sometimes be filled with the granular preparation.

Liquids.—The combustion tube having been rinsed out with cupric oxide, a layer of the latter from two to four inches long is placed in its posterior end, and the weighing bulb then introduced in an upright position. The manner of opening the bulb depends upon the volatility of the substance. Usually (with substances the boiling-point of which lie between 50° C. and 150° C.), the neck of the weighing bulb is scratched with a file, and, the bulb being held within the combustion tube, is broken off at the scratch by pressure against the edge of the tube with the finger. The broken-off end is dropped, with the bulb, into the tube. If the substance is very volatile, the bulb (in this case sealed up with wax) is inserted closed, and the subsequent heat allowed to melt the wax, and thus permit the vapourised substance to escape.[1] When filled with a substance which boils at a temperature higher than 150° C., the bulb can be broken by being thrown with some force against a small piece of glass which has previously been dropped into the tube. Whichever method is employed, the free portion of the tube must be filled with granular cupric oxide as soon as possible after the introduction of the substance. The remaining processes are as before.

§ **161.** *The Combustion.*—Having ascertained that the apparatus is air-tight, the operator can now proceed with the combustion, beginning at the anterior end of the tube. If the combustion is being made with a Liebig's potash bulb, a cork is placed under the lower bulb of the latter, which corresponds to the smaller of the two upper bulbs, so as to give the apparatus an inclined position. The tube is first heated by low flames from the first two burners. If the apparatus has been well put together, the level of the liquid in the potash bulb should commence to change as soon as the combustion has begun.

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[1] The analysis of very volatile substances will be further discussed in the paragraph on analyses in an open tube.

The successive burners, beginning at the anterior end of the furnace, are slowly and cautiously lighted, one by one, each new flame being at first kept low (if the operation be hastened, the tube is almost sure to crack). As fast as a section of the tube becomes heated, it is covered with a tile. When the front portion has attained a red heat, that which holds the substance being still cold, the last burner is lighted and the heat gradually extended along from this end also, the corresponding tiles being placed in position at the same time. The real combustion now begins. Its course can be judged by the rapidity with which the gas bubbles pass through the potash bulb. So long as these can be counted the combustion is proceeding properly; if, on the contrary, they begin to pass too quickly to be counted the heat is too great, and the portion of the tube containing the substance must be cooled off, either by throwing back the tiles or turning the gas off entirely. As soon as the normal flow has returned the heat is again increased. Care must be taken during the combustion that no water condenses in the tube about the cork connecting the latter with the absorption apparatus; should this occur, it must be carefully driven over by an ordinary burner (great caution must be taken not to burn the cork). The entire tube slowly reaches a bright-red heat, and the rapidity with which the bubbles pass gradually diminishes, until at last no more are caused. The potash bulb must now be carefully watched. At the end of the combustion the air has been entirely displaced from the tube by carbon dioxide, and as the latter becomes absorbed in the alkali the liquid may be sucked back, not only into the upper bulb, but even into the calcium chloride tube. If a Liebig's bulb is being used, this danger can be prevented by placing the cork on which the apparatus rests under the opposite lower bulb (the one which corresponds to the larger upper bulb). This renders it possible for the air to enter the tube, and the operator can therefore cautiously commence to turn off the heat, beginning at the posterior end and having first thrown back the tiles. As soon as the tail has become sufficiently cool, a piece of rubber tubing is passed over it for the introduction of the oxygen, and its end crushed, either between the fingers or with a pair of pliers. Immediately after the current of oxygen has been turned on, the potash bulb must again be given the position which it had during the combustion. If a Geissler's bulb be employed, and the larger bulb, which must exceed in capacity that of all the lower ones together (attention must be paid to this point in purchasing the apparatus) is filled, access of air is secured to the tube at the end of the combustion without a change in the position of the potash bulb being necessary. If, on the contrary, the large bulb has too small a capacity, the oxygen must be passed through as quickly as possible after the heat has been turned off, since the alkali will otherwise recede into the calcium chloride tube. The oxygen drives all the carbon dioxide remaining in the combustion tube into the potash bulb. Its flow can be stopped as soon as its escape from the potash tube can be detected by a glowing match.

If the combustion is made in a charcoal furnace, the process is as follows: a screen is placed round the tube at a short distance from the anterior end of the furnace, and the intervening section is then surrounded by glowing pieces of charcoal. As soon as this portion has become hot, the screen is moved further along and more charcoal added. When a sufficiently long section of the tube has become red-hot, a second screen is placed near its posterior end, and this section also ignited, as when a gas furnace is used. The heat is then gradually extended toward the substance from each side. The perforations in the bottom of the furnace must be watched throughout the combustion, to see that they do not become choked by ashes and the draught thus be shut off. Fresh coals must be continually added, and if necessary, the heat increased by means of a pair of bellows. In other regards, such as observance of the process of combustion, the indications that it is finished, the displacement by oxygen, etc., combustions with charcoal are exactly like those made in a gas furnace.

When the analysis is finished, the absorption apparatus is carefully taken apart, wiped off, and the oxygen which it contains displaced by air. The rubber caps are then slipped over the tubes, and the apparatus taken into the balance room. When it has attained the same temperature as the latter, or in about a quarter of an hour, the two pieces are weighed. The rubber caps must first be removed.

COMBUSTION WITH LEAD CHROMATE IN A TUBE SEALED AT ONE END

§ **162.** The advantages which the use of lead chromate in analyses possesses over that of copper oxide have already been mentioned. Owing to its very slight hygroscopicity it can be obtained in a thoroughly dry state, and therefore affords much more accurate results in the determination of water. The combustion of bodies of the following classes *must* be made with lead chromate, as in these cases the results obtained with cupric oxide are very unreliable. In the analysis of compounds containing sulphur, the latter, when ignited with cupric oxide, is converted to sulphur dioxide, which becomes absorbed in both the potash bulb and the calcium chloride tube, and the results obtained for both carbon and hydrogen are thus affected. If the combustion be made with lead chromate, on the contrary, the sulphur is held back as lead sulphate, which is stable at a high temperature. Another case in which lead chromate must be employed is in the analysis of organic salts of the alkali and alkaline earth metals. The use of cupric oxide is here prevented by the fact that among the products of combustion the carbonates of these metals are formed, and can either be only partially decomposed, or, at the temperature which the tube reaches, remain entirely unaffected. Such substances are ignited with lead chromate which has been mixed with one-tenth its weight of potassium dichromate, the excess of chromic acid in the latter completely displacing the carbonic acid in the carbonates.[1] In exceptional cases, where perfect combustion is only difficultly effected, lead chromate and cupric oxide can be employed simultaneously. When this method is to be resorted to, the substance is mixed only with the lead chromate, and the anterior half of the tube filled with cupric oxide (preferably in the granular form).

The length and shape of the tube used in combustions with lead chromate is the same as that employed with cupric oxide.

Drying of the lead chromate.—The finely-pulverised salt is heated for fifteen minutes in a porcelain or iron dish over a gas flame, and with continual stirring by means of a glass rod. As the yellow powder grows hot it becomes gradually darker

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[1] The combustion of these salts is now sometimes performed with cupric oxide; the potash bulb having been weighed, the quantity of carbon dioxide remaining combined with the metal in the tube is calculated and added to the weight of that absorbed in the bulb. This method, however, is less accurate than the combustion with lead chromate.

and darker: when the whole mass has assumed an even, coffee-brown tint the flame is removed, and the dish, after having cooled off a little, is placed under a bell-jar over sulphuric acid. The mixture with the substance should be made while the chromate is barely warm.

The substance is weighed off while the lead chromate is cooling. Respecting the other operations, the tube is rinsed out; the mixture effected; the tightness of the apparatus tested, in the manner already described in the foregoing paragraphs. Caution must be used not to heat the tube too strongly at first; and, except at the end of the combustion, the chromate must not be brought into fusion, as the surface presented for the oxidation of the still incompletely decomposed products will so be reduced, and therefore the combustion itself be less thorough.[1] At the close of the combustion, however, the heat is increased until the chromate is well fused, and the operation then interrupted. In the analysis of salts, finally, some patience is required in waiting for the end of the operation, since the last traces of carbonic acid give way very slowly to the chromic acid. If the combustion was complete, the use of a current of oxygen is superfluous, and the gas can be replaced by air, as it serves merely to drive the carbon dioxide remaining in the tube into the absorption apparatus.

DETERMINATION OF CARBON AND HYDROGEN IN SUBSTANCES WHICH CONTAIN NITROGEN OR HALOGENS

§ **163.** To determine carbon and hydrogen in substances which contain nitrogen or the halogens, a slight modification must be introduced into the method above explained. The combustion of haloid compounds results in part in the liberation of the halogens themselves, which affects the accuracy of both the carbon and water determinations. Nitrogenous substances give off nitric oxide, and as the latter is absorbed by potassium hydroxide, it will render the results for carbon too

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[1] Caution is required at this point for another reason: if the lead chromate has once been fused, the heat cannot be decreased without causing the tube to crack and thus the loss of the analysis. In learning the method, therefore, the student should make his first combustions with the pure and difficultly fusible lead chromate, instead of its mixture with potassium dichromate.

high. These errors are avoided by the use of metallic copper, which unites with the halogens to form haloid salts, and, when in a state of ignition, decomposes nitric oxide with formation of free nitrogen and cupric oxide. The metallic copper is best employed in the form of plugs.

Preparation of the copper plugs.—Copper filings have, until recently, been resorted to, but the pure metallic netting which can now be readily obtained is much more convenient. The copper employed for the plugs must be pure and lustrous. To prepare them, pieces of the netting about four inches long and one wide are cut out and rolled compactly about a thin tube, the diameter of which must be governed by that of the combustion tube; the plugs must entirely fill out the latter. When thus prepared the netting is superficially oxidised by ignition (which also destroys the coating of grease always found on copper netting). The oxidised plugs are then placed in an open tube and reduced in a current of hydrogen. The tube, one end of which is somewhat drawn out, is connected at the other end with a hydrogen generator,[1] and placed in a combustion furnace. When the air in the tube has been completely displaced by hydrogen (in 10-15 minutes) heat is applied, beginning at the open end, and finally extended the whole length of the tube, the flow of hydrogen being maintained throughout. As soon as the reduction has been accomplished (its completion is easily seen), the flames are gradually extinguished, and the tube allowed to cool in the atmosphere of hydrogen. The plugs are preserved in a vessel provided with a ground glass stopper. Thus prepared they can be used only once, and must be reduced again before a new analysis.[2]

Instead of the above plugs, metallic copper which has been prepared by the reduction of granular cupric oxide may

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[1] The hydrogen is obtained by the action of dilute sulphuric acid upon zinc. (1 part H_2SO_4, 5 parts H_2O). It is dried by passage through a Wolf's bottle containing concentrated sulphuric acid and then led directly into the tube.

[2] Since, when reduced in hydrogen, the plugs always occlude traces of the gas, it is advantageous, in making an exact determination of the hydrogen in an organic compound, to further subject them to ignition in an atmosphere of formic acid.

It has recently been proposed to use silver instead of copper plugs in the analysis of bodies containing halogens. These are prepared by winding silver wire tightly over a rod and then drawing the spiral out. Silver obtained by the reduction of the chloride by zinc can also be employed.

be used with equal advantage. It is made ready and preserved in the same manner as the plugs.

The analysis of organic substances which contain nitrogen or a halogen requires a tube from twenty-four to twenty-eight inches long. This is prepared in the manner already described, except that after the mixture has been effected it is filled with cupric oxide only to within about five inches from the end. Three or four of the copper plugs, which have been dried at 100° C., shortly before the analysis, are placed in the remaining space. The course of the analysis is not at all changed, but care must be given that during the combustion the plugs are kept at a red heat. When the oxygen is passed through the tube at the close of the analysis the flames below the plugs must be turned out and the tiles thrown back, to prevent unnecessary oxidation of the copper halogenides, in case haloid substances are being analysed; or, in general, of the plugs themselves, which will otherwise soon become unfit for use.

COMBUSTION IN AN OPEN TUBE

§ **164.** When the substance to be analysed is non-volatile, like fat or coal, the combustion can be made in an open tube, by the method proposed by Marchand. This method is also sometimes used (when but little of the substance is at hand) in the analysis of the salts of organic acids; its convenience in such cases lies in the fact that the carbon, hydrogen, and metal, can all be determined by one operation. We also give the modification of the method by which it can be employed in analysing very volatile substances. The process is not generally applicable, since with readily volatile or easily distilled substances loss cannot be guarded against. The reason for this will be explained later.

The combustion is made with cupric oxide or lead chromate, the choice depending upon the compound to be analysed, and being subject to the rules already enumerated. Two gasometers, one filled with air, the other with oxygen, are required. The air is conducted through the tube during the main period of the analysis; the oxygen, only at its end, as in the foregoing method. The two gases must be dried before passing into the tube. For this purpose only one drying apparatus is required, both gasometers being attached to it by means of rubber tubing and a so-called T-tube.

The process of combustion.—A tube of from twenty-five to twenty-eight inches in length is selected, and its edges well rounded by fusion. At a point about two inches from one end is placed a layer of asbestos (if the substance contains a halogen, copper plugs are employed). The first step in the analysis is the drying of the cupric oxide. The tube is filled with the oxide to within about 20 cm. from the other end, laid in the combustion furnace, and corks, through which pass glass tubes, are inserted in each end. One of these tubes is then connected with the air-gasometer. The section of the combustion tube which contains the cupric oxide is next gradually heated to redness, and finally allowed to cool in a current of dry air. During this time the absorption apparatus can be weighed. When the cupric oxide has grown cold, the connection with the gasometer is broken, the absorption apparatus brought into connection with the anterior end of the tube, and a platinum or porcelain boat containing the substance inserted into the posterior end. The boat is pushed in nearly to the layer of asbestos by means of a rod, and one or two oxidised copper plugs placed behind it. The tube is then connected with the air-gasometer, the tightness of the apparatus tested, and a slow current of air turned on. The anterior portion of the tube is next heated to dull redness, the posterior end gradually warmed, and the heat finally extended to the boat. The combustion must be carefully conducted, and its rapidity closely watched by means of the bubbles passing through the first bulb of the potash apparatus. As soon as the contents of the boat have volatilised, or when only carbon, the combustion of which cannot be effected in an atmosphere of air, remains, the current of the latter is replaced by one of oxygen. The analysis may be considered finished when the oxygen begins to escape from the potash bulb.

If a metallic salt is being analysed, both the absorption apparatus and the boat must be weighed, in order to determine not only the carbon and hydrogen, but also the metal (the latter may be left as carbonate, oxide, or in the metallic state, according to the nature of the salt).

This method is obviously very convenient in one respect; a second combustion can be made directly after the first, provided only that other absorption apparatus is at hand. It is, nevertheless, comparatively rarely resorted to, one objection to its use being that the current of gas passes very quickly through the potash bulb, and, carrying away traces of moisture which escape retention in the safety tube, causes a loss. The rapidity of the current of air or oxygen is, on the other hand, insufficient to prevent bodies which are very volatile, or capable of distillation, from condensing in the end of the tube nearest the gasometers, and as the condensed traces escape combustion, loss ensues from this cause as well. The method is expedient, however, in the instances cited at the beginning of this paragraph.

Cloëz has proposed to use an iron tube instead of one of glass in this method, and has also introduced some variations in the process. For a full description of his method we must refer to the original article (*Annales de Chimie et de Pharmacie*, T. 68, p. 394).

When employed for the analysis of very volatile substances this method must be subjected to the following modifications. The combustion tube is prepared as usual in Marchand's process. The substance is introduced into a thin U-tube, the ends of which are bent at right angles to the main direction of the limbs. The quantity taken of the substance is found from two weighings; one of the empty tube, the other after it has been filled (and its ends sealed up). The filled tube is connected by means of a cork or piece of caoutchouc tubing to the combustion tube. The cupric oxide is then ignited, as before, and when it has reached a dull-red heat, the end of the U-tube is broken off by gently crushing it against the side of the combustion tube. To prevent the too rapid volatilisation of the substance it should at first be surrounded by ice or water, which toward the end of the operation is removed, and the U-tube then very cautiously heated with a flame. As soon as all the contents of the U-tube have evaporated, its free end is broken off and connected with a gasometer, and the combustion finished in a current of oxygen.

DETERMINATION OF CARBON AND HYDROGEN BY KOPFER'S METHOD

The results obtained by the methods just described are not always satisfactory when the substance under analysis is a difficultly combustible body, such as the solid aromatic carbohydrates or the albuminoids. Kopfer's method is especially adapted to the analysis of such compounds, though also applicable in ordinary cases, and contains many points of advantage, both in convenience and accuracy. The combustion is effected in oxygen in an open tube, by means of platinised asbestos, or asbestos which has been well shaken with platinum black in a vessel provided with a glass stopper. The furnace used has a peculiar form, consisting of two iron boxes or sections. The anterior section, in which the substance is heated, is provided with a movable burner which can be pushed along in a slit below the tube. The second contains three fixed burners, which fall below the greater share of the platinised asbestos. The combustion tube is about twenty inches long and fairly large in diameter. At a point about two inches from one end is placed an asbestos plug wound about with platinum wire, and followed by twelve inches of the mixture of platinum and asbestos. Another asbestos plug, fitting somewhat more tightly than the first, is then inserted, and, after the introduction of the platinum boat containing the substance, the tube is closed by a third plug. It is then placed in the furnace, and the portion lying in the posterior box protected by a double wrapping of wire gauze, while that in the first section rests in a trough of the same material. Ordinary absorption apparatus can be used. At its anterior end the tube is connected with a drying apparatus and oxygen gasometer, from which it is first filled with oxygen. The current of the gas is then regulated so that two bubbles pass the absorption apparatus per second, and the burners finally lighted. The movable flame is first placed in front of the boat, and gradually pushed along until it stands directly beneath it. The greater part of the substance now either carbonises or distils over into the section of the tube behind the middle asbestos plug. When this point is reached, the tube must be entirely covered with wire gauze and the substance subjected to the full flame of the movable burner. If the oxidation becomes so rapid that the platinum begins to glow, the violence of the reaction can be lessened by sliding the movable burner away from the substance. After the combustion has been finished, the tube is allowed to cool in an atmosphere of either air or oxygen, and is then ready for a second analysis. If the substance contains a halogen, the latter is kept back by strips of silver foil which are mixed with the platinised asbestos. If nitrogen or sulphur is present, the tube must be somewhat longer than in ordinary combustions, and the portion projecting beyond the furnace, at the end to which the absorption apparatus is attached, is then filled with lead dioxide. The latter is heated by a burner outside the furnace, the heat being regulated by the intervention of wire gauze, and the nitrogen and sulphur thus retained as lead nitrate and sulphate respectively. The operations are more fully described in the *Ber. d. deutsch. chem. Gesell.* 1876, S. 1377, and *Zeits. f. anal. Chemie,* 1878, Bd. 17. S. 1.

DETERMINATION OF NITROGEN

§ **165.** The nitrogen of organic compounds is usually present in one of the three forms given in § 97. It occurs (1) in ammonia and derivatives of ammonia (amines, amides, acid amides, amido-acids, ammonium salts, etc.); (2) in the form of cyanogen (cyanogen compounds, nitrils, carbylamines, etc.); and (3) as the radical of nitric or nitrous acid (nitro-, nitroso-, azo-, and diazo-compounds).

Nitrogen can be estimated by one of two methods. The first, that of Dumas, which is applicable to any compound of nitrogen whatever, consists in the complete combustion of the organic substance and liberation and measurement of free nitrogen (determination from the volume). The second method was devised by Varrentrapp and Will; it is based upon the conversion of the nitrogen to ammonia by means of soda-lime, and determination of the ammonia, either as its platinichloride or by volumetric means. The method can be employed only when the nitrogen is present in one of the first two of the above forms, *i.e.*, as ammonia or cyanogen. It is inapplicable to the analysis of nitro-, azo-, and diazo-bodies, since soda-lime will not convert all the nitrogen in these compounds into ammonia. A third method, originated by Kjeldahl, is to decompose the nitrogenous substance with concentrated sulphuric acid, which also converts the nitrogen to ammonia.

Qualitative detection of nitrogen.—To detect nitrogen in organic substances we make use of its power of forming an alkali cyanide when acted upon by metallic sodium or potassium at a high temperature; the cyanide formed being recognised by its conversion to ferric ferrocyanide. The test is made as follows. The substance to be examined is placed, together with a small piece of sodium or potassium (the latter is to be preferred), in a test-tube and heated. The metal fuses and a slight explosion ensues, a portion of the substance being reduced to carbon. As soon as the residue has cooled, water is added, whereupon the excess of metal passes into its hydroxide. The solution is then filtered, if necessary, from the carbon, and small quantities of ferrous and ferric salts (partially oxidised ferrous sulphate) are added to the filtrate. This causes a precipitate of iron hydroxides, which dissolve on addition of hydrochloric acid, and leave that of ferric ferrocyanide which forms in the acid solution plainly visible. This general reaction is applicable to the detection of nitrogen in any one of its forms, except, as Gräbe has recently observed, that of diazo-compounds. Its insufficiency in this case is apparently due to the fact that the diazo-compounds decompose and liberate their nitrogen before the action of the potassium sets in. The nitrogen in compounds which are decomposed by soda-lime with formation of ammonia can also be detected by this reaction.

DETERMINATION OF NITROGEN FROM ITS VOLUME

(*Dumas's Method*)

§ **166.** This method, as we have already pointed out, can be used for the determination of the nitrogen in any nitrogenous substance whatever.

The organic substance is burned to carbon dioxide, water, and nitrogen. The gaseous products of the combustion are received in a graduated tube, where the carbon dioxide is absorbed by potassium hydroxide and the volume occupied by the nitrogen measured. The weight of the gas is then deduced by calculation.

Apparatus.—The nitrogen is determined by the combustion of the organic substance in a tube from twenty-eight to thirty-two inches long. The combustion tube is sealed at one end, and the other end closed by a cork through which passes a thin, doubly bent tube, to lead the nitrogen and accompanying gases into the apparatus in which the former is to be measured. The gas is collected in a graduated tube which is filled with mercury and a small quantity of caustic potash, the latter to absorb the carbon dioxide. It is fastened in a vertical position to a standard, and dips at its lower end in a bath of mercury. The nitrogen, after being collected in this tube, is measured according to the directions given below.

Weighing the Substance and filling the Combustion Tube.—To determine nitrogen, enough of the substance should be taken to yield from twenty to thirty cubic centimeters of the gas, this requiring, in most cases, 0·2 — 0·3 gr. The substance is weighed in the same apparatus as is used in estimating carbon and hydrogen, and under ordinary circumstances a like quantity is taken.

The combustion tube is filled in the following manner. A layer of sodium bicarbonate or, more advantageously, magnesite about six or eight inches long is first introduced into the tail of the tube. This serves to generate carbon dioxide, by means of which all the air is driven from the tube at the commencement of the analysis, and all the nitrogen forced into the graduated cylinder at its close.[1] An asbestos plug and from two to four inches of cupric oxide are then introduced,[2] and on top of this the mixture of cupric oxide and the substance. Solid substances can be mixed with the oxide in a mortar; liquids are dropped into the tube in a small bulb, as explained in § 158. The mixture having been poured in, the mortar is rinsed out and a layer of cupric oxide (preferably the granulated) about seven inches long next added. The remainder of the tube (from six to seven inches) is finally filled with freshly-reduced copper plugs and the cork supporting the conducting tube inserted.[3] The tube is then

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[1] Magnesite is preferable to sodium bicarbonate, but as it is often difficultly obtained in a pure state the latter must sometimes be resorted to. The sodium bicarbonate must be dried over sulphuric acid in a bell-jar (not at 100° C., as the heat would drive off a large portion of the carbonic acid). Even when thoroughly dried, it contains more or less water, which, if the operator is at all negligent during the combustion, may easily come in contact with the red-hot portion of the tube, crack it, and thus make the whole analysis worthless.

[2] When obtained by ignition of the nitrate cupric oxide may contain occluded nitrogen: that prepared in a muffle furnace should be taken.

[3] The remarks made on p. 477 respecting the copper plugs must be held in mind. When they are being prepared for use in a nitrogen determination,

gently tapped, to secure a passage for the gases, and placed in the furnace. The delivery tube having been so adjusted that its free end dips below the surface of the mercury in the mercury trough, the generation of the carbon dioxide is commenced (see below), and the operator at the same time fills the graduated cylinder with mercury.[1] For this purpose the cylinder is clamped in a vertical position, with the mouth above, and a funnel, the stem of which reaches to the bottom of the tube, passed into it. Mercury is then poured through the funnel, and when the cylinder is almost filled, the metal is freed from the bubbles of air which it contains by slightly inclining the cylinder. The mouth of the latter is then covered by the palm of the hand, and when it has again been restored to its vertical position on the support, the last minute air bubbles are removed by means of a platinum wire (or a clean fish bone, a feather, or the like). When the mercury presents a perfectly smooth, shining surface throughout the cylinder, the latter is filled as completely as possible, and a ground glass plate slid over its mouth (cutting the meniscus). The operator, holding the plate in his right hand and the tube in his left, turns the latter over into an inverted position, and dips the plate below the mercury in the trough.[2] This operation requires some practice. The cylinder is finally clamped in position, and from twenty to thirty cubic centimeters of potassium hydroxide (1 part KOH to 2 parts water) are passed into it by means of a pipette with a curved end.

The Combustion.—While the cylinder is being filled, the mouth of the delivery tube, as we have already said, is kept below the surface of the metal in the mercury trough, and the portion of the combustion tube which contains the sodium bicarbonate or magnesite gently heated. The evolution of carbon dioxide must be maintained for 15-20 minutes to drive out all the air. The complete expulsion of the latter

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carbon dioxide must be passed through the tube after their reduction in hydrogen, to remove the latter gas. Perkins recommends, as a very good substitute for these plugs, the use of pieces of pumice which have been soaked in a solution of potassium monochromate and then dried; or lumps of cupric oxide which have undergone reduction and cooled off in an atmosphere of carbon dioxide.

[1] The tube must either be graduated in cubic centimeters or, if an arbitrary unit be taken, the relations between its divisions and a cubic centimeter must be known.

[2] To avoid wasting the mercury, the tube should be filled over a stand surrounded by a ridge, so that the metal spilled may easily be collected.

is recognised as follows: a test-tube is filled with mercury, placed in an upright position over the mercury trough, and a few cubic centimeters of caustic potash passed into it from a pipette. If, on the mouth of the delivery tube being placed under the test-tube, all the escaping gas is absorbed by the alkali, the air has been completely displaced in the combustion tube. Should any of the gas resist absorption, on the other hand, the current must be maintained for some time and the test repeated. As soon as the air has been completely removed, the mouth of the delivery tube is placed beneath that of the cylinder, and the combustion commenced. Heat is first applied to the anterior portion of the tube (that containing the copper plugs), and at the same time the flames below the layer of magnesite or sodium bicarbonate are gradually lowered and finally extinguished. When the copper plugs and the adjoining layer of cupric oxide have become red-hot, the layer back of the substance is brought into ignition and the heat gradually extended to the substance itself, as in ordinary combustions. Care must be taken that the metallic copper remains red-hot throughout the combustion, and toward the close of the analysis the mixture of the substance and cupric oxide must be exposed to the highest possible temperature. The pressure within the tube becomes comparatively great during the combustion, and care should therefore be taken, if the glass of the tube happens to be too easily fusible, to prevent the heat from becoming so intense as to cause the tube to burst, and the consequent loss of the analysis.

Measurement of the Nitrogen.—The combustion can be considered finished as soon as there is no further increase in the volume of the gas collected in the cylinder. The layer of sodium bicarbonate is then heated again, in order to drive the nitrogen remaining in the combustion tube into the cylinder. Great caution is required at this point, as the water given off by the carbonate is apt to crack the glass. The current of carbon dioxide is maintained for about twenty minutes, and the operation then interrupted. The cylinder is allowed to stand for an hour or two without removal from the trough, in order to allow any carbon dioxide which has remained with the nitrogen to become absorbed. The mercury and alkali in the cylinder must finally be replaced by water. For this purpose the cylinder, its mouth being protected by a small porcelain dish, is carefully transferred from the mercury trough to a vessel of greater capacity (a large mortar or a wooden bowl) containing water. The porcelain dish is then removed from its mouth, and the mercury and alkali allowed to flow out, the water rising into the tube at the same time. The porcelain dish is finally pressed tightly over the mouth of the cylinder again, and the latter transferred to a narrow and deep glass vessel filled with water. It is here fastened to a support in such a way that the level of its contents will be at exactly the same height as that of the water in the outer vessel. A thermometer having been placed in the latter, the apparatus is allowed to stand for two or three hours (preferably in a room where the temperature will remain constant).

To determine the weight of the nitrogen obtained, the temperature and height of the barometer are noted, and the quantity of the gas calculated from the following well-known formula:

$$W = \frac{V(H - h)}{760(1 + 0{\cdot}00367 \times t)} \times 0{\cdot}00125749$$

V = Volume of the nitrogen in cubic centimeters.
H = Barometric height.
h = Tension of aqueous vapour at the temperature at which the measurement was made.
t = Temperature observed.

Tension of Aqueous Vapour between 5° and 30° C.

Temp.	Mm.	Temp.	Mm.	Temp.	Mm.
5	6·534	13·5	11·530	22	19·659
5·5	6·763	14	11·908	22·5	20·265
6	6·998	14·5	12·298	23	20·888
6·5	7·242	15	12·699	23·5	21·528
7	7·492	15·5	13·112	24	22·184
7·5	7·751	16	13·536	24·5	22·858
8	8·017	16·5	13·972	25	23·550
8·5	8·291	17	14·421	25·5	24·261
9	8·574	17·5	14·882	26	24·988
9·5	8·865	18	15·357	26·5	25·738
10	9·165	18·5	15·845	27	26·505
10·5	9·474	19	16·346	27·5	27·294
11	9·792	19·5	16·861	28	28·101
11·5	10·120	20	17·391	28·5	28·931
12	10·457	20·5	17·935	29	29·782
12·5	10·804	21	18·495	29·5	30·654
13	11·162	21·5	19·069	30	31·548

The determination of nitrogen by Dumas's method is very accurate. Whatever error it involves is due chiefly to the fact that it is impossible to obtain the nitrogen in a perfectly pure state, a small quantity of air always being present (coming from the apparatus, or left in the cylinder on its being filled). The oxides of nitrogen also escape complete reduction at times, and the two sources of error give rise as a rule to an excess of weight which equals 0·2 – 0·3 per cent. In determining the nitrogen in bodies containing sulphur, the combustion must be very slowly conducted, and the gases passed over as long as possible a layer of lead chromate, to prevent the reduction of the carbon dioxide to its monoxide by the sulphurous acid formed.

The above explanation of Dumas's classical method for determining nitrogen follows his own description. The unpleasant operations which it involves have led to the invention of various forms of apparatus in which to collect the nitrogen, that proposed by Schiff (*Berl. Ber.* xiii. 885) and modified by Gattermann (*Zeits. f. anal. Chemie,* xxiv. 57) being the best. This apparatus is shown in the accompanying figure.

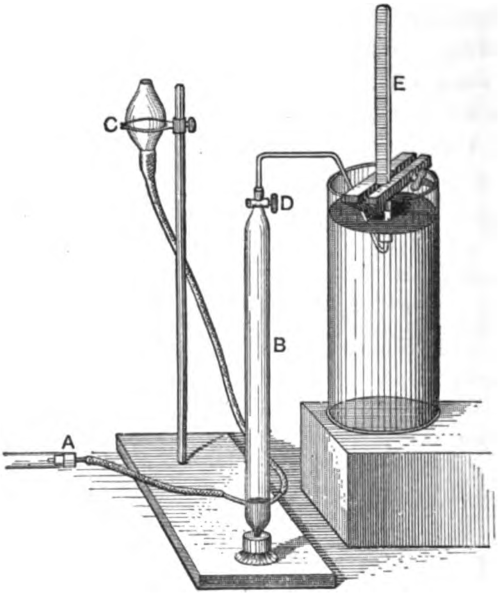

Fig. 1.

The combustion tube, A, having been connected with the cylinder, B, which is filled as far as the arm leading to A with mercury, for the rest with caustic potash, the cock

D is opened and the bulb C lowered until the level of the alkali stands about one centimeter above that of the mercury. A rapid current of carbon dioxide is then sent through the apparatus for fifteen or twenty minutes. After closing the cock, the bulb is next elevated and the alkali allowed to ascend to D. The quantity of air which the tube contains after five minutes have elapsed is then observed. As soon as none is left, the bulb is raised somewhat higher, the cock opened, and the delivery tube to E thus filled with the alkali. The combustion can now be commenced. It is continued in the usual manner until the volume of gas collected in B no longer increases, whereupon the tube between the combustion tube and cylinder is closed by a pinch-cock and the apparatus allowed to stand for about an hour. The cock D is then carefully opened again, while the bulb C is still elevated. The nitrogen obtained thus passes into the measuring cylinder E, where its volume is determined as usual.

DETERMINATION OF NITROGEN BY CONVERSION TO AMMONIA

(Method of Varrentrapp and Will)

§ **167.** This method is based upon the conversion of the nitrogen of an organic substance to ammonia by the action of a caustic alkali at a high temperature. The ammonia is received in an acid, and can be determined by either a gravimetric or volumetric method. The carbon of the substance is oxidised at the expense of the oxygen of the alkali, and its hydrogen goes to form the ammonia, or is in part released in the free state (or in the form of hydrocarbons). The conversion of the nitrogen to ammonia is often preceded by the formation of a metallic cyanide. We will refer to these complicated reactions again in explaining the method.

Varrentrapp and Will's method, as has already been remarked, is inapplicable to the analysis of nitro-, nitroso-, azo-, or diazo-compounds.

Preparation of the soda-lime.—Calcium oxide is slaked with a concentrated solution of pure sodium hydroxide (in the proportion, 2 parts CaO to 1 part NaOH). The mixture is then evaporated to dryness in an iron dish, ignited in a Hessian crucible, and finally broken up and sifted. The powder obtained is used for mixing with the substance; the coarser granules and lumps to fill the remainder of the combustion tube. The preparation must be preserved in a tightly closed vessel.

Commercial soda-lime which contains nitrites or nitrates cannot be employed, as it evolves ammonia of itself. It can best be tested by ignition with pure sugar, the conditions for the determination of nitrogen being observed: if ammonia forms, the preparation is unfit for use.

Instead of soda-lime, a mixture of equal parts of sodium carbonate (obtained from the bicarbonate) and dried slaked lime can also be employed.

The Tube and Absorption Apparatus.—The combustion is performed in a difficultly fusible tube, from sixteen to twenty inches long, and one end of which tapers to a narrow point and is bent upwards. The other end is joined, by means of a well-fitting perforated cork, with a Varrentrapp and Will's absorption apparatus, in which the ammonia is received. This apparatus consists of three bulbs, lying in the same vertical plane, the intermediate one being much smaller than the other two. From each of the larger bulbs passes a tube, one to connect the apparatus with the combustion tube, and the other, which is long, tapering, and very thin, being the outlet. The ammonia is absorbed in dilute hydrochloric or sulphuric acid, the former being used when the determination is to be made as ammonium platinichloride, the latter if a volumetric method is to be employed. The gravimetric determination as the platinichloride is the better, for reasons which will be explained below. The hydrochloric acid used should be dilute, not the fuming acid; and of about the sp. gr. 1·10. It is introduced into the bulbs by suction through the thin tube. The amount taken must be such that it will neither be drawn into the combustion tube by the violent absorption of ammonia, nor ejected from the other end in case the flow of gas becomes too rapid. After filling the bulbs, therefore, air must be drawn and forced through the apparatus, to ascertain the probable behaviour of the acid. The subsequent operations will be described later. If standard sulphuric acid is to be used, twenty cubic centimeters of it are required (the ammonia is found by titration of the residual acid). The quantity of substance to be taken varies between 0·2 gr. and 0·4 gr., according to its richness in nitrogen.

Filling the Tube. The Combustion.—Before the combustion tube is filled, the soda-lime must be heated, with continual stirring, in a porcelain or iron basin over a Bunsen burner, to drive off hygroscopic water and ammonium salts (the latter are always present if the substance has been kept in the laboratory for some time). When the preparation has become sufficiently cool, the combustion tube is rinsed out with a portion of it and an asbestos plug then placed in the tail. A layer of granular soda-lime about two inches long is next introduced, and on top of this is brought the mixture of the substance with powdered soda-lime (eight inches), the mixture having been effected in a warm porcelain mortar. (Fluids are introduced, as usual, in glass bulbs.) The mortar is then rinsed out two or three times with powdered soda-lime, and the tube filled for the rest of its length with the granular preparation. An asbestos plug having been inserted to prevent any of the alkaline dust from being carried into the absorption apparatus, the tube is connected with the latter by means of a well-fitting cork and, after a passage for the gases has been secured by a few gentle taps,[1] is laid in the furnace, and its anterior part heated. As soon as the forward third of the tube (not as far as the substance) has become red-hot, the flames at the rear of the furnace are lighted and the ignition gradually extended to the whole tube. Care must be taken that the combustion proceeds evenly, so that the current of gas generated will pass into the absorption apparatus without cessation. If the heat becomes irregular and the flow of gas interrupted, the sudden absorption of the ammonia in the tube may draw the acid out of the bulbs into the former (means of preventing this accident will be explained below). In addition to this precaution, the water which forms during the combustion and condenses in the anterior portion of the tube must be carefully driven over into the absorption-apparatus by means of a small flame, as it always dissolves some of the ammoniacal gas. Toward the close of the combustion the portion of the tube which contains the substance must be

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[1] The necessity of forming this passage has recently been doubted.

ignited as strongly as possible, until the carbon which has previously separated out becomes fully consumed and leaves the contents of the tube white or grayish-white. Neglect at this point may lead to the loss of more or less nitrogen which has combined with the alkalies to form cyanides, the latter compounds being decomposed to ammonia only on protracted and intense ignition. If the operation has been properly conducted, *i.e.*, if a current of gas passed through the bulbs steadily, during the whole of the combustion, the analysis may be interrupted when the acid in the absorption bulbs is seen to be gradually receding toward the combustion tube. A piece of caoutchouc tubing is then slipped over the free end of the absorption bulbs, and, the tail of the combustion tube having been broken off, a current of air is drawn steadily through the apparatus for five minutes, either by the mouth or with an aspirator.

Determination of the Ammonia.—If the ammonia is to be gravimetrically determined, the contents of the absorption bulbs are poured into a porcelain casserole, the apparatus rinsed out three times, and the wash-water added to the main solution. The liquid is then evaporated almost to dryness, precipitated with platinum chloride,[1] and the ammonium platinichloride washed with alcohol and ether, etc., as directed in § 116. The quantity of nitrogen is calculated from the weight of the metallic platinum obtained on ignition of the precipitate (the determination on a weighed filter is less accurate, as will be explained below):

194·8 parts Platinum = 28 parts Nitrogen.

If a volumetric method is to be employed, the ammonia is received in a standard solution of sulphuric acid. The contents of the bulbs are poured, together with the wash-water, into a beaker, where the solution is coloured by litmus and the residual free sulphuric acid titrated with standard sodium hydroxide. The difference between this quantity and that placed in the bulb before the analysis represents the amount saturated by the ammonia. From this value the weight of nitrogen is easily calculated.

98 parts Sulphuric acid = 28 parts Nitrogen.

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[1] The platinum chloride solution must contain no *aqua regia*. It should be prepared from the crystallised salt.

While under favourable circumstances this method is very accurate, it can at the same time be employed only with great caution. One of the greatest difficulties in the process lies in correctly regulating the temperature and preventing the liquid in the absorption bulbs from suddenly changing its level. Substances which are poor in nitrogen are in this respect easily analysed; but those which contain a large quantity (20 per cent and over) must be mixed with some non-nitrogenous body, to decrease the rapidity of the formation of ammonia and the consequent danger of too sudden an absorption. For this purpose, sugar, oxalic acid, or calcium oxalate, can be employed, the preparation having first been thoroughly dried. Another drawback to Varrentrapp and Will's method is presented in the complicated reactions which take place between the soda-lime and nitrogenous compounds. Many of the latter (indigo, quinine, morphine, etc.) are decomposed in part to ammonia, in part to compound ammonias; it is for this reason that the precipitated platinichloride cannot be directly weighed, but must be determined from the platinum left after its ignition. The same cause may also lead to errors in the volumetric determination. The possibility of an error arising from the formation of these compound ammonias cannot be prevented, as many members of this class of compounds form platinichlorides soluble in alcohol, so that loss ensues in washing the precipitate. This danger is partly, but only partly, obviated by the proposition made by A. W. Hofman, to wash the precipitate in such cases with ether, to which only a few drops of alcohol have been added. The determination of nitrogen by this method in very complicated compounds (especially of the aromatic series) is moreover accompanied, as I have often observed, by the separation of solid substances (hydrocarbons, napthaline, etc.) which get into the absorption bulbs and must necessarily be filtered off; the filtrate is then apt to contain substances, on evaporation with which the platinum of the platinichloride suffers reduction. Great discrimination is, therefore, required in the use of Varrentrapp and Will's method, especially when a new compound is to be investigated. In the analysis of substances which evolve only ammonia (such as oxamide and analogous compounds) it nevertheless affords very accurate results.

Kjeldahl's Method

§ **168.** The substance (about 0·5 gr.) is weighed off in an ordinary flask of about 100 c.c. capacity, and oxidised, in the same vessel, with boiling concentrated sulphuric acid (10 c.c.) For this purpose the flask is placed on a support covered with wire gauze, and first heated with a small flame. The operation must be performed under a hood, as sulphurous acid is liberated in the reaction. The liquid is boiled for about two hours, until the evolution of gas has entirely ceased and the dark colour which the acid at first assumed has been lost, indicating that the decomposition of the organic substance is complete.

The flame is next extinguished, and pulverised potassium permanganate added to the acid in small quantities at a time. The reaction, which is violent but not dangerous, colours the solution at first red, and finally dark-green; the appearance of the latter colour showing that enough has been added. As soon as the liquid has cooled off, it is diluted with water and transferred to a distilling flask holding about seven hundred cubic centimeters, where an excess of sodium hydroxide (about 40 c.c., of sp. gr. 1·3) is added, and the ammonia distilled into a receiver containing an acid. To perform this operation safely a few zinc filings are added, which causes a gentle evolution of hydrogen. The ammonia in the distillate can be determined by either the gravimetric or volumetric method.

According to the observations of Arnold and Wedemeyer, potassium sulphate can be used instead of the permanganate. To 40 gr. of sulphuric acid, 20 gr. of the salt are added at once, 15 gr. more after the lapse of about twenty minutes. The solution is completely without colour. It is also preferable to use the zinc in the form of dust instead of filings in the process of distillation. The oxidation can be still more quickly effected by the addition (to 40 gr. H_2SO_4) of 20 gr. K_2SO_4, 1 gr. mercuric oxide, and 1 gr. cupric sulphate (method of Guning-Arnold).

This method, the original and full description of which can be found in the *Zeitschrift f. anal. Chemie*, 1883, S. 366 possesses many advantages. It is especially convenient for the determination of nitrogen in fertilisers, milk, flesh, etc., as it is easily carried out, requires little time, and does not necessitate fine division of the substance. It is still far too imperfectly elaborated, however, for use in the analysis of purely organic chemical compounds. The author obtained good results by its means in the analysis of triethylamine, asparagine, uric and hippuric acids, and urea, but found too little nitrogen in that of quinine hydrochloride. According to Asbott's experiments the method can be used for the determination of nitrogen in all organic substances, except the pyridine and quinoline groups; and these compounds also can be analysed by the method as modified by Guning-Arnold.

DETERMINATION OF THE CARBON, HYDROGEN, AND NITROGEN OF ORGANIC SUBSTANCES IN ONE OPERATION.

(Method of P. Jannasch and Victor Meyer)

This method is intended, not to displace the processes which we have already described, but for use when only a small quantity of the substance is available, and simultaneous determination of the three elements is therefore desirable. The substance is ignited as usual with cupric oxide, in a tube about forty inches long. The products of combustion first pass through a calcium chloride tube and a potash bulb, and the nitrogen is finally received in a cylinder connected with the latter. A current of pure dry oxygen is first led through the apparatus, and when the air has been driven out, the bayonet of the tube is sealed up, and the posterior end, containing a mixture of equal parts of potassium permanganate and dichromate, is slightly heated. The arrangement of the different parts of the apparatus and reagents is the same as in Dumas's method, with the exception that the cylinder receiving the nitrogen is filled with a hydrochloric acid solution of chromous chloride, $CrCl_2$, instead of sodium hydroxide. This reagent serves to absorb the excess of oxygen. The process is the same as in Dumas's method. The hydrogen is determined from the increase in weight of the calcium chloride tube; the carbon from that of the potash bulb; and the nitrogen measured as such. The details of the method can be found in the *Ann. d. Chem. u. Pharm.* Bd. 233, S. 375.

DETERMINATION OF THE HALOGENS

§ **169.** The halogens in organic substances are rarely present in a form which permits their direct detection and estimation by means of silver nitrate. Compounds in which this can be effected are the haloid salts of organic bases and the acid haloids, or haloid anhydrides of the acids, which are decomposed to the respective hydrogen acids by water. In these few cases the halogens are detected and estimated by precipitation with silver nitrate under the usual conditions (§ 127).

In general, however, the halogens in organic compounds, whether in aqueous or alcoholic solution, show no reaction with silver nitrate; and their detection and estimation must therefore be preceded by complete decomposition of the compound.

Detection of the halogens.—When organic haloid compounds are burned they very often tinge the flame green, the colour being particularly distinct on the border. In accordance with Beilstein's proposition, the conditions of the reaction have been altered as follows. A piece of cupric oxide is ignited in the loop of a platinum wire, and some of the substance to be examined then placed upon it. If it be again held in the outer mantle of the flame, no change is at first observed in the latter, but the haloid salt of the copper soon commences to volatilise and colours the flame green or blue. The purity of the cupric oxide must be tested before each experiment, the piece to be used being for this purpose ignited in both the oxidising and reducing flame, either alone or after it has been moistened with water or alcohol. The halogens in organic compounds can also be detected by combustion with calcium oxide (it is not always applicable; for instance, with monochlorobenzene). The method is described below, in connection with the quantitative determination.

Determination of the Halogens. *Method of Carius.*—This method is the one most frequently used. It consists in decomposing the substance with concentrated nitric acid at a high temperature, and finally determining the halogen as its silver salt with silver nitrate. The decomposition is effected in a sealed tube.

The quantity of the substance to be taken depends on its richness in the halogen. From 0·2 gr. to 0·3 gr. are weighed off, in a thin glass bulb (of difficultly fusible glass) if the substance be liquid, or in a small tube sealed at one end if a solid. It is then placed in a tube of about one half inch in diameter, which is sealed at one end. Enough crystallised silver nitrate to precipitate the whole of the halogen, and from twenty to sixty times as much nitric acid as substance, having been added, the open end is drawn out to a thick capillary tube and then sealed. The concentration of the nitric acid must be governed by the readiness with which the substance will undergo oxidation; the specific gravity should be 1·3-1·37 (or greater). The liquid must not occupy more than a third or two-fifths of the tube. The latter is placed in the iron tube of an air-bath (having first been shaken, for the purpose of breaking the bulb, if a liquid is being analysed), and kept at a temperature of 150°-250° C. for from ten to thirty hours. The degree and duration of the heat to be employed depends upon the ease with which the substance can be decomposed. When the reaction is considered over, the tube is allowed to become entirely cold while still inside the air-bath, and then opened. For this purpose it is wrapped in a towel (as a precaution in case of explosion), and its capillary end held in a gas flame. As the glass melts the compressed gas within the tube forces a hole through it and escapes. As soon as this occurs the tube is scratched with a file and broken off cleanly by holding the red-hot end of a glass rod against the mark made. The precipitated silver haloid is then carefully transferred from the tube to a small filter, washed, and determined according to § 127. If the substance .under analysis was a liquid, the pieces of glass from the bulb must also be collected on the filter and weighed with the precipitate. As the weight of the bulb while whole is known, the quantity of the silver salt is found by subtracting this value from the combined weight (of the bulb and precipitate). The quantity of the halogen found is deduced in the usual manner.

The method of Carius is more accurate than other processes, and the halogens are therefore almost always determined by its means. Its chief objection is that for every substance the proper concentration of the nitric acid, and also the time necessary to ensure decomposition, must be ascertained by experiment. It is inapplicable in cases where the substance will not be completely destroyed by the nitric acid. Carius has proposed to use in such instances a mixture of 3-4 parts of nitric acid (sp. gr. 1·4), 1 part of potassium dichromate, and the requisite amount of silver nitrate. Since with this mixture silver chromate is also formed, however, the liquid must be boiled for an hour with alcohol (5-10 c.c.) before being filtered. This modification is rarely employed, as the process below is more convenient. A modification of the latter method which can also be used in estimating the halogens is described in the paragraph on the determination of sulphur.

Determination by Ignition with Calcium Oxide.—The calcium oxide (anhydrous) must contain no halogens, and is usually prepared from pure marble. The ignition is performed in a tube of difficultly fusible glass, which is sealed at one end and from sixteen to twenty inches long. A layer of pure calcium oxide is first introduced, and then the mixture of the substance with more of the oxide. The mixture is prepared in a porcelain mortar if the substance be solid, and a bulb employed for liquids. The mortar having been rinsed out with lime, and the latter poured into the tube, the remaining space is filled with the oxide and closed by an asbestos plug. A passage over the substance is then obtained by tapping the tube, and the latter ignited, the heat being first applied to the forward end. When the whole tube has become red-hot the flames are extinguished and the hot tube inserted, mouth downward, in a glass cylinder containing water. This completely shatters it, and its contents instantly become soaked. Nitric acid is then added until the calcium oxide has completely dissolved, the solution filtered from the glass splinters and residual carbon, and the halogens in the filtrate determined with silver nitrate according to § 127.

Method of E. Kopp.—A mixture of the substance with ferric oxide, obtained by the ignition of ferrous sulphate, is placed in a glass tube which is sealed at one end. The mixture should fill from five to seven inches of the tube. An iron wire plug about nine inches long is then inserted, and the remaining space filled with pieces of anhydrous sodium carbonate. The iron wire is first heated, and the ignition gradually extended toward the substance. The halogens are obtained as their iron compounds. When the combustion is finished, the contents of the tube are extracted with boiling water, filtered, and the filtrate acidified and precipitated with silver nitrate, as in § 127.

Kekulé's method. By means of sodium amalgam.—This method, while not always applicable, is very convenient when permitted. It is more especially suitable for the analysis of so-called substitution compounds, and is based upon the fact that by the action of sodium amalgam the halogen is displaced by hydrogen, the former uniting with the sodium. The substance is introduced into a flask containing sodium amalgam. Water is then added, and when the reaction, which requires some hours, is finished, the solution is neutralised with dilute nitric acid and precipitated with silver nitrate. (In determining iodine the process is reversed, the acid not being added until after the precipitation.)

In all these methods the halogen may be volumetrically determined by Volhard's method (§ 153). An excess of standard silver nitrate is first added to the liquid, and the residual silver then titrated with standard ammonium sulphocyanate.

DETERMINATION OF SULPHUR AND PHOSPHORUS

§ **170.** The widely-varying behaviour of sulphur and phosphorus compounds necessitates several different methods for their analysis. In all of them, however, the sulphur is converted to sulphuric acid and weighed as barium sulphate, the phosphorus to phosphoric acid and precipitated as ammonium magnesium phosphate. The qualitative detection of these substances is made in the same manner as their determination, and will therefore require no separate description. The oxidation of sulphur and phosphorus is effected under like conditions, and the following methods can be employed for the analysis of either element (and also of arsenic).

Method of Carius.—This process is particularly convenient for the estimation of sulphur. The substance is decomposed, as in determining the halogens, with concentrated nitric acid in a sealed tube. The varying readiness with which different sulphur compounds undergo decomposition necessitates the choice of one of several modifications, which are given below in the order of their power as a means of oxidation.

1. The substance is oxidised with nitric acid of sp. gr. 1·2, under the conditions explained in the determination of the halogens by this method (§ 169). The solution obtained is diluted with water and precipitated by barium chloride, and the barium sulphate filtered off, washed, and weighed.

2. Many substances, such as ethyl sulphide, cannot be decomposed in this way. In such cases the above process is supplemented by neutralising the liquid with sodium carbonate, evaporating to dryness, and fusing the residue in a silver dish over a glass flame. The cake obtained is then dissolved in water, neutralised with nitric acid (with addition of hydrochloric), filtered, and the filtrate precipitated with barium chloride. The barium sulphate must be purified, as directed in § 134.

3. A mixture of nitric acid of sp. gr. 1·4 and potassium dichromate is employed, as explained in § 169.

4. Nitric acid of sp. gr. = 1·5, obtained by gently heating the fuming acid in a flask, is employed. The tube should be eighteen or twenty inches long and have an internal diameter of one-half an inch. Not more than one and a half or two times as much of the acid as is theoretically necessary must be taken, the calculation being made on the hypothesis that each molecule of nitric acid contains one atom of active oxygen. For the complete oxidation of CH_4S, for instance, seven atoms of oxygen, and accordingly seven molecules of

nitric acid, are necessary. The temperature to which the tube must be heated is governed by the ease with which the substance can be decomposed: it ranges from 150° C. to 300° C., and is maintained for one and a half or two hours. When the operation is finished, the tube is opened and its contents diluted with a small quantity of water and treated as usual.

Oxidation with Sodium Carbonate and Potassium Nitrate.—1. This method, introduced by Liebig, is particularly suitable for the analysis of compounds which contain only a small percentage of sulphur, such as albuminoids, the aromatic sulpho-acids, etc. A quantity of pure potassium hydroxide, to which has been added one-eighth its weight of potassium nitràte and a little water, is fused in a silver crucible and allowed to cool. A weighed quantity of the substance is then added and the fusion repeated, the mixture being continually stirred with a glass rod until it has become perfectly white. When it has again grown cold it is dissolved in water, neutralised with hydrochloric acid, and precipitated with barium chloride. The barium sulphate obtained requires purification (§ 134).

2. If the compound be volatile the method must be subjected to the following modification (it has the objection of being longer). The substance is fused in a glass tube, about eighteen inches in length and sealed at one end, with a mixture of eight parts of sodium carbonate and one part of potassium nitrate or chlorate (a greater proportion of potassium chlorate would be apt to cause an explosion). The operations of filling the tube and preparing the mixture of the substance with the reagent are performed as described in § 169 (determination of the halogens by ignition with calcium oxide). Fluids are introduced into the tube in glass bulbs. The tube having been placed in a combustion furnace, the gas is lighted under its anterior end and the heat gradually extended its whole length. When the contents have become perfectly white the tube is thrust, while still hot, into a flask or cylinder containing water. The solution is then acidified with hydrochloric acid, filtered from the pieces of glass, and evaporated to dryness in a porcelain casserole (to convert the silica taken up from the glass into the insoluble state). The

residue is extracted with water and treated as usual. The barium sulphate requires purification (§ 134).

Clason's method.—This method consists in the complete oxidation of the sulphur compound in a current of oxygen and nitric oxide. Its details can be found in the *Zeitschrift f. anal. Chemie*, 1883, S. 177.

If sulphur and phosphorus are both present, the solution is precipitated, after the oxidation, with barium chloride, the precipitate filtered off, and the phosphoric acid thrown down from the filtrate as ammonium magnesium phosphate. The detailed description of the estimation of sulphuric acid will be found in § 118; that of phosphoric acid as ammonium magnesium phosphate in § 135.

DETERMINATION OF THE METALS

§ **171.** We shall consider only the most frequently occurring case, viz., the determination of the metals in salts of organic acids. The metals are determined in the same forms as in the methods described in Part II., Section I., the respective compounds often being obtained simply by ignition of the salts, *i.e.*, through the decomposition of the organic constituents at a high temperature.

The analysis is made with from 0·3 gr. to 0·7 gr. of the substance, according to the probable percentage of the metal and the method to be used.

If ignition is to be employed, the substance can be weighed directly in a platinum or porcelain crucible; if another method, in a weighing tube (§ 139).

Ignition.—The substance is first carbonised, by heating with a small flame in a covered porcelain or platinum crucible, the exact temperature to be employed varying with the nature of the compounds. This operation requires great care, as it is often attended by violent effervescence. When the vehemence of the reaction has subsided the heat is increased, and the crucible placed somewhat obliquely, to assist the combustion of the carbon. This is further hastened by inclining the cover to the crucible. The final residue (metallic oxide or carbonate) is then treated as below.

Zinc, cadmium, and lead salts cannot be directly ignited until the carbon has been completely oxidised, as loss is otherwise apt to ensue from volatilisation of the metal. The process to be here followed is given under the respective metals. Mercury salts, obviously, must not be subjected to ignition: they are analysed by the wet way.

Potassium; sodium.—The ignition of the salts of these metals usually converts them to the carbonates. The salts of certain acids which contain nitrogen, however, yield cyanides, and those containing sulphur leave a residue of varying composition. It is therefore advantageous to convert the carbonate to sulphate before it is weighed. For this purpose the contents of the crucible are treated, after they have been ignited and grown cold again, with a few drops of concentrated sulphuric acid[1] and the cover put on the crucible. When the evolution of carbon dioxide has ceased, the crucible is placed in an oblique position, and its upper half cautiously heated with a small flame, the temperature being regulated according to the rapidity of the acid's volatilisation. When the fumes have entirely disappeared, the residue is ignited somewhat more strongly. It still contains more or less of the acid sulphate, however, and to convert this to the neutral salt pieces of ammonium carbonate must from time to time be added and volatilised within the covered crucible. The crucible must be continually covered during the ignition of potassium sulphate. Sodium sulphate is very readily fusible. The operation can be very conveniently performed in a cup-shaped open air-bath, or in a muffle, as explained in § 116.

Barium is preferably determined by precipitation with dilute sulphuric acid from its aqueous or hydrochloric or nitric acid solution, as in § 118. The determination can also be made by igniting the salt and treating the residue with sulphuric acid, as is done with potassium. A platinum crucible should not be used for the ignition of barium salts, as it is apt to be attacked by the barium oxide formed. In very rare cases (such, for instance, as in the analysis of haloid substitution products of the acids), the barium is precipitated by ammonia and ammonium carbonate, and weighed as its carbonate (§ 118).

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[1] It must be ascertained that the sulphuric acid leaves no residue on ignition.

Calcium, magnesium.—Calcium salts are ignited over an ordinary flame until the combustion of the carbon is complete, and then heated before the blow-pipe in an uncovered crucible for an hour (§ 118). The ignition is repeated again after the calcium oxide has been weighed, to ascertain whether the weight remains constant. The determination can be somewhat more accurately made as sulphate than by the above method. The residue left on ignition of the salt is for this purpose treated with hydrochloric acid, a few drops of dilute sulphuric acid added, and the liquid evaporated to dryness and ignited. Magnesium is determined by igniting the salt and weighing the residual magnesium oxide.

Aluminium, chromium, iron.—The salts are ignited and the residual oxides weighed.

Zinc.—The zinc in salts with volatile organic acids is determined by precipitation with sodium carbonate (§ 123) and weighing as oxide. When combined with non-volatile acids, the best method is to separate it as zinc sulphide (§ 123). Ignition is apt to lead to too low results. If it must be employed, the operation is performed as described under Lead.

Lead is most conveniently estimated in the wet way, by precipitation as lead sulphate from the aqueous or nitric acid solution of its organic salt. The directions given in § 127 must be observed. In the determination of lead as the oxide by ignition, the substance is carefully ignited in a porcelain crucible to carbonisation. The cover is then removed and, when the further combustion has ceased and the flame been taken away, a few pieces of recently-fused ammonium nitrate are added and the cover replaced. When the reaction, which is at first violent, has subsided, the ignition is repeated and the residue finally weighed as lead oxide.

Copper can rarely be precipitated from the solution of its organic salts by means of sodium hydroxide (§ 117). It is usually determined by igniting the salt in a porcelain or platinum crucible, the residue first obtained being moistened with nitric acid and reignited before the weighing. To avoid the risk of a loss occurring through spirting, it is advisable to perform this operation while the crucible is standing inside another and somewhat larger one, with which it must also be weighed. The oxidation can also be effected with mercuric oxide (which must leave no residue on ignition).

Mercury is determined exclusively in the wet way. The aqueous or nitric acid solution of the salt to be analysed is precipitated by freshly-prepared hydrogen sulphide water, and the mercuric sulphide determined on a weighed filter, according to § 127.

Silver, gold, platinum.—When organic compounds containing these elements are ignited, the latter are left in the metallic state and can be weighed as such. For the details to be fulfilled in the ignition of compounds containing gold, see § 131; of those of platinum, §§ 131 and 116. In the determination of silver the metal must be dissolved in dilute nitric acid after being weighed, to ascertain that no carbon has been left from the ignition.[1] The ignition of silver salts must be performed with the utmost care, since many of them explode on being heated. If the explosion is only slight, the salt can safely be analysed by this method, but in violently explosive bodies the silver must be determined by precipitation from aqueous or nitric acid solution with hydrochloric acid (§ 127).

In order to determine both the chlorine and platinum in the platinichlorides of organic bases, the following method, proposed by Wallech, may be employed. The salt is weighed off in a platinum dish, covered with alcohol, and treated with 0·5-1·0 gr. of metallic sodium in alcoholic solution. The dish is then set upon the water-bath, where the excess of alcohol is driven off. As soon as crystals are observed to form, the residual alcohol is lighted. When it has entirely burned away, the residue is ignited, allowed to cool, extracted with water, and filtered. The chlorine is determined in the filtrate by the usual method. The platinum remains upon the filter, with which, after being dried, it is ignited in a platinum crucible and weighed.

According to Wolff this method must also be employed in many cases for the analysis of aurichlorides, since in the determination of the gold by ignition it is sometimes impossible to avoid a loss.

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[1] When using a Bunsen burner for the ignition in determining silver I have never yet observed a case in which the combustion of the carbon was incomplete.

ATOMIC WEIGHTS OF THE ELEMENTS

	0=16	0=15·96		0=16	0=15·96
Aluminium	27·08	27·04	Molybdenum	96·1	95·9
Antimony	120·29	119·6	Nickel	58·37	58·19
Arsenic	75·0	74·9	Niobium	94·2	93·7
Barium	137·42	136·9	Nitrogen	14·041	14·02
Beryllium	9·10	9·08	Osmium	191·6	190·3
Bismuth	209·02	208·37	Oxygen	16·0	15·96
Boron	11·0	10·9	Palladium	106·7	106·35
Bromine	79·963	79·76	Phosphorus	31·03	30·96
Cadmium	112·08	111·8	Platinum	194·83	194·5
Cæsium	132·88	132·7	Potassium	39·136	39·03
Calcium	40·00	39·91	Rhodium	103·0	102·74
Carbon	12·003	11·97	Rubidium	85·44	85·2
Cerium	140·2	139·9	Ruthenium	101·6	101·4
Chlorine	35·453	35·37	Selenium	7·907	78·87
Chromium	52·15	52·0	Silicon	28·40	28·3
Cobalt	59·85	59·67	Silver	107·938	107·66
Copper	63·60	63·45	Sodium	23·058	23·0
Fluorine	18·99	19·06	Strontium	87·52	87·3
Gallium	69·9	69·9	Sulphur	32·063	31·98
Germanium	72·32	72·3	Tantalum	182·8	182·
Gold	196·85	196·7	Tellurium	125·0	125·0
Hydrogen	1·0032	1·00	Thallium	204·15	203·7
Indium	113·7	113·6	Thorium	232·4	231·9
Iodine	126·864	126·54	Tin	119·17	118·8
Iridium	193·18	192·5	Titanium	48·13	48·0
Iron	56·0	55·88	Tungsten	184·0	183·6
Lanthanum	138·5	138·2	Uranium	239·4	238·8
Lead	206·911	206·4	Vanadium	51·21	51·1
Lithium	7·030	7·01	Yttrium	89·0	88·9
Magnesium	24·38	24·2	Zinc	65·38	65·3
Manganese	55·09	54·8	Zirconium	90·67	90·4
Mercury	200·4	199·8			

TABLE FOR THE CALCULATION OF ANALYTICAL RESULTS

Elements.	Atomic Weights.	Weighing-form.	Molecular Weight.	Factor.
Aluminium .	27	Al_2O_3	102	$\frac{54}{102}=0\cdot5294$
Antimony . .	120	Sb_2S_3	336	$\frac{10}{14}=0\cdot7142$
Arsenic . . .	75	As_2S_3	246	$\frac{75}{123}=0\cdot60975$
„ . . .	...	$MgNH_4AsO_4 . \frac{1}{2}H_2O$	190	$\frac{15}{38}=0\cdot3947$
Barium . . .	137·4	$BaSO_4$	233·4	$\frac{137\cdot4}{233\cdot4}=0\cdot5887$
Bismuth . . .	209	Bi_2O_3	466	$\frac{209}{233}=0\cdot897$
Boron . . .	11	...	...	...
Bromine . . .	80	AgBr	188	$\frac{20}{47}=0\cdot4255$
Cadmium . .	112	CdO	128	$\frac{7}{8}=0\cdot8750$
Calcium . . .	40	CaO	56	$\frac{5}{7}=0\cdot7143$
„ . .	...	$CaCO_3$	100	$\frac{2}{5}=0\cdot4000$
Carbon . . .	12	CO_2	44	$\frac{3}{11}=0\cdot2727$
Chlorine . . .	35·5	AgCl	143·5	$\frac{7\cdot1}{28\cdot7}=0\cdot2474$
Chromium . .	52·1	Cr_2O_3	152·2	$\frac{104\cdot2}{152\cdot2}=0\cdot6846$
Cobalt . . .	59·8	Co_3O_4	243·4	$\frac{179\cdot4}{243\cdot4}=0\cdot7370$
Copper . . .	63·6	CuO	79·6	$\frac{63\cdot6}{79\cdot6}=0\cdot799$
Fluorine . . .	19	CaF_2	78	$\frac{19}{39}=0\cdot4871$
Gold	197	...	...	...
Hydrogen . .	1	H_2O	18	$\frac{1}{9}=0\cdot1111$
Iodine . . .	127	AgI	235	$\frac{127}{235}=0\cdot5404$
Iron	56	Fe_2O_3	160	$\frac{7}{10}=0\cdot7000$
Lead	207	$PbSO_4$	303	$\frac{69}{101}=0\cdot6831$

TABLE FOR THE CALCULATION OF ANALYTICAL RESULTS—*Continued.*

Elements.	Atomic Weights.	Weighing-form.	Molecular Weight.	Factor.
Magnesium . .	24·4	$Mg_2P_2O_7$	222·8	$\frac{48\cdot8}{222\cdot8}=0\cdot2190$
Manganese .	55	Mn_3O_4	229	$\frac{165}{229}=0\cdot7205$
Mercury . .	200·4	HgS	232·4	$\frac{200\cdot4}{232\cdot4}=0\cdot8623$
"	...	HgCl	235·9	$\frac{200\cdot4}{235\cdot9}=0\cdot8494$
Nickel . . .	58·5	NiO	74·5	$\frac{58\cdot5}{74\cdot5}=0\cdot7852$
Nitrogen . . .	14	$(NH_4)_2PtCl_6$	443·9	$\frac{28}{443\cdot9}=0\cdot063077$
"	...	Pt	194·9	$\frac{28}{194\cdot9}=0\cdot14366$
Ammonia	17	$(NH_4)_2PtCl_6$	443·9	$\frac{34}{443\cdot9}=0\cdot076594$
"	...	Pt	194·9	$\frac{34}{194\cdot9}=0\cdot17455$
Cyanogen	26	AgCy	134	$\frac{13}{67}=0\cdot1940$
Oxygen . . .	16	...	...	...
Phosphorus . .	31	$Mg_2P_2O_7$	222·8	$\frac{31}{111\cdot4}=0\cdot2782$
Platinum . . .	194·9	...	...	...
Potassium . .	39·1	K_2SO_4	174·2	$\frac{39\cdot1}{87\cdot1}=0\cdot4489$
Silicon . . .	28·4	SiO_2	60·4	$\frac{28\cdot4}{60\cdot4}=0\cdot4702$
Silver . . .	108	AgCl	143·5	$\frac{108}{143\cdot5}=0\cdot7526$
Sodium . . .	23	Na_2SO_4	142	$\frac{23}{71}=0\cdot3239$
Strontium . .	87·5	$SrSO_4$	183·5	$\frac{17\cdot5}{36\cdot7}=0\cdot4768$
Sulphur . . .	32	$BaSO_4$	233	$\frac{32}{233}=0\cdot1373$
Tin	119	SnO_2	151	$\frac{119}{151}=0\cdot7881$
Zinc	65·4	ZnO	81·4	$\frac{65\cdot4}{81\cdot4}=0\cdot8034$

The weight of the element is found by multiplying that of the compound by either the fraction or decimal given in the last column; these constants express the ratio between the atomic weight of the element and the molecular weight of its weighing-form.

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