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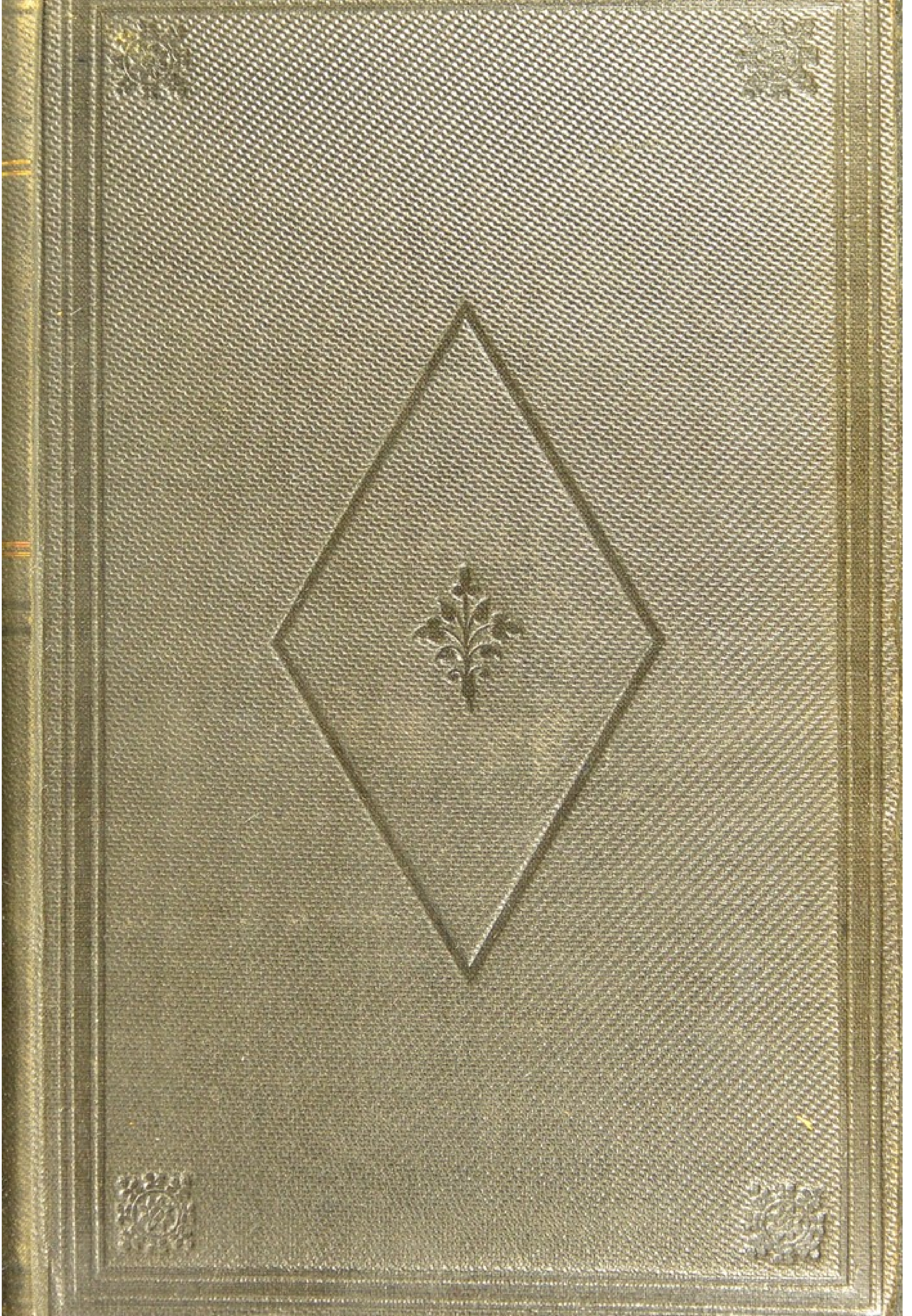
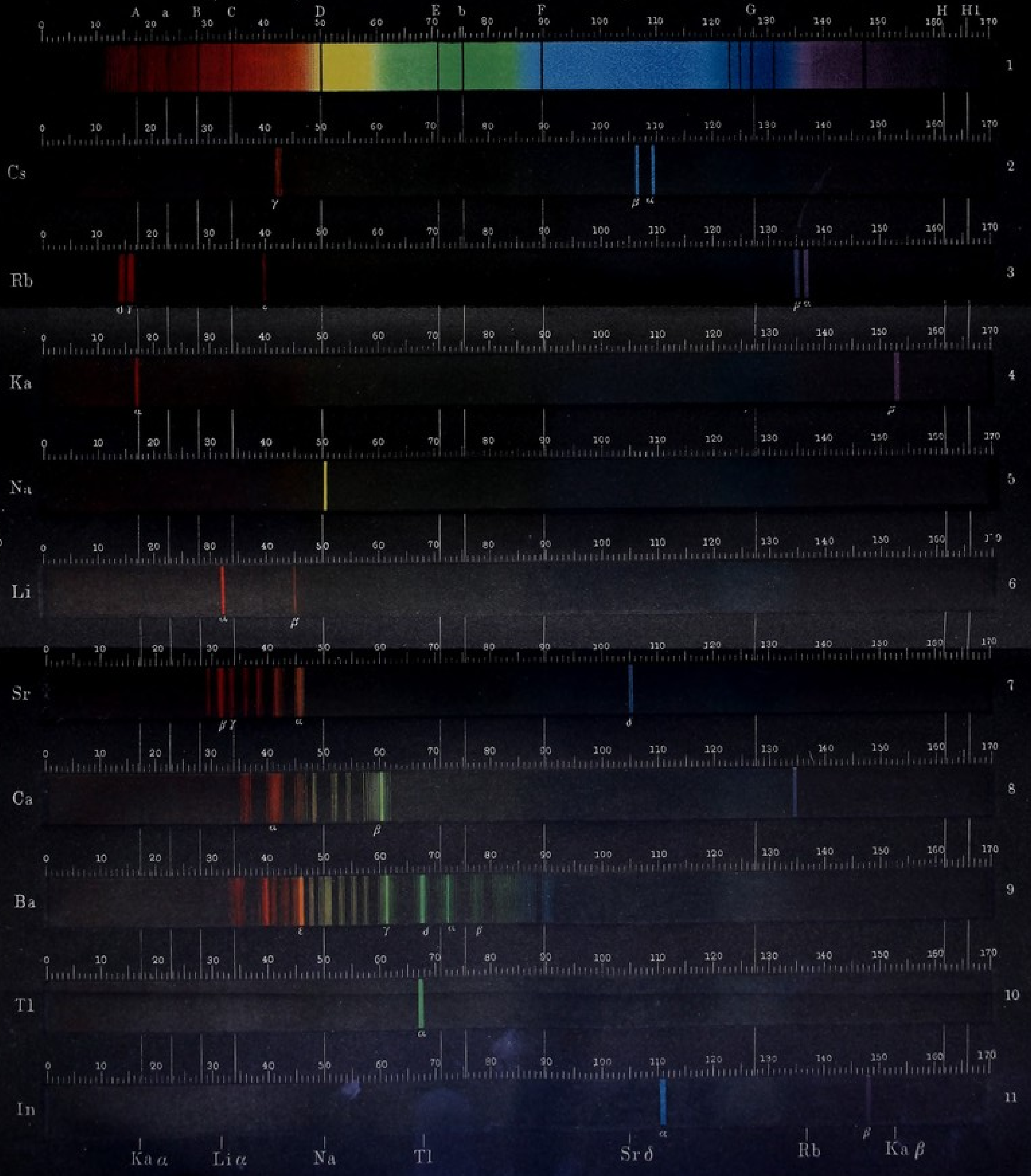


QUALITATIVE
CHEMICAL ANALYSIS

Fig. 2.


Sr
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170
β γ
α
δ

Fig. 1


A a B C D E b F G H H1
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170
1
Cs
γ
β α
2
Rb
δ γ
ε
β α
3
Ka
α
β
4
Na
5
Li
α
β
6
Sr
β γ
α
δ
7
Ca
α
β
8
Ba
ε
γ
δ
α
β
9
Tl
α
10
In
α
β
11
Ka α
Li α
Na
Tl
Sr δ
Rb
Ka β

QUALITATIVE
CHEMICAL ANALYSIS

BY

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Tenth Edition

TRANSLATED FROM THE FIFTEENTH GERMAN EDITION

AND EDITED BY

CHARLES E. GROVES, F.R.S.

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PREFACE TO THE TENTH ENGLISH EDITION.

In this translation of the Fifteenth German Edition of Fresenius's Qualitative Analysis, every care has been taken to adhere strictly to the original text; this contains many emendations and additions, especially in the concluding portions of the work devoted to the reactions of the alkaloïds and the systematic methods of detecting them; but although these portions have been practically re-written, the original plan of the work is retained.

The present English Edition has been almost entirely re-written, and various styles of type and other typographical improvements have been introduced, in the hope that the book might thereby be rendered more handy and useful to students. The Index also has been made as complete as possible.

In conclusion, I have to thank Mr. Arnold Philip, F.I.C., for the valuable assistance he has rendered me in translating much of the new matter.

CHARLES E. GROVES.

Guy's Hospital,
July, 1887.

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PART I.

QUALITATIVE CHEMICAL ANALYSIS.

PRELIMINARY.

PART I.

INTRODUCTORY.

PRELIMINARY REMARKS.

Definition, General Principles, Objects, Utility, and Importance of Qualitative Chemical Analysis—Conditions and Requirements for a successful Study of that Science.

Chemistry, as is well known, is the science which treats of the various materials of which the earth is formed, their composition and decomposition, and especially their mutual relations to one another. A special branch of this science is designated ANALYTICAL CHEMISTRY, inasmuch as it has a distinct and definite object, that is the analysis of compounds, and the determination of their component elements. Analytical chemistry, again, is subdivided into two branches, namely, QUALITATIVE ANALYSIS, which treats of the nature and properties of the component parts of various substances ; and QUANTITATIVE ANALYSIS, by which the amount of every individual constituent present is determined. The object of qualitative analysis, therefore, is to present the constituents of a substance of unknown composition in forms of known composition, from which definite conclusions may be drawn as to the constitution of the substance examined, and the presence of the several elements of which it is composed. The value of the method depends on two conditions, in the first place, it must attain the object in view with certainty, and secondly in the most expeditious manner possible. Quantitative analysis, on the other hand, exhibits the elements revealed by the qualitative investigation in forms which will permit of the accurate determination of their weight, or in some other way to ascertain the amount of them present.

Of course, the way in which these different ends are attained varies greatly. The study of qualitative analysis must, therefore, be pursued separately from that of quantitative analysis, and must naturally precede it.

Having thus generally defined the meaning and scope of qualitative analysis, we have to consider, in the first place, the preliminary information necessary to qualify a student for its successful cultivation, the rank which it holds in the domain of chemistry, and its utility and importance: and, in the second place, the substances that fall within the sphere of its operations, and the principal parts into which its study is divided.

For the successful pursuit of qualitative investigations, it is above all things indispensable that the student should have some knowledge of the chemical elements, and of their most important combinations, as well as of the general principles of chemistry; also that he should have some practice in the mechanism of chemical reactions. It demands moreover strict order, the greatest cleanliness, and a certain skill in manipulation. If in addition to these qualifications the student has the habit of invariably ascribing his failures to some defect in his operations, or rather, to the absence of some condition or other indispensable to the success of the experiment—and a firm belief in the immutability of natural laws cannot fail to create this habit—he will have all the qualities necessary to render his study of analytical chemistry successful.

Now, although chemical analysis is based on general chemistry, and cannot be cultivated without some previous knowledge of the latter, yet, on the other hand, we must regard it as one of the foundation stones upon which the entire structure of the science rests, since it is of almost equal importance for all branches of chemistry whether theoretical or practical. It is unnecessary to expatiate here on the advantages which the technical chemist, the physician, the pharmaceutist, the mineralogist, the metallurgist, the skilful farmer, and many others derive from it.

This consideration would surely in itself be sufficient to recommend a thorough and diligent study of analysis, even if its cultivation lacked those attractions which it unquestionably possesses for every one who devotes himself zealously and ardently to it. The human mind is constantly striving after truth; it delights in solving problems; and where do we meet with a greater variety of them, some easier, some more difficult to solve, than in the province of chemistry? But as a problem to which, after long pondering, we fail to discover the key, wearies and discourages the mind; so, in like manner, do chemical investigations, if the object in view is not attained—if the results do not bear the stamp of truth, of unerring certainty. A half-knowledge in every department of science, but more especially in this must be considered worse than no knowledge at all; so that a mere *superficial* acquaintance with chemical analysis must be particularly guarded against.

A qualitative investigation may be made with a twofold object, either to prove that a certain compound is or is not contained in a substance, for example, lime in spring-water; or to ascertain *all* the constituents present in a chemical compound or mixture. Any substance may of course become the object of a chemical analysis.

All elements, however, are not equally important in practical chemistry, a certain number only of them being found more widely disseminated in nature, and more generally employed in metallurgy, in pharmacy, in the arts and manufactures, and in agriculture, whilst the others are met with only as constituents of rarely occurring minerals. The elements of the former class, therefore, and the more important of their compounds, will alone be considered fully in the present work, whilst those of the latter class will be discussed more briefly and in such a manner as to enable the learner to separate, without difficulty, the study of the former from that of the latter. This arrangement will render the study of the science easier for beginners, and lighten the labours of practical chemists.

The study of qualitative analysis is most properly divided into four principal parts—viz.,

1. Chemical Operations.
2. Reagents and their uses.
3. Reactions, or behaviour of the various substances with reagents.
4. Systematic course of qualitative analysis.

It will now be readily understood that the pursuit of chemical analysis requires practical skill and ability as well as theoretical knowledge; so that a merely theoretical study of it can be as little expected to lead to success as purely empirical experiments. To attain the desired end, theory and practice must be combined.

SECTION I.

OPERATIONS.

§ 1.

The operations of analytical chemistry are essentially the same as those of synthetical chemistry, although modified to a certain extent in order to adapt them to the different object in view, and to the small quantities operated on in analytical investigations.

The following are the principal operations in qualitative analysis.

§ 2.

1. Solution.

The term solution, in its broadest sense, denotes the perfect union of a substance whether gaseous, liquid, or solid, with a fluid yielding a homogeneous liquid. If the substance dissolved is gaseous, the term absorption is generally employed; whilst if it is liquid it is called a mixture. The application of the term solution, in its usual and more restricted sense, is confined to the perfect union of a solid with a liquid.

The more minutely the substance to be dissolved is divided, the more readily is solution effected. The liquid by means of which the solution is effected, is called the solvent, and if the solvent enters into chemical combination with the substance dissolved we call the solution *chemical*; if no definite combination takes place, it is said to be *simple*.

In a simple solution, the dissolved substance exists in the free state, and retains all its original properties, except those dependent on its form and cohesion; when the solvent is withdrawn it separates unaltered. Common salt dissolved in water is a familiar instance of a simple solution. The salt in this case imparts its peculiar taste to the liquid, and on evaporating the water, the salt is left behind in its original form. A simple solution is said to be *saturated* if the solvent has taken up as much as it can retain of the dissolved substance. But as liquids generally dissolve larger quantities of a substance the higher their temperature, the term saturated, as applied to simple solutions, is only relative, and refers invariably to a certain temperature. It may be laid down as a general rule that elevation of temperature facilitates and accelerates simple solution.

A chemical solution contains the dissolved substance in a different state and with different properties from what it had before; it is no longer free, but intimately combined with the solvent which has also lost its original properties; a new substance has thus been produced, and the solution therefore has now the properties of this new substance. Chemical dissolution* also may be accelerated by elevation of temperature; this indeed is usually the case, since heat generally promotes the action of substances on one another, but the amount of substance dissolved always remains the same in proportion to the solvent, whatever may be the difference of temperature—the combining proportions of substances being invariably and altogether independent of the temperature. The reason of this is, that in a chemical solution the solvent and the substance on which it acts have invariably opposite properties, which they strive mutually to neutralize; when this tendency of mutual neutralization is satisfied, dissolution ceases. The solution is in this case also said to be saturated or, rather, *neutralized*, and the point which denotes it to be so is termed the point of saturation or neutralization.

The substances which produce chemical solutions are, in most cases, either acids or alkalies. With few exceptions, they must first be reduced to the liquid form by means of a simple solvent. When the opposite properties of acid and base are mutually neutralized, and the new compound is formed, the actual transition to the liquid state will ensue only if the new compound has the property of forming a simple solution with the liquid present; for example, if solution of acetic acid in water is brought into contact with oxide of lead, there ensues, first, a chemical combination of the acid with the oxide, and then a simple solution of the newly-formed acetate of lead in the water present.

In chemical laboratories, solutions are usually made by digesting or heating the substance to be dissolved along with the liquid in a beaker, flask, test-tube, or dish. In preparing chemical solutions, the best way generally is to mix the substance to be dissolved in the first place with water (or with whatever other indifferent liquid may happen to be used), and then gradually to add the chemical agent. In this way, a large excess of the latter is avoided, the action is not too violent, and dissolution takes place readily and completely. It sometimes happens in chemical combinations that the product formed does not dissolve if an excess of the chemical solvent is present; in this case the particles of the new salt first formed, being soluble in the menstruum present, surround the portion still unacted on, thereby weakening or altogether preventing further action. Thus, for instance, witherite (carbonate of baryta) dissolves readily if water is poured on to the pulverized mineral and hydrochloric acid is added gradually; but on the contrary it dissolves with difficulty and imperfectly if it is projected into a concentrated solution of hydrochloric acid in water; since chloride of barium, although it dissolves readily in water, does not do so in hydrochloric acid.

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* The word *solution* is commonly used to signify both the act of dissolving, and the liquid obtained by that process. It seems advisable to restrict the use of the word solution to the latter and to employ *dissolution* for the act of dissolving [Editor].

Crystallization and Precipitation are usually the reverse of solution, as they have for their object the conversion of a liquid or dissolved substance to the solid state. As both depend generally on the same cause, namely, the want of a solvent, it is impossible to assign exactly the limit to either; in many cases, they merge into one another. Here, however, we must consider them separately, as they differ essentially in their extreme forms, and as the special objects which we purpose to attain by their application are generally very different.

§ 3.

2. Crystallization.

We understand generally by the term crystallization, any process whereby compounds assume fixed, mathematically definable, regular forms. But as the forms, which we call crystals, are more regular, and consequently more perfect, the more slowly the operation is carried on, the term crystallization is always connected with the accessory idea of a slow separation—of a gradual conversion to the solid state. The formation of crystals depends on the regular arrangement of the ultimate particles of compounds, and can only take place when these particles possess perfect freedom of motion, and therefore, as a rule, only when a substance passes from the liquid or gaseous to the solid state. Those instances in which the mere ignition, or the softening or moistening of a solid substance is sufficient to allow of such a regular arrangement of the ultimate particles (crystallization), are to be regarded as exceptions —such, for example, as when moistened barley-sugar turns white and opaque.

To induce crystallization, the agent which causes a substance to assume the liquid or gaseous form must be removed. These are either *heat*, as in the case of fused metals; or *solvents*, as in the case of an aqueous solution of common salt; or *both combined*, as in the case of a hot saturated solution of nitrate of potassa in water. In the first case, we obtain crystals by cooling; in the second by evaporation; and in the third by either of these means. The most frequently occurring case is that of crystallization by cooling hot saturated solutions. The liquid which remains after the separation of crystals is called the mother-liquor. The term amorphous is applied to such solid substances as have no crystalline form.

We usually have recourse to crystallization either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same solvent. In many cases also, the form of the crystals, their optical properties or their behaviour on exposure to the air—that is, whether they remain unaltered or effloresce or deliquesce —will afford an excellent means of distinguishing between compounds otherwise closely resembling each other; for instance, between sulphate of soda and sulphate of potassa. Crystallization is usually effected in evaporating dishes, or, for very small quantities, in watch-glasses.

When the quantity of liquid to be operated on is but small, the surest way of getting well-formed crystals is to let the solution evaporate in the air, or, better still, under a bell-glass, under which is also placed an open vessel half-filled with concentrated sulphuric acid. Minute crystals are examined best with a lens, or under the microscope.

§ 4.

3. Precipitation.

This operation differs from the preceding in that the substance dissolved assumes the solid state, not slowly and gradually, but suddenly, and that whether the precipitate is crystalline or amorphous, whether it sinks to the bottom of the vessel or ascends, or remains suspended in the liquid. Precipitation is either caused by some change in the solvent —thus on adding alcohol to a solution of sulphate of lime in water, it separates immediately; or it takes place in consequence of the separation of an insoluble substance formed by simple or double decomposition —thus metallic copper is precipitated if zinc is immersed in a solution of chloride of copper; and when oxalic acid is added to a solution of acetate of lime, oxalate of lime is precipitated; and chromate of lead is thrown down if chromate of potassa in solution is mixed with solution of nitrate of lead. In decompositions of this kind, induced by simple or double affinity, one of the new compounds generally remains in solution, like the chloride of zinc, the acetic acid, and the nitrate of potassa in the instances just mentioned. It may, however, happen also that both the products are precipitated, and nothing remains in solution; as, for instance, when a solution of sulphate of magnesia is mixed with baryta water, or when a solution of sulphate of silver is precipitated with chloride of barium.

The object of precipitation is either, as with crystallization, to obtain a substance in the solid form, or to separate it from other substances dissolved in the same menstruum. But in qualitative analysis, we have recourse to this operation more particularly for the purpose of detecting and distinguishing substances by the colour, and especially by the properties and general behaviour which they exhibit when precipitated either in an isolated state, or in combination with other substances. The solid separated by this process is called the precipitate, and the substance which acts as the immediate cause of the separation is termed the precipitant. Various terms are applied to distinguish precipitates of different nature; thus we speak of crystalline, pulverulent, flocculent, curdy, gelatinous precipitates, &c. Precipitates which appear pulverulent to the naked eye, will often be seen to consist entirely of regular crystals when examined under the microscope; precipitates of this kind may frequently be distinguished from each other in this way.

The terms turbid and turbidity, or cloudy and cloudiness, are made use of to designate the state of a liquid which contains a precipitate so finely divided and so small in amount, that the suspended particles, although impairing the transparency of the fluid, yet cannot be clearly distinguished. The separation of flocculent precipitates may generally be promoted by vigorous agitation; that of crystalline precipitates, by stirring the solution, and rubbing the inside of the vessel with a glass rod; lastly, the separation of most precipitates is promoted by warming the solution. According to circumstances, precipitation is conducted either in test-tubes, flasks, beakers, or dishes.

The two operations described in §§ 5 and 6, namely, Filtration and Decantation, serve to effect the mechanical separation of liquids from suspended matter.

§ 5.

4. Filtration.

This operation consists in passing the liquid from which we wish to remove the solid particles mechanically suspended therein through a filtering apparatus, usually formed of a circular piece of unsized paper, called a filter, properly folded and placed in a funnel. An apparatus of this description allows the liquid to trickle through with ease, but completely retains the solid particles. Both smooth filters and plaited filters are employed; the former when the separated solid substance is required, the latter—which is more expeditious—when the filtrate (the clear solution which passes through) only is wanted. To make a plaited filter, is more easily shown than described. Smooth filters are prepared by double-folding a circular piece of paper, with the folds at right angles; they must fit close to the funnel in every part. In cases where the contents of the filter have to be washed, the paper must not project above the edge of the funnel. It is in most cases advisable to moisten the filter before passing the solution through it, for this not only tends to accelerate the process, but also prevents the solid particles from being carried through the pores of the filter. The paper selected for filters must be as free as possible from inorganic matter, especially such as is dissolved by acids, like sesquioxide of iron and lime. The common filtering paper of commerce is seldom equal to our requirements in this respect, and it is better therefore always to wash it with acid and water whenever it is intended to use it in *accurate analyses;* for this purpose, the apparatus shown in fig. 1 will be found convenient. A is a bottle with the bottom out, *a* and *b* are glass plates, between which lie the filters previously cut and folded, *d* is a glass tube fitted into the cork *c*, and *e* is a piece of flexible tube, which is closed by a clip or a piece of glass rod. The vessel is filled with a mixture of one part of hydrochloric acid, sp. gr. 1·12, and two of water, in which the filters are allowed to soak twelve hours, the acid being then run off and replaced by common water. After an hour, this is replaced by fresh water, and so on until the washings are barely acid. The washing is then continued with distilled water until the washings are free from hydrochloric acid—that is, until they no longer become turbid when mixed with a few drops of

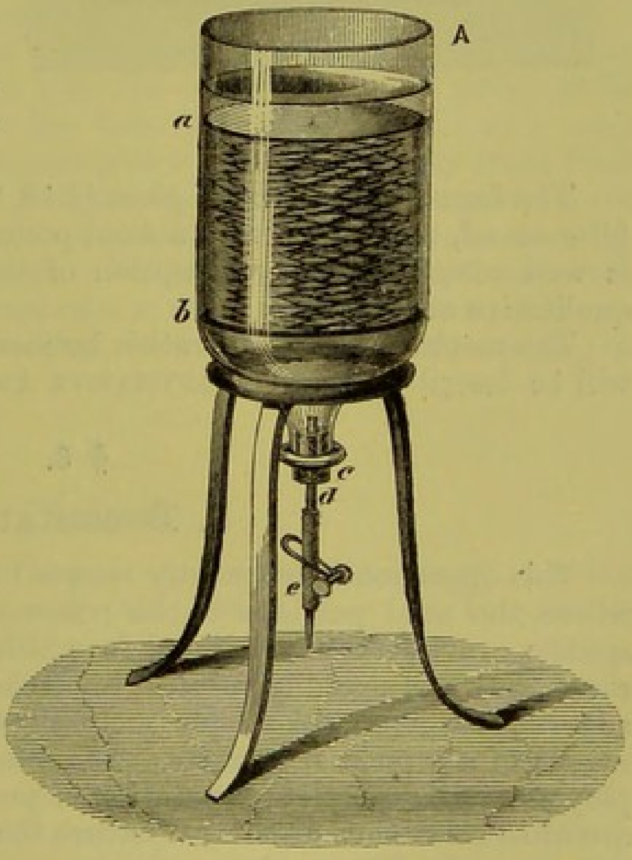

Fig. 1.

solution of nitrate of silver. Finally, the filters are drained, turned out on to blotting paper, covered with the same, and dried in a sieve in a warm place. When two or three filters only have to be washed, they are placed in a funnel, as in filtering, one inside the other, moistened with dilute hydrochloric or nitric acid, and after some time well washed with distilled water. If filtering paper is good, it must, besides being pure, allow liquids to pass through readily, and yet completely retain even the finest precipitates, such as sulphate of baryta, oxalate of lime, &c. Where a paper satisfying these requirements cannot be readily procured it is advisable to keep two sorts, one of closer texture, for the separation of very finely divided precipitates, and another more porous for the speedy separation of coarser particles.

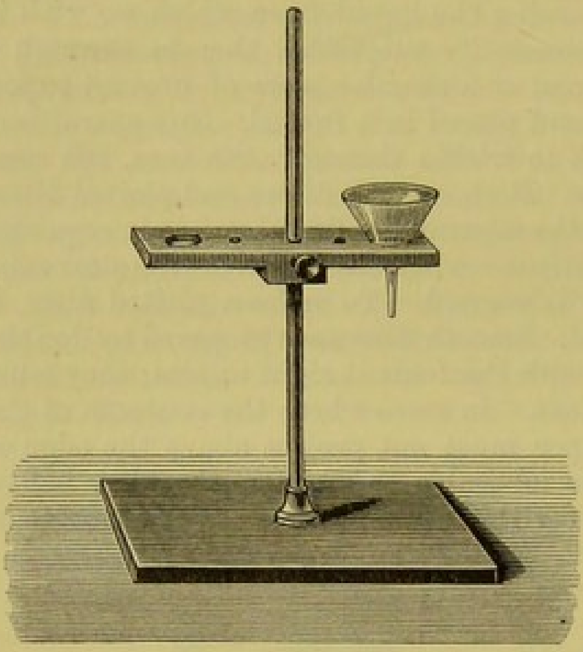

Fig. 2.

The funnels should be of glass (§ 18, 9); they are usually placed on a filter-stand, to keep them in a fixed position. The stand shown in fig. 2 is well adapted for the reception of the small-sized funnels used in qualitative analyses.

The method of rapid filtration by means of an exhausting apparatus will be described in the Quantitative Analysis.

§ 6.

5. Decantation.

This operation is frequently resorted to instead of filtration, in cases where the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended; in such cases they will speedily subside, rendering it easy either to decant the supernatant liquid by simply inclining the vessel, or to draw it off by means of a syphon or pipette. Decantation has frequently to be employed for the complete separation of precipitates, especially when they are of so gelatinous or slimy a nature that they would immediately stop the pores of a filter, and prevent the passage of the liquid. Occasionally, decantation and filtration are combined by allowing the precipitate to settle, and then pouring off the supernatant liquid on to a filter so as to render it quite clear.

§ 7.

6. Washing.

In cases where filtration or decantation is resorted to for the purpose of obtaining the solid substance, the latter has to be freed from the adhering liquid by repeated *washing*. Precipitates collected on a filter are usually washed by means of the wash-bottle (fig. 3).

The drawing scarcely needs explanation. The outer end of the tube *a* is drawn out to a fine point. If it is desired to have a movable jet, the short tube is divided at *a* and the two parts connected by means of a piece of caoutchouc tubing. By blowing air into the flask through the other tube, a fine jet of water is expelled through *a*, with a certain degree of force, which is particularly well suited for washing precipitates. Wash-bottles of this construction have also the advantage that they can be used equally well with hot water. For this purpose, they are either furnished with a handle, or some cork is bound round the neck. The best way of washing by decantation is, after the supernatant liquid has been poured off, to stir up the precipitate with water or whatever liquid may be used for the washing, allow it to settle, pour off again, and so on.

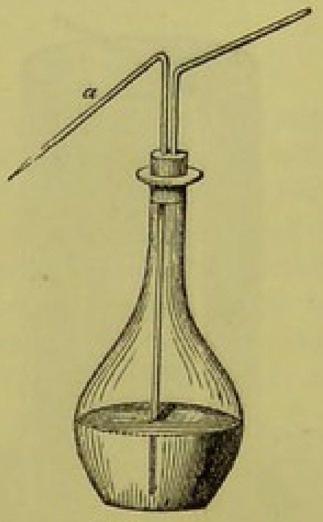

Fig. 3.

As the success of an analytical operation often depends absolutely on the proper washing of a precipitate, it may be as well to mention at once that the operation ought never to be considered complete until this has been actually attained; as a rule, this is the case only when the precipitate has been entirely freed from the adhering solution. The operator should, in this respect, never trust to mere belief or guessing, but should always make quite sure by properly testing the last washings. With non-volatile substances, it is generally enough to slowly evaporate a drop of the last washings on platinum-foil; if there is no residue, it will show that the washing is completed.

§ 8.

7. Dialysis.

Dialysis is an operation which is occasionally employed for the separation of substances from each other when they are in solution together; at first sight it appears to have some resemblance to filtration, but in reality it differs essentially from it. This operation was introduced to the scientific world by Graham,[*] and depends on the difference in the behaviour of different substances dissolved in water towards moist membranes. A certain class of compounds, the crystalloïds, have the power of penetrating suitable membranes with which their solution may be placed in contact; whilst another class, the colloïds, do not possess that property. Hence the two classes may be separated by means of dialysis. To the class of crystalloïds belong all crystallizable substances; to the colloïds all non-crystallizable substances, as gelatin, gum, dextrin, caramel, tannin, albumin, extractive matters, hydrated silicic acid, &c. The septum must consist of a colloïd material, such as an animal membrane, or, better still, parchment paper or gold-beater's skin, and it must on the other side be in contact with water. Graham

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[*] Phil. Mag. Fourth Series, Nos. 153–155; also Ann. Chem. Pharm. **121**, 12.

explains the action on the assumption that the crystalloïds appropriate to themselves the water absorbed by the colloïd septum, acquiring thereby a medium for diffusion, whilst the dissolved colloïds are unable to separate the water from the septum, and fail therefore to penetrate the latter. Figs. 4 and 5 exhibit suitable forms of apparatus for this operation. In fig. 4, the dialyser consists of the top of a bottle closed below with parchment paper; in fig. 5, it consists of a hoop covered with parchment paper so as to resemble a sieve. The hoop may be of wood, or better of gutta-percha. The disc of parchment paper used should measure three or four inches in diameter more than the space to be covered; it is moistened, stretched over and fastened by a string or by an elastic band, but it should not be secured too firmly. The parchment paper must not be porous; its soundness may be tested by sponging the upper side with water, and observing whether wet spots show on the other side. Defects may be remedied by applying liquid albumin and coagulating this by heat. When the dialyser has thus been prepared, the substance to be examined is poured into it. If the mass is quite liquid, the apparatus fig. 4 may be used, but if it contains undissolved solid matter, the hoop is to be preferred. The depth of liquid in the dialyser should not be more than half an inch, and the membrane should dip a little way below the surface of the water in the outer vessel, which should be at least four times the bulk of the liquid to be dialysed. The dialyser in fig. 4 is suspended in the manner indicated—the hoop is simply floated on the water. After twenty-four hours, half or three-fourths of the crystalloïds will be found in the external water, while the colloïds remain in the dialyser—at most only traces pass into the external liquid. If the dialyser is brought successively in contact with fresh supplies of water, the whole of the crystalloïds may be finally separated from the colloïds. This operation is often of considerable service in chemico-legal investigations for the extraction of poisonous crystalloïds from parts of a dead body, food, vomit, &c.

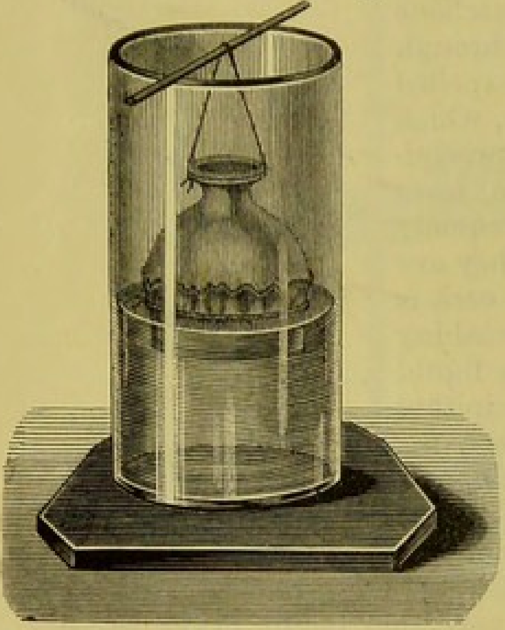

Fig. 4.

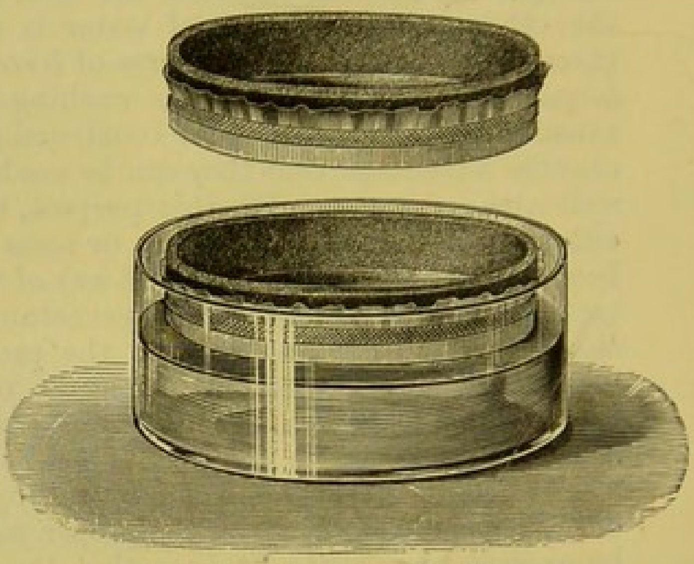

Fig. 5.

There are four operations which serve to separate volatile from less volatile or non-volatile substances—namely, Evaporation, Distillation, Ignition, and Sublimation. The two former refer exclusively to liquids, the two latter exclusively to solids.

§ 9.

8. Evaporation.

This is one of the most common operations in analytical chemistry, and is employed to separate volatile liquids from less volatile or non-volatile substances (no matter whether solid or liquid), in cases where the residue alone is of importance, whilst the substance volatilized is entirely disregarded;—thus, for instance, we have recourse to evaporation if we want to remove from a saline solution part of the water, so as to bring about crystallization of the salt; or if we wish to obtain a non-crystallizable substance in a solid form, by the removal of the whole of the water from the solution. The evaporated water is entirely disregarded in both cases, the only object being to obtain, in the one case a more concentrated solution, and in the other the dry substance. Evaporation is invariably attained by converting into vapour the liquid which is to be removed, generally by the application of heat; sometimes, however, by leaving the solution freely exposed to the air for a time, or in contact with an enclosed volume of air kept dry by hygroscopic substances, such as concentrated sulphuric acid, chloride of calcium, &c.; or, lastly, in many cases, by placing the solution in air, under diminished pressure, along with hygroscopic substances. As it is of the greatest importance in qualitative analysis to guard against the slightest contamination, and as there is the greater chance of this the longer the operation lasts, it is usual to evaporate the solution as quickly as possible, in porcelain or platinum dishes, over the flame of a spirit or gas-lamp, in a separate place free from dust, preferably in a cupboard provided with a draught. If there is no place of the kind, recourse must be had to the much less suitable proceeding of covering the dish; the best way of doing this is to suspend over the dish a large glass funnel by means of a retort-holder, so as to leave sufficient space between the rim of the funnel and the border of the dish; the funnel is placed slightly aslant, that the drops running down its sides may be received in a beaker. Or the dish may be covered with a sheet of filter-paper previously freed from inorganic substances by washing with dilute hydrochloric or nitric acid (see p. 7); were common and unwashed filter-paper used for the purpose, the sesquioxide of iron, lime, &c., contained in it would dissolve in the vapours evolved (more especially if acid), and

Fig. 6.

the solution dripping down into the evaporating liquid would speedily contaminate it. These precautions are necessary of course only in accurate analyses. Large quantities of liquid are evaporated best over a charcoal fire or gas-flame, in flasks standing aslant, and covered with a cap of purified filter-paper, or in tubulated retorts with the neck inclined obliquely upwards, and the tubulure open. Evaporation at 100° is conducted in a suitable steam apparatus, or in the water-bath shown in fig. 6, on which porcelain or copper rings may be laid if the dish is small. Evaporation to dryness is not usually conducted over the naked flame, but generally either on the water-bath, or the sand-bath, or on an iron plate.

There is a circumstance connected with the subject which should be noted here; namely, that porcelain and glass vessels—which we can hardly avoid using for the evaporation of large quantities of liquid—are slightly attacked, and in this way their contents become more or less contaminated; this is a source of great trouble in delicate work. It will be more fully discussed in the Quantitative Analysis, but it may be noted here that alkaline liquids should never be evaporated in glass vessels, as these are attacked considerably at a boiling temperature.

§ 10.

9. Distillation.

This operation serves to separate a volatile liquid from a less volatile or a non-volatile substance (no matter whether solid or liquid) where the object is to recover the volatile liquid. For this purpose, it is necessary to convert the volatilized solvent to the liquid state again. A distilling apparatus consists consequently of three parts, whether they are separable or not. These are; first, a vessel in which the liquid to be distilled is heated, and thereby converted into vapour; secondly, an apparatus in which this vapour is cooled again or condensed, and thus reconverted to the liquid state; and thirdly, a receiver or vessel to receive the liquid thus reproduced by the condensation of the vapour (the distillate). For the distillation of large quantities of liquid metallic apparatus are used (copper stills with head and condenser of tin), or large glass retorts; in analytical investigations we either use small retorts with receivers, or more usually an apparatus such as that shown in fig. 7. The liquid to be distilled is boiled in A, and the vapour escapes through

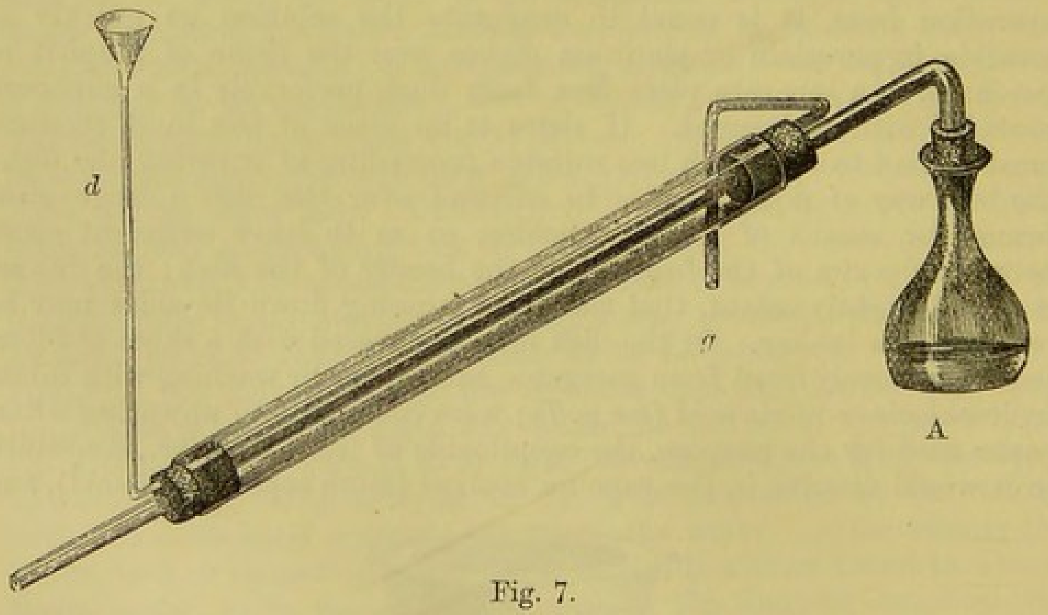

Fig. 7.

the tube which is fitted into the cork; this tube is surrounded with a wider tube which is filled with cold water. In proportion as the water cools the inner tube, it becomes heated itself, and requires to be renewed either continuously or occasionally, which is done by pouring cold water in through *d*, after placing a vessel under *g* to catch the hot water which will run out. A small flask serves as a receiver.

§ 11.

10. Ignition.

Ignition, to a certain extent, has the same relation to solids that evaporation has to liquids; since it serves, at least generally, to separate volatile from less volatile or non-volatile substances in cases where the residue alone is of importance. The process of ignition always presupposes the application of a high temperature, in which respect it differs from drying. The form or state which the eliminated substance assumes on cooling—whether it remains gaseous, as in the ignition of carbonate of lime; or assumes the liquid state, as in the ignition of hydrate of lime; or solidifies, as in the ignition of a mixture containing chloride of ammonium—is a matter of perfect indifference as regards the name given to the operation.

The process of ignition is mostly employed, as has just been said, to effect the elimination of a volatile compound. In some instances, however, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place; thus sesquioxide of chromium is converted by ignition into the so-called insoluble modification, &c. In analytical investigations, substances under examination are often ignited, that the operator may draw some conclusion as to their nature from their behaviour at a red heat, such as their fixity, their fusibility, the presence or absence of organic matter, &c.

Crucibles are the vessels generally made use of in ignition. In operations on a large scale, Hessian or black-lead crucibles are used, heated by charcoal or gas; in analytical experiments, small-sized crucibles or dishes of porcelain, platinum, silver, or iron are chosen, or glass tubes sealed at one end, according to the nature of the substance to be ignited; these crucibles, dishes, or tubes are heated over a Berzelius spirit-lamp, or a gas-lamp, or a bellows blowpipe.

§ 12.

11. Sublimation.

If a solid substance is converted into vapour by the application of heat, and subsequently recondenses to a solid on cooling, the process is termed sublimation, and the substance volatilized and recondensed is called a sublimate. Sublimation may be defined, therefore, as the distillation of solid substances, and is used mostly to effect the separation of compounds which have different degrees of volatility. It is of the greatest importance in analysis for the detection of certain substances, such as arsenic. The vessels used in sublimation are of various shapes, according to the degree of volatility of the substance operated on. In sublimations for analytical purposes, glass tubes closed at one end are generally employed. When the sublimation is performed with the aid of a current of hydrogen or carbonic acid, open glass tubes are used; these are usually made narrower just behind the part to which the heat is applied.

§ 13.

12. Fusion.

Fusion is the conversion of a solid substance to the liquid state by the application of heat; it is most frequently used to effect combination or decomposition. The term is also applied in cases where substances insoluble or sparingly soluble in water and acids, are by fusion along with some other compound modified or decomposed in such a manner that they or the new-formed compounds will subsequently dissolve in water or acids. Fusion is conducted either in porcelain, silver, or platinum crucibles, according to the nature of the compound. The crucible is supported on a triangle of moderately stout platinum wire, resting on, or attached to, the iron ring of the Berzelius spirit-lamp or the gas-lamp. Triangles of thick iron wire, especially when laid upon the stouter brass ring of the lamp, carry off too much heat to allow of the production of very high temperatures. Small quantities of substance are also often fused in glass tubes sealed at one end.

Resort to fusion is especially required for the analysis of the sulphates of the alkaline earths, and also for that of many silicates and alumina compounds. The flux most commonly used is carbonate of soda or carbonate of potassa, or, better still, a mixture of both in equal atomic proportions (see § 76). In certain cases, hydrate of baryta is used instead of the alkaline carbonates.

For the fusion of aluminates, bisulphate of potassa or bisulphate of soda is frequently used.

A platinum crucible is used for the fusion, whether alkaline carbonates, hydrate of baryta, or alkaline bisulphates are employed.

It is as well to mention here a few necessary precautions for the prevention of damage to the platinum vessels used in these operations. No substance evolving chlorine ought to be treated in platinum vessels; nitrates of the alkalies, hydrate of potassa and soda, metals, or sulphides of metals or cyanides of the alkali metals must not be fused in such vessels; neither should readily deoxidizable metallic oxides, nor salts of the heavy metals with organic acids be ignited in them, nor phosphates in presence of organic compounds. It is also detrimental to platinum crucibles, and especially to their covers, to expose them to the direct action of intense charcoal fire, as the ash of the charcoal is likely to give rise to the formation of silicide of platinum, which renders the vessel brittle. It is always advisable to support platinum crucibles used in ignition or fusion on triangles of platinum wire. When a platinum crucible has been made white hot over the bellows blowpipe, it is unwise to cool it too quickly by suddenly turning off the gas, and allowing the cold blast to play upon it, since the crucible is under these circumstances very liable to become slightly cracked. Platinum crucibles are cleaned by rubbing with wet sea-sand, the round grains of which do not scratch the metal. Where this fails to remove the stains, the desired object may be attained by fusing bisulphate of potassa or borax in the crucible, boiling subsequently with water, and finally polishing with sea-sand.

We have still to speak here of another operation which bears some affinity to fusion, namely—

§ 14.

13. Deflagration.

By deflagration, in the widest sense, is meant every process of decomposition attended with noise or detonation—the cause of the decomposition being a matter of perfect indifference as regards the application of the term in this sense. The same term, however, is used, in a more restricted sense, to designate the oxidation of a substance in the dry way, at the expense of the oxygen of another substance mixed with it (usually a nitrate or a chlorate), and is connected with the idea of a sudden and violent combustion attended with vivid incandescence and noise or detonation.

Deflagration is resorted to either to produce the desired oxide—thus sulphide of arsenic is deflagrated with nitrate of potassa to obtain arsenate of potassa; or it is applied as a means to prove the presence or absence of a certain substance—thus salts are tested for nitric or chloric acid by fusing them with cyanide of potassium, and observing whether they deflagrate, &c. For the first, the perfectly dry mixture of the substance with the deflagrating agent is projected in small portions at a time into a red-hot crucible. Experiments of the latter description should invariably be made with minute quantities, preferably on a piece of thin platinum foil, or in a small spoon.

§ 15.

14. Use of the Blowpipe.

This operation belongs exclusively to analytical chemistry, and is of paramount importance in many analytical processes. We have to consider the apparatus required, the way it is applied, and the results obtained.

The blowpipe fig. 8 is a small instrument, usually made of brass or German silver. It was originally used for soldering, whence it derived the name of *soldering pipe* (*Löthrohr*), by which the Germans designate it. It consists of three distinct parts; viz., 1st, a tube *a b*, fitted, for greater convenience, with a horn or ivory mouthpiece, through which air is blown from the mouth; 2nd, a small cylindrical vessel *c d*, into which *a b* is screwed air-tight, and which serves as an air-chamber and to retain the moisture of the breath; and 3rd, a smaller tube *f g*, also fitted into *c d*. This small tube, which is at right angles with the larger one, is furnished at its aperture either simply with a finely perforated platinum plate, or more conveniently with a finely perforated platinum nozzle, *h*. The construction of this nozzle is shown in fig. 9. It costs a little more than a simple plate, but it is much more durable. If the opening of the nozzle gets stopped up, the obstruction may generally be removed by heating it to redness before the blowpipe.

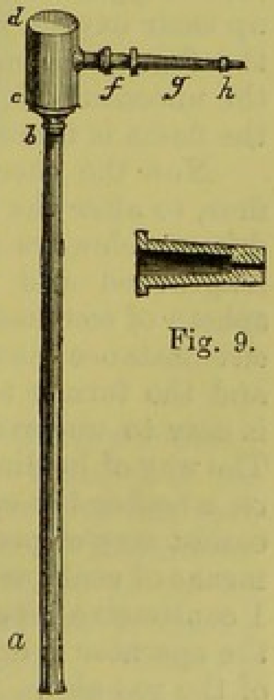

Fig. 8.

Fig. 9.

The proper length of the blowpipe depends on the distance to which the operator can see with distinctness; it is usually from 20 to 25 centimetres. The form of the mouthpiece varies. Some chemists like it of a shape to be encircled by the lips; others prefer a trumpet-shaped mouthpiece, which is only pressed against the lips. The latter requires less exertion on the part of the operator, and is, therefore, generally chosen by those who have a great deal of blowpipe work to do.

The blowpipe serves to conduct a continuous slender current of air into a gas-flame, or into the flame of a candle or lamp, or sometimes into a spirit-of-wine flame. The flame of a candle (and also that of gas or of an oil lamp), burning under ordinary circumstances, consists of three distinct parts, as shown in fig. 10, viz., 1st, a dark nucleus in the centre, *a*; 2nd, a luminous cone, *e f g*, surrounding this nucleus; and, 3rd, a feebly luminous mantle, *b c d*, encircling the whole flame. The dark nucleus is formed by the gases which the heat evolves from the wax or fat, and which cannot burn here for want of oxygen. In the luminous cone, these gases come in contact with a certain amount of air insufficient for their complete combustion; in this part, therefore, it is principally the hydrogen of the hydrocarbon product which burns, whilst the carbon separates in a state of intense ignition, and imparts to the flame the luminous appearance observed in this part. In the outer coat, the access of air is no longer limited, and all the matter not yet burned is consumed here. This part of the flame is the hottest, and the extreme apex is the hottest point of it. Oxidizable bodies oxidize therefore with the greatest possible rapidity when placed in it, since all the conditions of oxidation are here united, that is, high temperature and an unlimited supply of oxygen. This outer part of the flame is therefore called the *oxidizing flame*. On the other hand, oxides having a tendency to yield up their oxygen are reduced when placed within the luminous part of the flame, the oxygen being withdrawn from them by the carbon and the unconsumed hydrocarbons there present. The luminous part of the flame is therefore called the *reducing flame*.

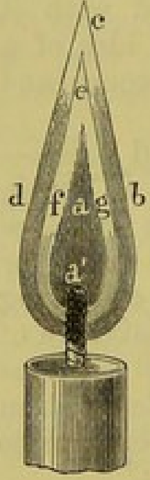

Fig. 10.

Now the effect of blowing a thin stream of air across a flame is, first, to alter the shape of the flame, as, from tending upward, it is now driven sideways in the direction of the blast, being at the same time lengthened and narrowed; and, in the second place, to extend the sphere of combustion from the outer to the inner part. As the latter circumstance causes an extraordinary increase in the heat of the flame, and the former a concentration of that heat within narrower limits, it is easy to understand the very energetic action of the blowpipe flame. The way of holding the blowpipe and the nature of the blast will depend on whether the operator wants a reducing or an oxidizing flame. The easiest way of producing the most efficient flames of both kinds is by means of coal-gas delivered from a jet, shaped as in fig. 11, the slit being 1 centimetre long and 1½ to 2 millimetres wide; as with the use of gas the operator is enabled to regulate not only the current of air, but that of the gas also. The task of keeping the blowpipe steadily in the proper position may be greatly facilitated by firmly resting it upon some moveable metallic support, such, for instance, as the ring of the Bunsen gas-lamp intended for supporting dishes, &c.

Fig. 11 shows the flame for reducing, fig. 12 the flame for oxidizing.

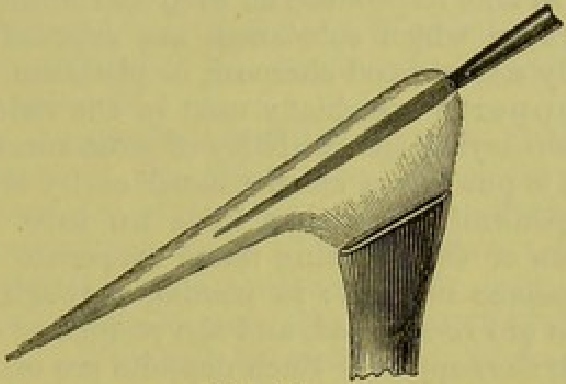

Fig. 11.

The reducing flame is produced by keeping the jet of the blowpipe just on the border of a tolerably strong gas flame, and driving a moderate blast across it. The resulting mixture of the air with the gas is only imperfect, and there remains between the inner bluish part of the flame and the outer barely visible part a luminous and reducing zone, of which the hottest point lies somewhat beyond the apex of the inner cone.

To produce the oxidizing flame, the gas is lowered somewhat, the jet of the blowpipe pushed a little further into the flame, and the strength of the blast somewhat increased. This effects an intimate mixture of the air and gas, and an inner, pointed, bluish cone, slightly luminous towards the apex, is formed, and surrounded by a thin, pointed, pale-blue, barely visible mantle. The hottest part of the flame is at the apex of the inner cone. Difficultly fusible substances must be exposed to this part of the flame to effect their fusion; but those which have to be oxidized are held a little beyond the apex, that there may be no want of air for their combustion. An oil-lamp with broad wick of proper thickness may be used instead of gas; a thick wax-candle also will do. When an oxidizing flame is required, a small spirit-lamp will in most cases answer the purpose.

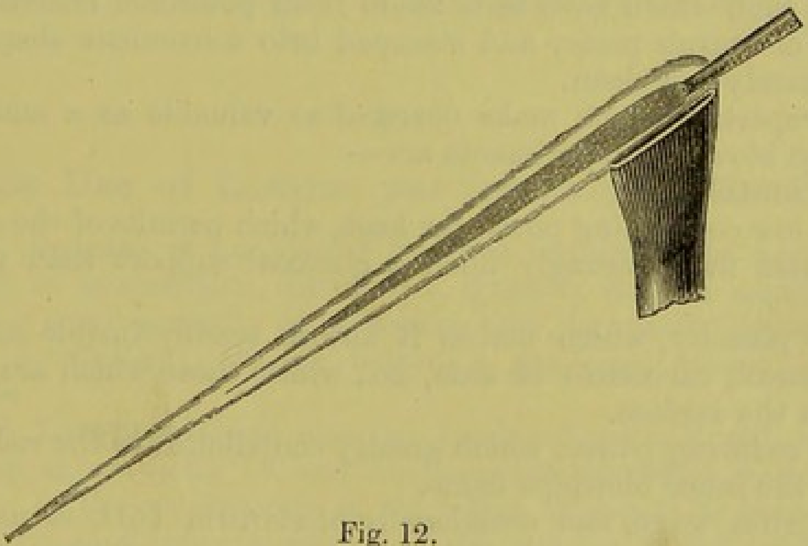

Fig. 12.

The blast is produced with the muscles of the cheek alone, and not with the lungs. The way of doing this may be easily acquired by practising for some time to breathe quietly with distended cheeks and with the blowpipe between the lips; with practice and patience, the student will soon be able to produce an even and uninterrupted current.

The supports on which substances are exposed to the blowpipe flame are generally either wood charcoal, or platinum wire or foil.

Charcoal supports are chiefly used in the reduction of metallic oxides, &c., or when trying the fusibility of substances. The substance to be operated on is put into a small conical cavity scooped out of the charcoal with a penknife or with a little tin tube. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part as their oxides become reduced: in passing through the outer flame, the metallic fumes are re-oxidized, and the re-formed oxide is deposited around that left on the support. Such deposits are called incrustations; and as many of these exhibit characteristic colours, they serve for the detection of the metals. None but thoroughly-burnt pieces of charcoal should be used, otherwise they are apt to decrepitate and throw off the substance. The charcoal from the pine, linden, or willow is far preferable to that of harder woods, or such as are richer in ash. Smooth pieces ought to be selected, as knotty pieces are apt to decrepitate when heated and throw off the substance. The most convenient way is to saw the charcoal of well-seasoned and straight-split pinewood into parallelopipedic pieces, and to blow or brush off the dust; they may then be handled without soiling the hands. Those sides alone are used on which the annual rings are visible on the edge, as on the other sides the fused matters are apt to spread over the surface of the charcoal (Berzelius). Small charcoal supports are sometimes sold, which have been made from powdered charcoal, mixed with rice or starch paste, and stamped into convenient shapes—they are very handy and clean.

The properties which make charcoal so valuable as a material for supports in blowpipe experiments are—

1. Its infusibility.

2. Its low conducting power for heat, which permits of the substance being heated more strongly upon a charcoal support than upon any other.

3. Its porosity, which makes it absorb readily fusible substances, such as borax, carbonate of soda, &c., whilst those which are infusible remain on the surface.

4. Its reducing power, which greatly contributes to the reduction of oxides in the inner blowpipe flame.

Platinum wire, and occasionally platinum foil, is used in all oxidizing processes before the blowpipe; also when fusing substances with fluxes, with a view to try their solubility in them, to watch the phenomena attending the dissolution, and mark the colour of the bead; lastly, to introduce substances into the flame, to see whether they will colour it. The wire should be cut into lengths of 8 centimetres, and each length twisted at both ends into a small loop (fig. 13). When required for use, the loop is moistened with a drop of water, then dipped into the powdered flux (where a flux is used), and the portion

Fig. 13.

adhering fused in the flame of a gas- or spirit-lamp. When the bead produced, which remains in the loop, is cold, it is moistened again, a portion of the substance to be examined is added, and the bead gently heated; lastly it is exposed to the inner or to the outer blowpipe flame according to circumstances.

What renders the application of the blowpipe particularly useful in chemical experiments is the great expedition with which the results are obtained. These are of two kinds, either affording us simply an insight into the general properties of the substance, so as to enable us to determine whether it is fixed, volatile, fusible, &c.; or the phenomena observed enable us at once to recognize the particular substance which is under treatment. We shall have occasion to describe the various phenomena, when treating of the behaviour of the different substances with reagents.

When using the mouth blowpipe, one hand is always necessarily engaged, and the production of a continued blast requires practice and some slight exertion; moreover it is not very easy to maintain the blowpipe flame for any length of time perfectly steady, so that the substances exposed to it may be invariably kept in the desired part of the flame. Owing to these difficulties, many chemists have endeavoured to devise self-acting blowpipe apparatus, and many contrivances of the kind have been proposed and used. In some, the air-current is produced by means of a gasometer, in others, by a caoutchouc balloon, in others again, by a species of hydrostatic blast, &c. In most cases, however, the blowpipe flame may be replaced by the Bunsen gas-lamp, which burns without luminosity and without soot. A description of this lamp follows in § 16.

§ 16.

15. The Use of Lamps, particularly of Gas-lamps.

As in processes of qualitative analysis requiring the application of heat, such as evaporation, distillation, ignition, &c., we usually have to deal with a small quantity of substance only, lamps are generally used, either a spirit-lamp, or, far better, a gas-lamp, where coal-gas is obtainable.

Spirit Lamps.—There are two kinds of spirit-lamps, the simple spirit-lamp, shown in fig. 16, and the Berzelius lamp with double draught (fig. 14). In the construction of the latter, it should be borne in mind that the part containing the wick and the vessel with the spirit must be in separate pieces, connected only by means of a narrow tube; otherwise troublesome explosions are apt to occur in lighting the lamp. The chimney, also, must not be too narrow, or the stopper fit air-tight on the opening through which the spirit is poured in. A lamp should be selected which can be readily moved up and down the pillar of the stand; this must be fitted with a moveable brass ring to support dishes and flasks, and a ring of moderately stout iron wire to support the triangle used to support crucibles in ignitions and fusions. Of the various forms of lamps in use, the one shown in fig. 14 is the best and most convenient. Fig. 15 shows a triangle of platinum wire fixed within an iron wire ring; this serves to support the crucible. Glass vessels, more particularly beakers, which have to be heated over the lamp, are most conveniently supported on a piece of gauze made of fine iron wire such as is used in making sieves of medium fineness.

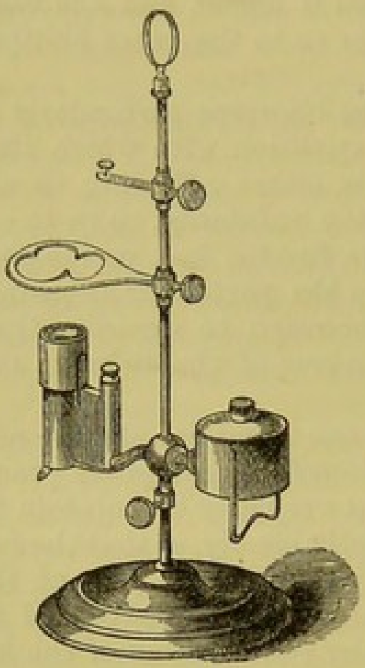

Fig. 14.

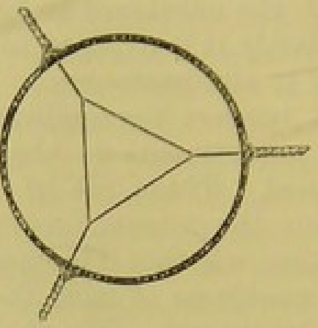

Fig. 15.

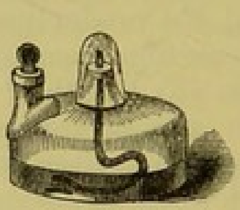

Fig. 16.

Gas Lamps.—Of the many gas-lamps proposed, Bunsen's, as shown in its simplest form in figs. 17 and 18, is one of the most convenient. $a\ b$ is a foot of cast iron measuring 7 cm. in diameter. In the centre of

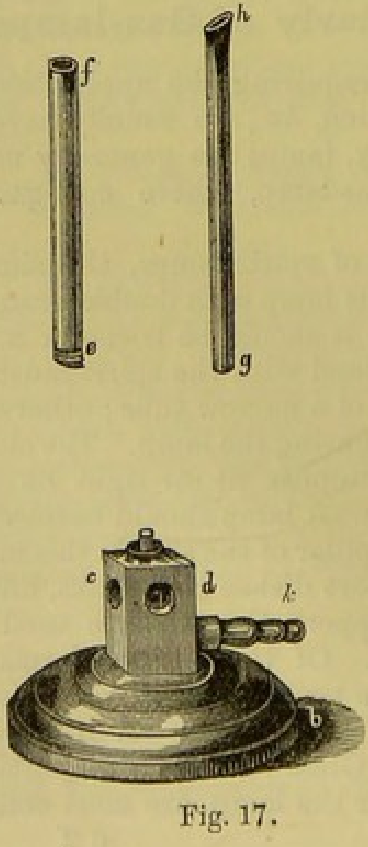

Fig. 17.

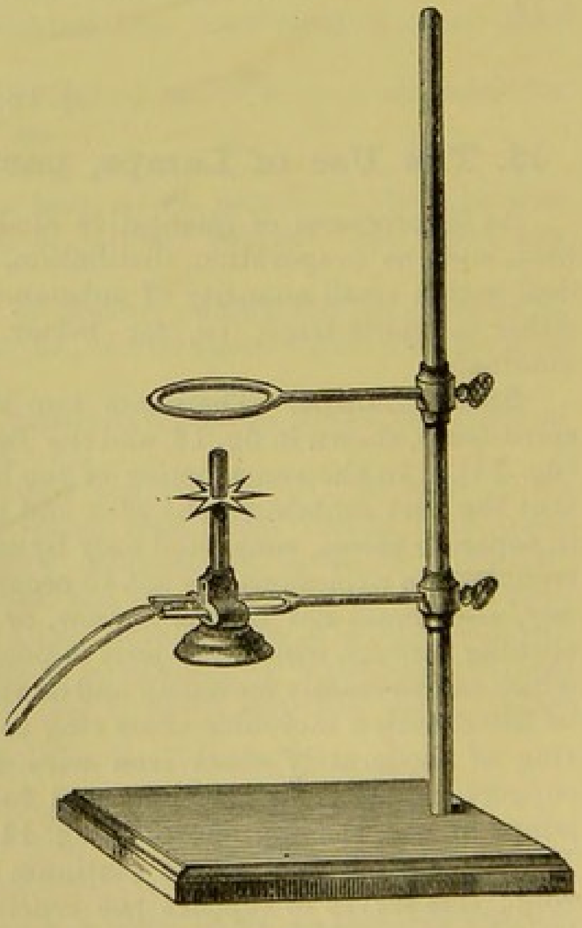

Fig. 18.

this is fixed a square brass box, *c d*, which slightly tapers towards the top; the sides of this box are 25 mm. high, and 16 mm. wide; it has a cylindrical cavity of 12 mm. deep and 10 mm. in diameter. Each side of the box has, 4 mm. from the upper rim, a circular aperture of 8 mm. diameter, leading to the inner cavity. One of the sides has fitted into it, 1 mm. below the circular aperture, a brass tube, which serves for the attachment of the india-rubber supply tube. This brass tube, which has a bore of 4 mm., is turned in the shape shown in fig. 17. The gas conveyed into it re-issues from a tube in the centre of the cavity of the box. This tube, which is 4 mm. thick at the top, but thicker at the lower end, projects 3 mm. above the rim of the box; the narrow opening from which the gas issues is in the form of three equidistant radii of a circle meeting in the centre; the length of each radius is 1 mm.; the opening of the slit is $\frac{1}{3}$ mm. wide; *e f* is a brass tube 95 mm. long, open at both ends with a bore of 9 mm.; the screw at the lower end of this tube fits into the upper part of the cavity of the box. With this tube screwed in, the lamp is completed. On opening the stop-cock, the gas rushes into the tube *e f*, where it mixes with the air coming in through the circular apertures below. When this mixture is kindled at *f*, it burns with an upright bluish flame, entirely free from soot, the size of which may be regulated at will by opening the stop-cock more or less; if this is partially open it suffices to give a flame fully answering the purpose of the common spirit-lamp; with the full stream of gas turned on, the flame, which will then be about 20 centimetres in height, affords a most excellent substitute for the Berzelius lamp. If the flame is made to burn very low, it will often occur that it "blows down;" in other words, that instead of the mixture of gas and air burning at the mouth of the tube *e f*, the gas takes fire on issuing from the slit, and burns below in the tube. This defect may be obviated by modifying the lamp as shown in fig. 22 (p. 22), in which the admission of air below can be regulated; or in the simple form of burner just described, by covering the tube *e f* at the top with a little wire-gauze cap. Flasks, &c., which it is intended to heat over the gas-lamp, are most conveniently supported on a wire-gauze plate. We give this name to a square piece of thin iron plate to which a piece of wire gauze of equal size is riveted, as shown in fig. 19. A thin iron plate, or a square of asbestos millboard, or a plain square piece of wire gauze can also be used, but the latter rapidly burns through in the middle, and beakers or flasks are more liable to crack. If it is wished to use the gas-lamp for blowpipe operations, the tube *g h* must be inserted into *e f*; this tube terminates in a flattened top slanting at an angle of 68° to the axis, and having an opening in it 1 cm. long, and $1\frac{1}{2}$ to 2 mm. wide. The insertion of *g h* into *e f* serves to close up the air-holes in the box, and gas unmixed with air, and burning with a luminous flame, issues from the top of the tube. Fig. 18 shows the Bunsen burner, fixed in the fork of an iron stand; this allows the lamp to be moved backwards or forwards along the prongs of the fork, and up and down the pillar of the stand. The moveable ring on the same pillar serves to support the objects to be heated. The six radii round the tube of the lamp support an iron-plate

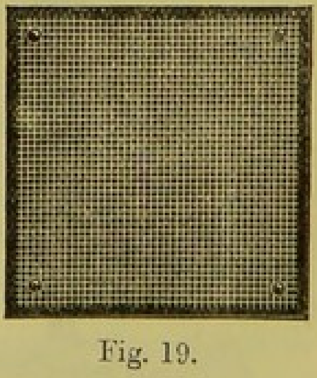

Fig. 19.

chimney (see fig. 23), or a porcelain plate used in quantitative analyses.

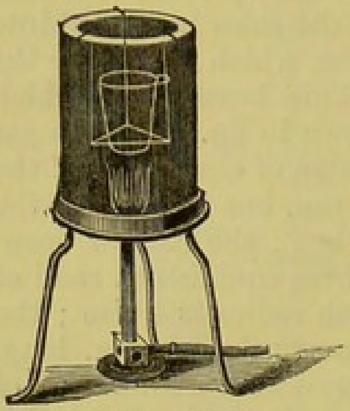

Fig. 20.

To heat crucibles to the brightest red heat, or to a white heat, the bellows blowpipe is used, but even without this the heating action of the gas-lamp may be considerably increased by surrounding the crucible with a small clay furnace, as recommended by O. L. Erdmann. Fig. 20 shows the simple contrivance by which this is effected. The furnaces are 115 mm. high, and measure 70 mm. diameter in the clear. The thickness of material is 8 mm. If the ordinary Bunsen burner is not sufficiently strong for any purpose, the triple Bunsen (fig. 21) may be used.

Bunsen has devised an improved form of his lamp* in which the flame is a more complete substitute for the blowpipe flame, for reducing, oxidizing, fusing, and volatilizing, and for the observation of the coloration of flame (§ 17). This improved form of lamp is shown in fig. 22, *a* is a sheath, which can be turned round for regulating the flow of air.

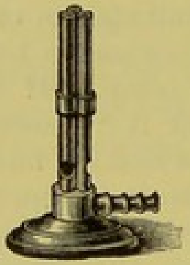

Fig. 21.

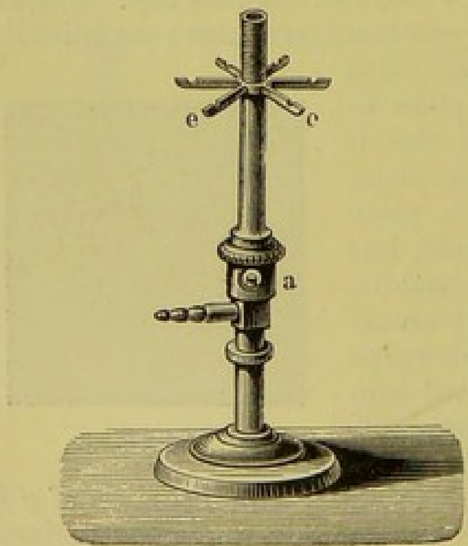

Fig. 22.

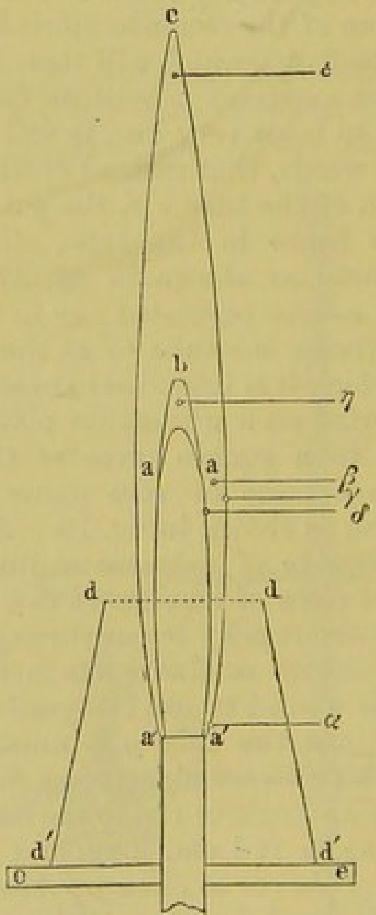

Fig. 23.

When in use, the conical chimney *d d d d* (fig. 23) is placed on *e e*; it is of such dimensions that the flame may burn tranquilly. Fig. 23

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* Ann. Chem. Pharm., **111**, 257 and **138**, 257. Also Zeit. anal. Chem., **5**, 351.

shows the flame half its natural size. In this, three zones can be distinguished, namely, 1. *a a a′ a′* the dark cone, which contains the cold gas mixed with about 62 per cent. of air, 2. *a′ c a′ b* the mantle formed by the burning mixture of gas and air, 3. *a b a* the luminous tip of the dark cone, which does not appear unless the air-holes are somewhat closed. The latter is useful for reductions.

Such are the three principal parts of this flame, but Bunsen distinguishes no less than six parts, which he names as follows:

1. The base at *α*, which has a relatively low temperature, because the burning gas is here cooled by the constant current of fresh air, and also because the lamp itself conducts the heat away. This part of the flame serves for discovering the colours produced by readily volatile substances when less volatile substances which colour the flame are also present. At the relatively low temperature of this part of the flame, the former volatilize alone instantaneously, and the colour thereby imparted to the flame is visible for a moment unmixed with other colours.

2. The fusing zone. This lies at *β*, at a distance from the bottom of somewhat more than one-third of the height of the flame, equidistant from the outside and the inside of the mantle, which is broadest at this part. This is the hottest part of the flame—namely, about 2300°, and it therefore serves for testing substances as to their fusibility, volatility, emission of light, and for all processes of fusion at a high temperature.

3. The lower oxidizing zone lies in the outer border of the fusing zone at *γ*, and is especially suitable for the oxidation of oxides dissolved in vitreous fluxes.

4. The upper oxidizing flame at *ε* consists of the non-luminous tip of the flame. Its action is strongest when the air-holes of the lamp are fully open. It is used for the roasting away of volatile products of oxidation, and generally for all processes of oxidation where the very highest temperature is not required.

5. The lower reducing zone lies at *δ* in the inner border of the fusing zone next to the dark cone. As the reducing gases are here mixed with oxygen, they do not possess their full power, and, therefore, are without action on many substances which are deoxidized in the upper reducing flame. This part of the flame is especially suited for reduction on charcoal or in vitreous fluxes.

6. The upper reducing flame lies at *η* in the luminous tip of the dark inner cone, which, as already explained, may be produced by diminishing the supply of air. This part of the flame must not be allowed to get large enough to blacken a test-tube filled with water and held in it. It contains no free oxygen, is rich in separated incandescent carbon, and therefore has a much stronger action than the lower reducing zone. It is used more particularly for the reduction of metals collected in the form of incrustations.

With the help of a gas flame of this description, we can obtain as high a temperature as with the blowpipe, and even higher if the radiating surface of the substance is made as small as possible; and by the use of the different parts of the flame, processes of reduction and of oxidation may be carried out with the greatest convenience.

In order to study *the behaviour of substances at a high temperature*, namely, their emission of light, fusibility, volatility and power of colouring flame, they are introduced into the flame in the loop of a platinum wire, which should be barely thicker than a horse hair. Should the substance attack platinum, a little bundle of asbestos is used, which should be about one-fourth the thickness of a match. Decrepitating substances are first very finely powdered, then placed on a strip of moistened filter-paper about a square centimetre in surface, and this is cautiously burnt between two rings of fine platinum wire. The substance now presents the appearance of a coherent crust, and may be held in the flame without difficulty. For testing liquids to see whether they contain a substance which colours flame, the round loop of the fine platinum wire is flattened on an anvil to the form of a small ring. This is dipped into the liquid, and then withdrawn, when a drop will be found attached to the ring. This drop is held near the flame and allowed to evaporate without boiling, after which the residue may be conveniently tested.

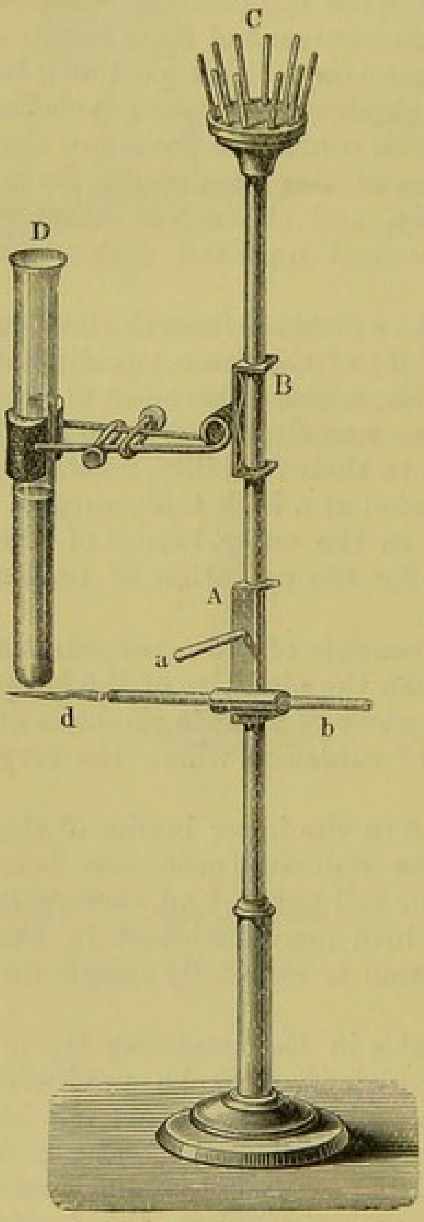

Fig. 24.

If a substance is to be exposed for a considerable time to the action of the flame, the stand, fig. 24, is used. *A* and *B* are provided with springs, and can be easily moved up and down. On *A* is the arm *a* intended for the support of the platinum wire fixed in a glass tube, fig. 25; also another little arrangement to hold the glass tube *b* with its bundle of asbestos fibres *d*. *B* bears a clip for the reception of a test-tube, which in certain cases has to be heated for a considerable time in a definite part of the flame. *C* serves to hold the various platinum wires fixed in glass tubes, and is capable of revolving on its axis.

Fig. 25.

Experiments on Reduction. — These are performed either by heating the substance with a suitable reducing agent in a small glass tube, or with the aid of a little stick of charcoal. In order to prepare the latter, Bunsen recommends that an ordinary wooden match from which the head has been removed should be smeared for three-fourths of its length with the wet mass produced by warming an uneffloresced crystal of carbonate of soda near the flame. If the match is then slowly rotated on its axis in the flame, a crust of solid carbonate of soda will be formed on the wood as it is carbonized, and on heating it in the fusing zone of the flame, this crust will be melted and absorbed by the charcoal. The little stick of charcoal will now in a measure be protected from combustion. The substance to be tested is made into a paste with a drop of melted crystallized carbonate of soda, and a mass about the size of a millet-seed is taken up on the point of the carbonized match, it is then first melted in the lower oxidizing flame, and afterwards moved through a portion of the dark cone into the opposite hottest part of the lower reducing zone. The reduction will be rendered evident by the effervescence of the carbonate of soda. After a few moments the action is stopped by allowing the substance to cool in the dark cone of the flame. If, finally, the point of the carbonized match is cut off and triturated with a few drops of water in a small agate mortar, the reduced metal will be obtained in the form of sparkling fragments which may be purified by elutriation, and if necessary more minutely examined.

Incrustations.—Volatile elements which are reducible by hydrogen and carbon may be separated as such or as oxides from their combinations, and deposited on porcelain. These deposits are called incrustations, they are thicker in the middle, and become thin towards the edges. They may be converted into iodides, sulphides, and other combinations, and may thus be further identified. These reactions are so delicate that in many cases a quantity of from $\frac{1}{10}$ to 1 mgrm. is sufficient to exhibit them.

The metallic incrustation is obtained by holding in one hand a small portion of the substance on asbestos in the upper reducing flame, and in the other hand a glazed porcelain dish, from 1 to 1·2 decimetres in diameter, filled with water, close over the asbestos in the upper reducing flame. The metals separate as sooty or mirror-like incrustations.

If the substance is held as just directed, and the porcelain dish is held in the upper oxidizing flame, an incrustation of oxide is obtained. In order to be sure of getting it, the flame must be comparatively small if the portion of substance is minute. To turn the incrustation of oxide into an incrustation of iodide, let the dish covered with the oxide cool, breathe on it, and place it on the wide-mouth bottle, fig. 26. This bottle contains iodide of phosphorus, which has been allowed to deliquesce and become converted into fuming hydriodic acid and phosphorus acid, it should have an air-tight glass stopper. If the hydriodic acid has become so moist that it has ceased to fume it may be restored to its proper condition by the addition of anhydrous phosphoric acid. To turn the incrustation of iodide into an incrustation of sulphide direct a current of air containing sulphide of ammonium upon it, breathing upon the dish occasionally, then drive off the excess of sulphide of ammonium by *gentle* warming.

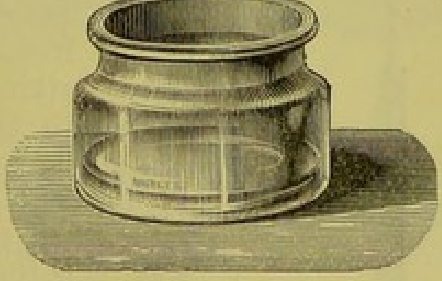

Fig. 26.

If a larger quantity of the metallic incrustation is required for further experiments, the porcelain dish is replaced by a test-tube half filled with water (D, fig. 24), in which a few pieces of marble should be placed to prevent bumping when the water is subsequently boiled. In this case, the asbestos *d*, with the substance on it, is fixed on a level with the middle of the upper reducing flame, the test-tube is fixed with its bottom just over the asbestos as shown in the figure, and then the lamp is moved just under the test-tube. In this way, the substance comes within the reducing flame and the metallic incrustation is formed on the bottom of the test-tube. By renewing the substance, the incrustation may be obtained of any thickness desired.

§ 17.

16. Coloured Flames and Spectrum Analysis.

Many substances have the property of colouring a colourless flame in a very remarkable manner. As most of these substances impart a different and distinct, and accordingly characteristic, tint to the flame, the observation of this coloured flame affords an excellent, easy, and safe means of detecting many of them; for instance, salts of soda impart to flame a yellow, salts of potassa a violet, salts of lithia a carmine tint, and they may thus be easily distinguished from each other.

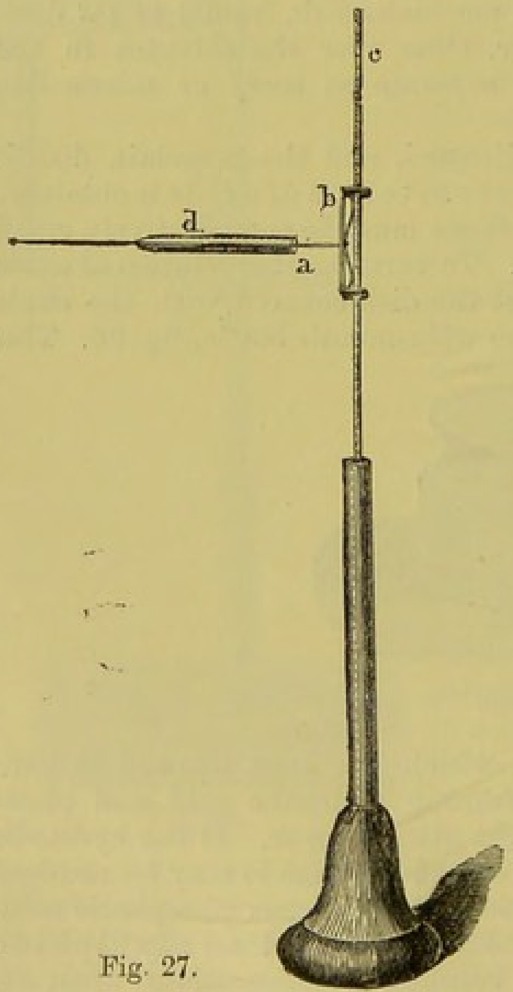

Fig. 27.

The Bunsen burner, with chimney, described on p. 22, and shown in fig. 22, is particularly well adapted for observations of the kind. The substances to be examined are put on the small loop of a fine platinum wire, and thus, by means of the holder shown in fig. 24, or the more simple one, fig. 27, placed in the fusing zone of the Bunsen flame. A particularly striking coloration is imparted to the flame by the salts of the alkalies and alkaline earths. If different salts of one and the same base are compared in this way, it is found that every one of them, if volatile at a high temperature, or at least if the base volatilizes, imparts the same colour to the flame, only with different degrees of intensity, the most volatile of the salts producing the most intense coloration; thus, for instance, chloride of potassium gives a more intense coloration than carbonate of potassa, and this again a more intense one than silicate of potassa. In the case of compounds which volatilize with difficulty, the coloration of the flame may often be brought about, or made more apparent, by adding some other substance which has the power of decomposing the compound under examination. Thus, for instance, in silicates containing only a small percentage of potassa, the latter cannot be directly detected by the colour imparted to the flame; but the base may be detected by adding a little pure gypsum, as this will cause the formation of silicate of lime and sulphate of potassa, a salt which is sufficiently volatile.

But however decisive a test the mere coloration of the flame affords for the detection of certain metals if present alone in a compound and unmixed with others, it becomes apparently useless in the case of mixtures of the compounds of several metals. Thus, for instance, mixtures of salts of potassa and soda show only the soda flame, mixtures of salts of baryta and strontia only the baryta flame, &c. This defect may be remedied, however, in two ways, with the greatest success.

The first method introduced by Cartmell,[*] and perfected afterwards by Bunsen [†] and by Merz,[‡] consists in looking at the coloured flame, through some coloured medium (coloured glasses, indigo solution, &c.). Such coloured media, by absorbing the flame coloration produced by the one metal, bring out that of the other metal mixed with it. For instance, if a mixture of a salt of potassa and a salt of soda is exposed to the flame, the latter will only show the yellow soda coloration; but if the flame be now looked at through a deep-blue cobalt glass, or through solution of indigo, the yellow soda coloration will disappear, and will be replaced by the violet tint of potassa. A simple apparatus suffices for observations and experiments of this kind; all that is required for the purpose being,—

1. A hollow prism (fig. 28) made of plate glass, the chief section of which forms a triangle with two sides of 150 mm., and one side of 35 mm. length. The indigo solution required to fill this prism is prepared by dissolving 1 part of indigo in 8 parts of fuming sulphuric acid, adding to the solution 1500–2000 parts of water, and filtering. When using this apparatus, the prism is moved in a horizontal direction close to the eye, in such a way that the rays from the flame pass through successively thicker and thicker layers of the absorbent medium before entering the eye.

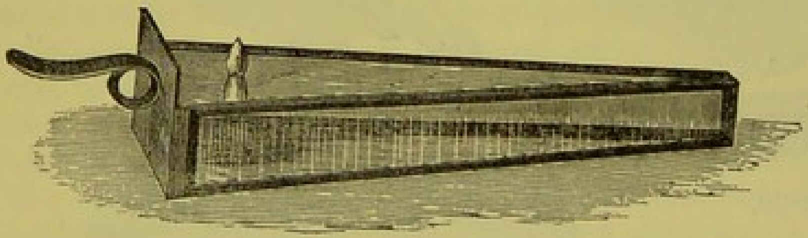

Fig. 28.

Cornwall § considers that a solution of permanganate of potassa is preferable to the indigo solution, as it absorbs the coloured rays emitted by the flame when sodium, lithium, and calcium are present, but not those due to potassium; the latter can therefore be readily detected in presence of the others. He recommends a hollow prism of 240 mm. in length and 30 mm. wide; the solution of permanganate of potassa should be of such a strength that a layer of 45 mm. in thickness completely extinguishes the light from the strongest sodium or lithium flame.

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[*] Phil. Mag., **16**, 382.

[†] Ann. Chem. Pharm., **111**, 257.

[‡] Jour. pr. Chem., **80**, 487.

[§] Amer. Chemist, **2**, 384, and Zeit. anal. Chem., **11**, 307.

2. A blue, a violet, a red, and a green glass. The blue glass is tinted with protoxide of cobalt; the violet glass with sesquioxide of manganese; the red glass (partly coloured, partly uncoloured) with suboxide of copper; and the green glass with sesquioxide of iron and protoxide of copper. The common coloured glass will generally be found to answer the purpose. Full information as to the tints imparted to the flame by different substances, when viewed through the aforesaid media, and the combinations by which these substances are severally identified, will be found in Section III., in the paragraphs treating of the several bases and acids.

Spectrum Analysis.—The second method, which is called Spectrum Analysis, was introduced by Kirchhoff and Bunsen. It consists in allowing the rays of the coloured flame to pass first through a narrow slit, and then through a prism, observing the refracted rays through a telescope. A distinct spectrum is thus obtained for every flame-colouring metal; this spectrum consists either, as in the case of baryta, of a number of coloured lines lying side by side; or, as in the case of lithia, of two separate, differently coloured lines; or, as in the case of thallium, of a single green line. These spectra are characteristic in a double sense, for the spectrum lines not only have a distinct colour, but they also occupy a fixed position.

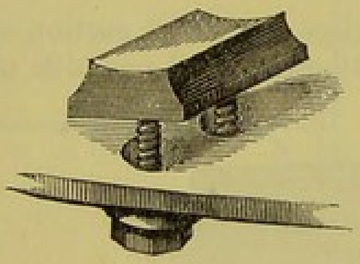

Fig. 29.

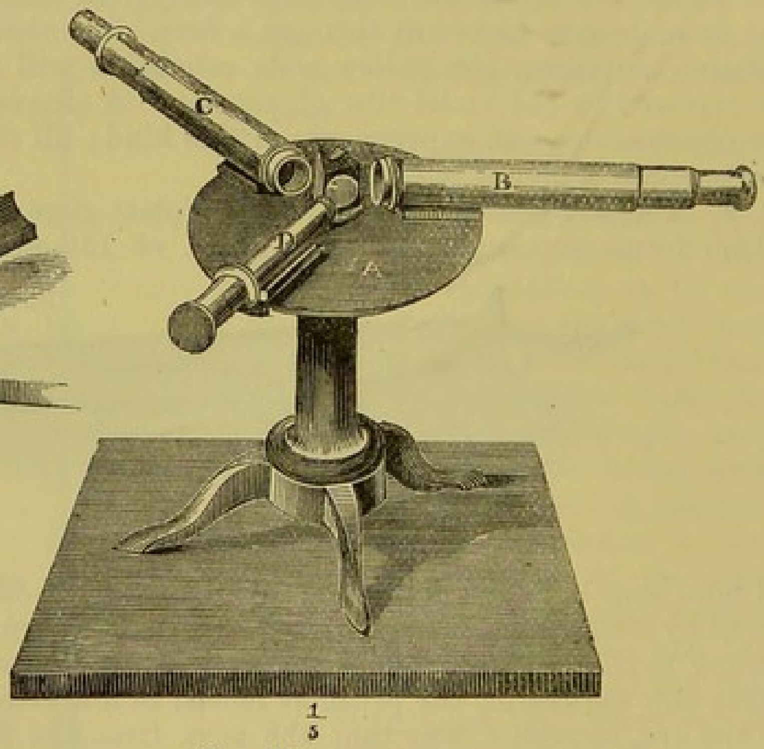

Fig. 29 *a*.

It is this latter circumstance which enables us to identify every individual metal without difficulty, in the spectrum observations of mixtures of flame-colouring metals; for instance, a flame in which a mixture of potassa, soda, and lithia salts is evaporated, will give, side by side, the spectra of the several metals in the most perfect purity.

Kirchhoff and Bunsen have constructed two kinds of apparatus, which are both of them suited for spectrum observation, and enable the operator to determine by measure the positions in which the spectrum lines make their appearance. Both are constructed on the same principle. A description, with illustration, of the larger of the two, which is also the more perfect, has been published in *Poggendorff's Annalen*, **113**, 374, and in the *Zeitschrift für analytische Chemie*, 1862, 49. The smaller, more simple, and less costly apparatus suffices for all common purposes, and is used most in chemical laboratories. It is shown in fig. 29 *a*.

A is an iron disk, in the centre of which a prism, with circular refracting faces of about 25 mm. diameter, is fastened by a metal strap, which presses upon the upper face of the prism, and is secured below to the iron plate by a screw. The three tubes, *B*, *C*, and *D*, are also firmly fastened to the same disk. Each of these tubes is soldered to a metal block, of which fig. 29 *b* gives an enlarged representation. This block contains the nuts for two screws, which pass through wider openings in the iron plate, and are firmly secured beneath when the tube has been adjusted in the proper position. *B* is the observation telescope; it has a magnifying power of about 6, with an object-glass of 20 mm. diameter. The tube *C* is closed at one end by a tin-foil disk, into which the perpendicular slit is cut through which the light is admitted.* The tube *D* carries a photographic copy of a millimetre scale, produced in the camera obscura on a glass plate of about one-fifteenth the original dimensions. This scale is covered with tin-foil, with the exception of the narrow strip upon which the divisional lines and the numbers are engraved. It is lighted by a gas- or candle-flame placed close behind it.

The axes of the tubes *B* and *D* are directed, at the same inclination, to the centre of one face of the prism, whilst the axis of the tube *C* is directed to the centre of the other face. This arrangement makes the spectrum produced by the refraction of the coloured light passing through *C*, and the image of the scale in *D* produced by total reflection appear superimposed, so that the positions occupied by the lines of the spectrum may be read off on the scale. The prism is placed at the angle of minimum deviation of the rays of the sodium line; and the telescope is set in the direction in which the red and the violet potassium lines are about equidistant from the middle of the field of view.

The colourless flame into which the flame-colouring substances are to be introduced, is placed 10 cm. from the slit. The Bunsen lamp, shown in fig. 22, gives the best flame; it is adjusted so as to place the upper border of the chimney about 20 mm. below the lower end of the slit. When the lamp has been lighted, and a bead of substance—say of sulphate of potassa—introduced into the fusing zone by means of the holder shown in fig. 27, the iron disk of the spectrum apparatus, which, with all it carries, is moveable round its vertical axis, is turned until the point is reached where the luminosity of the spectrum is the most intense.

To cut off foreign light in all spectrum observations, the centre part of the apparatus should be covered with a black cloth or a cardboard box.

When sunlight is reflected through the slit of the spectroscope, a continuous rainbow-coloured spectrum is formed, in which a number of dark lines may be observed (see No. 1 on the plate of spectra). Each of these dark lines—the Fraunhofer lines—occupies a perfectly definite position, and therefore affords the means of accurately determining the relative positions of other lines. They are caused by the

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* This arrangement is not very strong. For laboratories, a more solid material such as brass knife edges is much better than tin-foil.

rays from the radiant solids or fluids in the sun, which themselves yield a continuous spectrum, having to pass through the solar atmosphere; the elements in the latter absorb, from the white light passing through their vapours, rays of the same refrangibility as they themselves emit.

If the reflected sunlight (or indeed artificial lamplight) is passed through liquids before entering the spectroscope, the light is either unaffected or is partially absorbed. In the latter case, dark stripes and bands appear in the spectrum, and as these dark portions are due to the extinction of rays of known refrangibility, they occupy definite positions in the spectrum, and may thus serve to indicate the presence of many substances. For the observation of absorption spectra of this nature, the liquids to be examined are placed in colourless glass cells having perpendicular and parallel sides.

Besides the spectroscopes constructed by Bunsen and Kirchhoff, many others have been suggested and employed,[*] and among these the universal spectroscopic apparatus of H. W. Vogel[†] may be particularly mentioned, and also that of C. H. Wolff,[‡] with which both flame and absorption spectra can be very conveniently observed.

The spectra produced by the alkalies, the alkaline earths, thallium and indium are shown in the coloured plate at the commencement of the book. The solar spectrum has been added to serve as a guide to the position and bearings of the lines. The spectra are represented as they appear in the apparatus furnished with an astronomical telescope. In the Third Section, in the chapters treating of the several substances, attention will be called to the lines most characteristic of each metal, but the method by which the highest degree of certainty is imparted to spectrum analysis may be mentioned here. This consists in exposing the beads of the pure and unmixed metallic compounds to the flame, and marking on copied scales the position which the most striking spectrum lines occupy on the scale of the apparatus, in the manner shown, by way of illustration, in No. 2 of the plate, with regard to the strontium spectrum. It is self-evident that the spectrum of an unknown substance can only pass for the strontium spectrum if the characteristic lines not only agree with those of the latter in point of colour, but appear also in exactly the same position where they are marked on the strontium scale.

The drawings of such scales every operator must, of course, make for his own apparatus; and they become useless for the intended purpose if any alteration is made in the position of the prism or the scale. It is therefore always advisable to set the apparatus so that it can be easily readjusted to its original position, which is most readily done by making the left border of the sodium line coincide with the number 50 of the scale.

With the introduction of spectrum analysis, a new era has, in many respects, begun for chemical analysis, for by no other method can such minute quantities of substances be detected. Spectrum analysis is marked moreover by a certainty free from all doubt, and gives results in a few seconds, which could formerly be obtained only, if at all, after hours or days of labour.

[*] Comp. Zeit. anal. Chem. **2**, 64, 190 and 353; **3**, 443; **5**, 329; **12**, 432; **13**, 48 and 442; **14**, 335; **16**, 463; **17**, 187; **19**, 72; **20**, 99.

[†] *Ibid.* **17**, 187.

[‡] *Ibid.* **20**, 99.

APPENDIX TO SECTION I.

§ 18.

Apparatus.

As many students of chemical analysis might find some difficulty in the selection of the proper apparatus, a list of the articles which are actually required for the performance of simple experiments and investigations, is here given, together with instructions to guide the pupil in their purchase.

1. A Bunsen burner with stand and special tube for blowpipe experiments as represented in § 16, figs. 17, 18, and 22.

Where gas is not available, a Berzelius spirit lamp (fig. 14, p. 20), or a glass spirit lamp (fig. 16, p. 20) may be used.

2. A blowpipe (see § 15).

3. A platinum crucible. A crucible should be selected which will contain about a quarter of an ounce of water, with a cover shaped like a shallow dish; it must not be too deep in proportion to its breadth.

4. Platinum foil, as smooth and clean as possible, and not very thin: length about 40 mm.; width about 25 mm.

5. Platinum wire (see pp. 18 and 24). Three stronger wires and three finer wires are amply sufficient. They are kept most conveniently in a glass filled with water, as this will dissolve most of the beads if left in contact with it for some time; in this way the wires are always kept clean.

6. A stand with twelve test-tubes—16 to 18 cm. is about the proper length of the tubes, from 1 to 2 cm. the proper width. The tubes must be made of thin white glass, and so well annealed that they do not crack when boiling water is poured into them. The rim must be quite round, and slightly turned over; it ought not to have a lip,

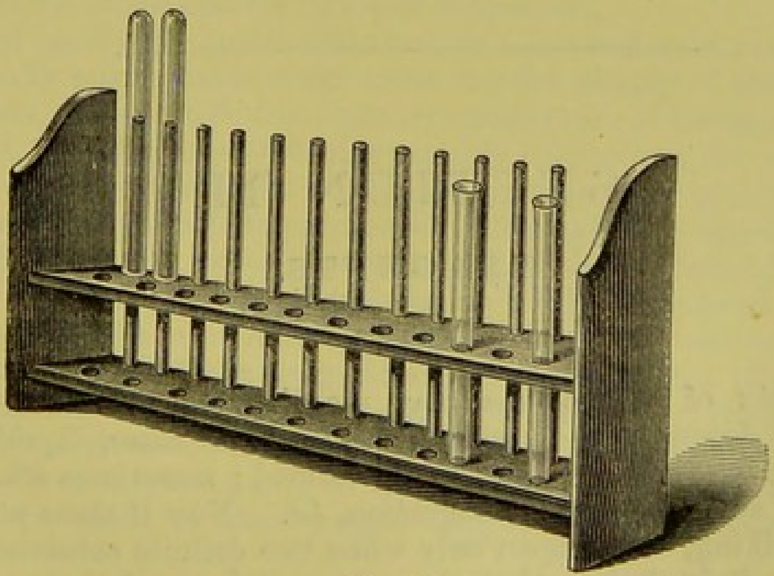

Fig. 30.

as this is useless and prevents the tube being closely stopped with the finger, and also interferes with shaking the contents. The stand shown in fig. 30 will be found most suitable. The pegs on the upper shelf serve for the clean tubes, which may thus be well drained.

7. Several beakers and small flasks of thin, well annealed glass.

8. Several porcelain evaporating dishes, and a variety of small porcelain crucibles. Those of Berlin porcelain are unexceptionable, both in shape and durability. Meissen and Nymphenburg porcelain will also answer the purpose.

9. Glass funnels of various sizes. The conical part must have an angle of 60°, and must not curve gradually into the neck, but be joined to it at a sharp angle (see fig. 2, p. 8).

10. A washing bottle of a capacity of from 300 to 400 c.c. (see § 7).

11. Several glass rods and glass tubes. The latter may be bent, drawn out, &c., over a Berzelius lamp or ordinary fish-tail gas-burner; the former are rounded at the ends by fusion.

12. A selection of watch-glasses.

13. A small agate mortar.

14. A pair of small steel or brass pincers, about four or five inches long.

15. A wooden filter stand (see § 5).

16. A tripod of thin iron, to support the dishes, &c., when being heated over the spirit or gas lamp.

17. A wire-gauze plate, or a square of wire gauze or asbestos millboard.

18. A platinum triangle.

19. The coloured glasses described in § 17, especially blue and green.

SECTION II.

REAGENTS.

§ 19.

A variety of phenomena may manifest themselves when substances are decomposed or combine. In some cases, liquids change their colour, in others precipitates are formed; sometimes effervescence takes place, and sometimes deflagration, &c. Now if these phenomena are very striking, and happen only when two definite substances act on one another, it is obvious that the presence of one of these substances may be detected by means of the other: if we know, for instance, that a white precipitate of certain definite properties is formed on mixing baryta with sulphuric acid, it is clear that, if we obtain a precipitate exhibiting these properties when baryta is added to any given solution, we may conclude that the solution contains sulphuric acid.

Those substances which indicate the presence of others by any striking phenomena are called reagents.

According to the different objects attained by the application of these reagents, we distinguish them as general or special reagents. General reagents are those which serve to determine the class or group to which a substance belongs; whilst special reagents are those which serve to detect individual substances. That the line between the two divisions cannot be drawn with any degree of precision, and that one and the same substance is often made to serve both as a general and as a special reagent, cannot be considered a valid objection to this classification, which is in fact simply intended to induce a habit of employing reagents always for a settled purpose—viz., either simply to find out the group to which the substance belongs, or to determine the latter individually.

Now whilst the usefulness of general reagents depends principally on their efficiency in strictly characterizing groups of substances, and often effecting a complete separation of those belonging to one group from those belonging to another, that of special reagents depends on their being characteristic and sensitive. We call a reagent *characteristic*, if the alteration produced by it—the substance tested for being present—is so distinctly marked as to admit of no mistake. Thus iron is a characteristic reagent for copper, and protochloride of tin for mercury, because the phenomena produced by these reagents—namely, the separation of metallic copper and of globules of mercury—admit of no mistake. We call a reagent *sensitive* or *delicate*, if its action is distinctly perceptible, even though a very minute quantity only of the substance tested for is present; such, for instance, is the action of starch on iodine.

Very many reagents are both characteristic and delicate; for instance, terchloride of gold for protoxide of tin; ferrocyanide of potassium for ferric oxide and for oxide of copper, &c.

It need hardly be mentioned that, as a general rule, reagents must be chemically pure, that is, they must consist simply of their essential constituents, and must be free from any admixture of foreign substances. We should, therefore, make it an invariable rule to test the purity of our reagents before we use them, no matter whether they be articles of our own production or have been purchased. Although the necessity of this is fully admitted on all hands, yet it is too often neglected in practice; thus it is by no means uncommon to see alumina entered among the substances detected in an analysis, simply because the solution of potassa or soda used as one of the reagents happened to contain that earth; or iron, because the chloride of ammonium used was not free from that metal. The directions given in this section for testing the purity of the several reagents refer, of course, only to the presence of foreign matter resulting from the mode of their preparation, and not to mere accidental admixtures.

One of the most common sources of error in qualitative analysis proceeds from missing the proper measure—the right quantity—in the application of reagents. Such terms as "addition in excess," "supersaturation," &c., often induce novices to suppose that they cannot add too much of the reagent; and thus some will fill a test-tube with acid, simply to supersaturate a few drops of an alkaline fluid, whereas every drop of acid added, after the neutralization point has once been reached, must be regarded as an excess of acid. On the other hand, the addition of an insufficient amount must also be avoided, since a reagent added in insufficient quantity often produces phenomena quite different from those which will appear if the same reagent is in excess: for example, a solution of chloride of mercury yields a white precipitate if tested with a small quantity of sulphuretted hydrogen; but if treated with the same reagent in excess, the precipitate is black. Experience has, however, proved that the most common mistake beginners make, is to add the reagents too copiously. One reason why this over-addition must impair the accuracy of the results is obvious; we need simply bear in mind that the changes effected by reagents are perceptible within certain limits only, and that therefore they may be the more readily overlooked the nearer we approach these limits by diluting the fluid. Another reason lies in the fact that a large excess of a reagent will often have a solvent or modifying action on a precipitate or colour, and will entirely prevent the exhibition of phenomena which a suitable quantity would produce without difficulty.

Although no special or definite rule can be given for avoiding this source of error, a general rule may be laid down, which will be found to answer the purpose, if not in all, at least in the great majority of cases. It is simply this: let the student always consider, before adding the reagent, for what purpose he applies it, what are the phenomena he intends to produce, and what will be the result if it is added in excess.

Reagents are divided into two classes, according as to whether the liquid state, which is indispensable for the manifestation of the action of reagents on the various bodies, is brought about by the application of heat, or by means of liquid solvents; we have consequently, 1, Reagents in the wet way; and 2, Reagents in the dry way. For greater clearness, these two principal classes are subdivided as follows:—

A. REAGENTS IN THE WET WAY.

I. Simple Solvents.

II. Acids and Halogens.

a. Oxygen acids.
b. Hydrogen acids and halogens.
c. Sulphur acids.

III. Bases and Metals.

a. Oxygen bases.
b. Sulphur bases.

IV. Salts.

a. Of the alkalies.
b. Of the alkaline earths.
c. Of the oxides of the heavy metals.

V. Colouring Matters and indifferent Vegetable Substances.

B. REAGENTS IN THE DRY WAY.

I. Fluxes.

II. Blowpipe Reagents.

The more important reagents and those in general use are described in the following sections; special reagents employed in isolated cases will be noticed when their use is considered.

A. REAGENTS IN THE WET WAY.

I.—SIMPLE SOLVENTS.

Simple solvents are liquids which do not enter into chemical combination with the substances dissolved in them; they will accordingly dissolve any quantity of matter up to a certain limit, which is called the point of saturation, and is in a measure dependent on the temperature of the solvent. The essential and characteristic properties of the dissolved substances (taste, reaction, colour, &c.) are not destroyed by the solvent. (See § 2.)

§ 20.

Water, HO [H_2O].

Preparation.—Pure water is obtained by distilling spring water from a copper still with a head and worm of pure tin, or from a glass retort, although the latter is not so good; about one-fourth should be left in the retort. If the distilled water is to be quite free from carbonic acid and carbonate of ammonia, the portions passing over first must be thrown away. In the larger chemical and in most pharmaceutical laboratories, the distilled water required is obtained from the steam apparatus which serves for drying, heating, boiling, &c. Rain water collected in the open air may in many cases be substituted for distilled water.*

Tests.—It must be colourless, odourless, and tasteless, and should not leave the smallest residue when evaporated in a platinum vessel. It should not be changed by sulphide of ammonium (copper, lead, iron), nor rendered turbid by baryta water (carbonic acid). No cloudiness should be produced even after long standing with addition of oxalate of ammonia (lime), chloride of barium and hydrochloric acid (sulphuric acid), nitrate of silver and nitric acid (chlorides). It should give no blue coloration with iodide of potassium, starch-paste and dilute sulphuric acid (nitrous acid), and no yellow coloration with Nessler test (ammonia).

Uses.—Water† is used principally as a simple solvent for a great variety of substances; most conveniently from the wash-bottle (see p. 9, fig. 3), which affords a ready means of applying the water in a thicker or thinner stream as desired. A special use for it is in the decomposition of certain neutral metallic salts (such as terchloride of antimony

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* As regards the preparation of water absolutely free from organic matter, see Stas, Zeit. anal. Chem., 6, 417.

† In analytical experiments distilled water only is used; whenever, therefore, the term water occurs in the present work, distilled water is meant.

and the salts of bismuth) whereby they are converted into soluble acid and insoluble basic compounds.

§ 21.

2. Alcohol, $C_4H_6O_2$* [C_2H_6O].

Preparation.—Two sorts of alcohol are used in chemical analyses, namely, spirit of wine of 0·83 or 0·84 sp. gr. = 91 to 88 per cent. by volume (*spiritus rectificatus* of the British Pharmacopœia); and absolute alcohol. The latter may be prepared most conveniently by mixing, in a distilling vessel, 1 part of fused chloride of calcium with 2 parts of rectified spirit of wine of about 90 per cent. by volume, digesting the mixture 2 or 3 days, until the chloride of calcium is dissolved, and then distilling slowly and in fractional portions. So long as the distillate shows a sp. gr. below 0·8037 (= 98 per cent. by volume), it may pass for absolute alcohol. The portions coming over after that are received in a separate vessel.

Tests.—Pure alcohol should volatilize completely, and ought not to leave an odour of fusel oil when allowed to evaporate on the palm of the hand; neither should it alter the colour of moist blue or red litmus paper. When kindled, it must burn with a faint bluish barely perceptible flame.

Uses.—Alcohol is useful (*a*) for separating substances soluble in it from others which do not dissolve—chloride of strontium from chloride of barium for example; (*b*) to precipitate from aqueous solutions many substances which are insoluble in dilute alcohol, such as gypsum, malate of lime; (*c*) to produce various kinds of ether—acetic ether, for example, which is characterized by its peculiar and agreeable smell; (*d*) to reduce, mostly with the co-operation of an acid, certain peroxides and metallic acids, such as binoxide of lead, chromic acid, &c.; (*e*) to detect certain substances which impart a characteristic tint to its flame, especially boric acid, strontia, potassa, soda, and lithia.

§ 22.

3. Ether, C_4H_5O [$C_4H_{10}O$].

4. Chloroform, C_2HCl_3 [$CHCl_3$].

5. Bisulphide of Carbon, CS_2 [CS_2].

These solvents find but limited application in the qualitative analysis of inorganic substances; their use indeed is confined almost entirely to the detection and isolation of bromine and iodine. Chloroform and bisulphide of carbon are preferable to ether in this respect. Ether is used for the detection of chromic acid by means of peroxide of hydrogen. As these reagents can be made much better on a large than on a small scale, it is more convenient to purchase them than to make them.

Tests.—Ether should be colourless, of sp. gr. of 0·720 to 0·725 at 17·5°, and require 12 parts of water for solution. The solution must not alter the colour of test papers. Ether must, even at the common

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* Methylated spirit may be substituted for alcohol, in almost all analytical operations, if it is used as a solvent merely.

temperature, rapidly and completely evaporate on a watch-glass. Chloroform should be colourless and transparent, and have a sp. gr. of 1·490 to 1·493 at 15°. If agitated with twice its volume of water, it must not be perceptibly diminished in volume; the water must neither have an acid reaction, nor should it render a solution of nitrate of silver turbid. It must even at the ordinary temperature evaporate readily and completely on a watch-glass. Bisulphide of carbon should be colourless, readily and completely volatile even at the ordinary temperature, and not alter the colour of carbonate of lead, or moistened blue litmus paper.

II.—Acids and Halogens.

§ 23.

The acids—at least those of more strongly pronounced character—are soluble in water. The solutions taste acid and redden litmus paper. Acids may be divided into oxygen acids, sulphur acids, and hydrogen acids.

The oxygen acids, produced generally by the combination of a non-metallic element with oxygen, combine with water in definite proportions to form hydrated acids. It is these hydrates that are usually employed in analytical processes; they are contained in the aqueous solutions of the acids, and are commonly designated by the simple name of the free acid, as the addition of water does not destroy their acid properties. In the action of hydrated acids on oxides of metals, the oxide takes the place of the water of hydration, and an oxygen salt is formed, $HO,SO_3 + KO = KO,SO_3 + HO$. Where these salts are produced by the combination of an acid with a strong base, their reaction (supposing the combining acid also to be a strong acid) is neutral; a salt formed with a weaker base, for instance, with the oxide of a heavy metal, generally has an acid reaction, but is nevertheless called a neutral salt if the oxygen of the base bears the same proportion to that of the acid as it does in the distinctly neutral salts of the same acid, or, in other words, if it corresponds with the saturation capacity of the acid. Although sulphate of potassa, KO,SO_3, has a neutral reaction, whilst the reaction of sulphate of copper, $CuO,SO_3 + 5aq$, is acid, yet the latter is called neutral sulphate of copper, because the oxygen of the oxide of copper is to that of the sulphuric acid as 1 : 3, which is the same as the oxygen of the potassa and that of the sulphuric acid in the confessedly neutral sulphate of potassa. According to the modern views of chemists the acid anhydrides are not regarded as acids, the true acids being the compounds which dualistic chemists call hydrates of the acids; the formation of salts consequently takes place by the substitution of a metal for the hydrogen of the acid, thus: $H_2SO_4 + Zn = ZnSO_4 + H_2$.

The hydrogen acids are formed by the combination of the halogens with hydrogen; most of them possess the characteristic properties of acids in a high degree. They neutralize oxygen bases, with formation of haloid salts and water;

$$HCl + NaO = NaCl + HO, \qquad 3HCl + Fe_2O_3 = Fe_2Cl_3 + 3HO$$
$$[2HCl + Na_2O = 2NaCl + H_2O] \qquad [6HCl + Fe_2O_3 = Fe_2Cl_6 + 3H_2O].$$

The haloid salts produced by the action of powerful hydrogen acids on strong bases have a neutral reaction; whilst the solutions of the haloid salts produced by the action of powerful hydrogen acids on feeble bases (such as alumina and sesquioxide of iron) have an acid reaction.

The sulphur acids are more frequently the result of the combination of metallic than of non-metallic elements with sulphur; they combine with sulphur bases to form sulphur salts;

$$AsS_5 + 3NaS = 3NaS,AsS_5.$$

The sulphur acids are analogous to the oxygen acids, and the views held by dualistic chemists and the modern school as to their constitution differ in the same way as already described in respect of the oxygen acids. As the sulphur acids are but feeble acids, all the soluble sulphur salts have an alkaline reaction.

a. OXYGEN ACIDS.

§ 24.

1. **Sulphuric Acid,** HO,SO_3 [H_2SO_4].

This is employed as—

a. Commercial concentrated sulphuric acid (oil of vitriol).

b. Pure concentrated sulphuric acid.

The following method may be recommended for preparing chemically pure sulphuric acid, but it may be observed that pure sulphuric acid can now be so readily obtained from the chemical manufacturer, that it is quite the exception for a chemist to have to prepare it for himself in the laboratory; moreover, to distil it from a glass retort is inconvenient and not without danger.

a. In order to destroy the oxides of nitrogen which are generally present in minute quantity in the commercial acid, 1000 grams of the acid are placed in a porcelain dish with 3 grams of sulphate of ammonia, and heated until copious fumes of sulphuric acid begin to come off. When cool, 4 or 5 grams of coarsely powered binoxide of manganese is added, and the mixture heated to boiling with stirring, in order to convert any arsenious acid present into arsenic acid. (Blondlot.) It is again allowed to cool, and the clear liquid poured off from the sediment into a coated retort, using a long funnel tube. The retort should not be more than half full, and is to be heated directly over charcoal. To prevent bumping, it is advisable to rest the retort on an inverted crucible cover, so that the sides may be heated more strongly than the bottom. The neck of the retort must project so far into the receiver that the acid distilling over drops directly into the body. To cool the receiver by means of water is unnecessary, and even dangerous. To prevent the receiver coming into actual contact with the hot neck of the retort, some asbestos in large fibres is placed between them. When about 10 or 15 grams has passed over, the receiver is changed, and three-fourths of the contents of the retort are then distilled over. This method depends on Bussy and Buignet's discovery that, if the sulphuric acid contains arsenic in the form of arsenic acid, no arsenic passes over when it is distilled.

β. One part of concentrated sulphuric acid is poured into 4 parts of water, and a slow stream of sulphuretted hydrogen is passed into the mixture for some time, keeping the liquid at 70°. The mixture is allowed to remain for several days, and the clear supernatant liquid is then decanted from the precipitate, which consists of sulphur, sulphide of lead, perhaps also sulphide of arsenic; finally the clear liquid is heated in a tubulated retort with the neck inclined obliquely upwards and the tubulure open, until sulphuric-acid fumes escape with the aqueous vapour. This purified acid is fit for many purposes of chemical analysis; if it is wished, however, to free it also from non-volatile substances, it may be distilled from a coated retort as in *a*. As soon as the drops in the neck of the retort become oily, the receiver is changed, and the concentrated acid which then passes over is collected in a separate vessel.

c. Dilute sulphuric acid.—This is prepared by gradually adding 1 part of concentrated sulphuric acid to 5 parts of water in a leaden or porcelain dish, stirring all the while. The sulphate of lead which separates is allowed to subside, and the clear dilute acid decanted.

Tests.—Pure sulphuric acid must be colourless; and when colourless solution of sulphate of protoxide of iron is poured upon it in a test-tube, there should be no brown tint at the plane of contact of the two liquids (nitric acid, hyponitric acid, nitrous acid). When diluted with 20 parts of water, it should not impart a blue tint to a solution of iodide of potassium mixed with starch paste (hyponitric acid, nitrous acid). When diluted with water and poured on to pure zinc, the hydrogen gas evolved must not deposit the slightest trace of arsenic on being passed through a red-hot tube. It must leave no residue when evaporated on platinum, and should remain perfectly clear when diluted with four or five parts of spirit of wine (oxide of lead, ferric oxide, lime). The presence of small quantities of lead is detected most easily by adding some hydrochloric acid to the sulphuric acid in a test-tube; if the plane of contact is marked by turbidity (chloride of lead), lead is present. Sulphurous acid is discovered by the odour after shaking the acid in a half-filled bottle; and selenious acid by the separation of a red deposit of selenium on adding sulphurous acid and hydrochloric acid.

Uses.—For most bases sulphuric acid has a greater affinity than almost any other acid; it is therefore used for the liberation and expulsion of other acids, especially phosphoric, boric, hydrochloric, nitric, and acetic acids. Several substances which cannot exist in an anhydrous state (such as oxalic acid) are decomposed when brought into contact with concentrated sulphuric acid; this decomposition takes place owing to the great affinity which sulphuric acid has for water. The nature of the decomposed substance may in such cases be inferred from the liberated products of decomposition. Sulphuric acid is also frequently used in the preparation of certain gases, more particularly hydrogen and sulphuretted hydrogen. It serves also as a special reagent for the detection and precipitation of baryta, strontia, and lead. What kind of sulphuric acid is to be used, whether the pure acid or the ordinary acid of commerce, whether concentrated or dilute, depends on circumstances which vary in each individual case. The necessary directions on this point will be given hereafter.

When using ordinary English sulphuric acid, it should never be forgotten that it is now often strongly contaminated with the acids of arsenic derived from the pyrites used in its manufacture. Arsenical sulphuric acid of this kind cannot be employed for delicate analytical purposes, and is quite unfit for the preparation of hydrogen, as its action on zinc in the presence of water gives rise to arseniuretted hydrogen, which contaminates the hydrogen.

§ 25.

2. Nitric Acid, HO,NO_5 [HNO_3].

Preparation.—*a.* Nitric acid of commerce sp. gr. at least 1·31,* and as free as possible from chlorine, is heated in a glass retort to boiling, with addition of some nitrate of potassa; the receiver should be kept cool, and the distillate tested from time to time until it no longer precipitates or gives a cloudiness with nitrate of silver solution. The receiver is then changed, and the distillation continued until a trifling quantity only remains in the retort. The distillate should be diluted with water until the sp. gr. is 1·2.

b. Commercial nitric acid of about 1·38 sp. gr. is diluted with two-fifths of its weight of water, and nitrate of silver solution added as long as a precipitate of chloride of silver continues to form; a little more nitrate of silver solution is then added, the precipitate allowed to subside, and the perfectly clear supernatant acid is decanted into a retort or an alembic with ground head; some nitrate of potassa free from chlorine is added, and the distillation proceeded with until only a small quantity remains in the retort, taking care to attend to the proper cooling of the acid which passes over. If necessary, the distillate is diluted with water, until it has a sp. gr. of 1·2.

Tests.—Pure nitric acid must be colourless and leave no residue when evaporated on platinum foil. The addition of solution of nitrate of silver or of nitrate of baryta to the acid diluted with 3 parts of water, should not cause the slightest turbidity. It is advisable to dilute the acid with water before adding these reagents, as otherwise the nitrates will be precipitated. To test for iodic acid and *traces* of sulphuric acid, some of the acid is evaporated to a small bulk, diluted, and a portion tested with nitrate of baryta; bisulphide of carbon is added to the remainder, then a little sulphurous acid, and the whole shaken; if iodic acid be present, the bisulphide will become violet. Nitrous acid is tested for by adding starch paste and iodide of potassium to the nitric acid previously diluted with 5 parts of water. Silver should be tested for by hydrochloric acid.

Uses.—Nitric acid serves as a chemical solvent for metals, oxides, sulphides, oxygen salts, &c. With metals and sulphides of metals, the acid first oxidizes the metal present, at the expense of part of its own oxygen, and then dissolves the oxide to a nitrate. Most oxides are dissolved by nitric acid at once as nitrates; and so are most of the insoluble salts with weaker acids, the latter being expelled by the nitric acid. Nitric acid also dissolves salts with soluble non-volatile acids, such as phosphate of lime, with which it forms nitrate of lime and acid phosphate of lime. Nitric acid is used also as an oxidizing agent: for instance, to convert ferrous into ferric oxide, protoxide of tin into binoxide, &c.

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* A weaker acid will not answer the purpose.

§ 26.

3. Acetic Acid, $HO,C_4H_3O_3 = HO,A$ [$C_2H_4O_2$].

Highly concentrated acetic acid is not required in qualitative analytical processes; the *acidum aceticum* of the British Pharmacopœia, which contains 33 per cent. of glacial acetic acid, and has a sp. gr. of 1·044, fully answers the purpose.

Tests.—Pure acetic acid should leave no residue when evaporated, and, after saturation with carbonate of soda, emit no empyreumatic odour. Sulphuretted hydrogen, nitrate of silver solution, and solution of nitrate of baryta should give no precipitate or cloud with the dilute acid, neither should it be discoloured by sulphide of ammonium after neutralization with ammonia. Solution of indigo must not lose its colour when heated with the acid. Empyreumatic matter is best detected by neutralizing the acid with carbonate of soda, and adding solution of permanganate of potash. If the solution loses its colour and afterwards deposits a brown precipitate, empyreumatic matter is present.

If the acid is not pure, add some acetate of soda and re-distil from a glass retort, but not quite to dryness; if it contains sulphurous acid (in which case sulphuretted hydrogen will produce a white turbidity in it), digest it first with binoxide of lead or finely-pulverized binoxide of manganese, and then distil with acetate of soda.

Uses.—Acetic acid possesses a greater solvent power for some substances than for others, and is used therefore to distinguish between them; thus it serves, for instance, to distinguish oxalate of lime from phosphate of lime. Acetic acid is also used occasionally to acidify liquids where the employment of mineral acids is undesirable.

§ 27.

4. Tartaric Acid, $2HO,C_8H_4O_{10} = 2HO,\bar{T}$ [$C_4H_6O_6$].

Commercial tartaric acid is sufficiently pure for analytical purposes. It should form a clear solution with water; and this should give no coloration, precipitate, or turbidity with sulphuretted hydrogen, oxalate of ammonia or chloride of barium. It is kept best in powder, as its solution suffers decomposition after a time. Before use, it is dissolved in a little water, warming gently.

Uses.—The addition of tartaric acid to solutions of ferric oxide, alumina, and various other oxides of metals, prevents the usual precipitation of these metals by an alkali; this non-precipitation is due to the formation of double tartrates, which are not decomposed by alkalies. Tartaric acid may therefore be employed to effect the separation of these metals from others the precipitation of which it does not prevent.

Tartaric acid forms a sparingly soluble salt with potassa, but not with soda; it is therefore one of our best reagents to distinguish between the two alkalies. Bitartrate of soda answers this latter purpose still better than the free acid. This reagent is prepared by dissolving one of two equal portions of tartaric acid in water, neutralizing the solution with carbonate of soda, then adding the other portion of the acid, and evaporating the solution to the crystallization point. For use, 1 part of the salt is dissolved in 10 parts of water.

b. HYDROGEN ACIDS AND HALOGENS.

§ 28.

1. Hydrochloric Acid, HCl [HCl].

Preparation.—A cooled mixture of 7 parts of concentrated sulphuric acid (free from arsenic and oxides of nitrogen) with 2 of water is poured on to 4 parts of chloride of sodium in a retort; the retort, with slightly raised neck, is then heated on a sand-bath until the evolution of gas ceases, the evolved gas being led by means of a bent tube into a flask containing 6 parts of water, taking care to keep this vessel cool. To prevent the gas from receding, the tube ought only to dip about one line into the water in the flask. When the operation is terminated, the sp. gr. of the acid must be ascertained, and it is then diluted with water until it marks from 1·11 to 1·12. If the acid is required absolutely pure, and perfectly free from every trace of arsenic and chlorine, care must be taken to use sulphuric acid which has been purified from arsenic and the oxygen compounds of nitrogen, according to the directions given in § 24. Pure hydrochloric acid may also be prepared from the crude commercial acid, which usually contains much arsenic. For this purpose a concentrated solution of stannous chloride is added to the crude hydrochloric acid in such quantity that, after remaining 24 hours, a sample of the acid gives a white precipitate with mercuric chloride, indicating that an excess of stannous chloride is still present; the brown precipitate which is formed, and which contains all the arsenic and some tin, is allowed to subside, and the acid separated by decantation and subsequent filtration through an asbestos filter; the acid is then transferred to a retort, from 1 to 5 per cent. of sodium chloride added, according to the amount of sulphuric acid present, and the mixture distilled, the distillate being collected in a receiver, which is not luted to the retort, and which contains 60 parts of water to every 100 parts of acid to be distilled. The distillation is continued until almost all the acid has passed over.*

Tests.—Hydrochloric acid must be perfectly colourless and should leave no residue on evaporation. If it turns yellow when evaporated, ferric chloride is present. It should not impart a blue tint to a solution of iodide of potassium mixed with starch paste (chlorine or ferric chloride), destroy indigo-blue (chlorine), or decolorize a solution made faintly blue with iodide of starch (sulphurous acid). Chloride of barium ought not to produce a precipitate in the highly diluted acid (sulphuric acid). Traces of sulphuric acid, however, cannot be detected in this way. In such cases a relatively large quantity of the hydrochloric acid must be evaporated to a small bulk on the water bath, water added, and the solution tested with chloride of barium. Sulphuretted hydrogen should produce no change in the diluted acid (arsenic). After neutralization with ammonia, sulphide of ammonium must not darken it (iron, thallium). With zinc free from arsenic, it should evolve pure hydrogen free from arsenic.

Uses.—Hydrochloric acid is useful as a solvent for a great many

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* It is advisable to keep concentrated hydrochloric acid in a dark place, as when exposed to a bright light it is apt to become contaminated with chlorine, especially if the bottle is only partly filled. See L. Backelandt, Bull. Acad. Roy. Belg. [3] 11, 194, and H. McLeod, J. Chem. Soc. 1886, Trans. p. 608 [EDITOR].

substances. It dissolves many metals and sulphides of metals forming chlorides, with evolution of hydrogen or of sulphuretted hydrogen. It dissolves oxides and peroxides forming chlorides, in the latter case generally with liberation of chlorine. Salts with insoluble or volatile acids are also converted into chlorides by hydrochloric acid, with separation of the original acid; thus carbonate of lime is converted into chloride of calcium, with liberation of carbonic acid. Hydrochloric acid dissolves salts of non-volatile and soluble acids apparently without decomposing them (phosphate of lime, for example); but the fact is that in cases of this kind a metallic chloride and a soluble acid salt of the acid of the dissolved compound are formed; thus, for instance, in the case of phosphate of lime, chloride of calcium and acid phosphate of lime are formed. With salts of acids which do not form a soluble acid compound with the base present, hydrochloric acid yields metallic chlorides, the liberated acids remaining free in solution (oxalate of lime). Hydrochloric acid is also used as a special reagent for the detection and separation of oxide of silver, mercurous oxide, and lead, and likewise for the detection of free ammonia, with which it produces dense white fumes of chloride of ammonium.

§ 29.

2. Chlorine, Cl, and Chlorine Water.

Preparation.—18 parts of common salt in lumps is mixed with 15 parts of finely pulverized good binoxide of manganese, free from carbonate of lime; the mixture is introduced into a flask, a completely cooled mixture of 45 parts of concentrated sulphuric acid with 21 parts of water is poured upon it, and the flask well shaken: a uniform and continuous evolution of chlorine gas will soon begin, which, when it slackens, may be easily increased again by the application of a gentle heat. This method of Wiggers is excellent, and can be highly recommended. The chlorine gas evolved is first passed through a flask containing a little water, and then into a bottle filled with cold water, the process being continued until the water is saturated. If chlorine water is required quite free from bromine, the washing flask is changed after about one-half of the chlorine has been expelled, and the gas which then passes over is led into a fresh bottle filled with water. If the chlorine water is wanted quite free from hydrochloric acid, the gas must be passed through a U tube containing binoxide of manganese. The chlorine water must be kept in a cellar and carefully protected from the action of light; for, if this precaution is neglected, it soon suffers decomposition, being converted into hydrochloric acid, with evolution of oxygen (resulting from the decomposition of water). Smaller quantities, intended for use in the laboratory, are best kept in a stoppered bottle protected from the influence of light by a case of pasteboard, or in a black glass bottle.

Tests.—Chlorine water should smell very strongly of chlorine, and when evaporated in a porcelain basin it must leave no residue. It should contain no hydrochloric acid, or only very little, so that after being agitated with metallic mercury until the odour of chlorine has disappeared, and filtered, the solution should be only faintly acid. When chlorine water is agitated with bisulphide of carbon and finely divided zinc, the bisulphide should not become even transiently red brown (bromine).

Uses.—Chlorine has a greater affinity than either iodine or bromine for metals and for hydrogen. Chlorine water is therefore a useful reagent for expelling iodine or bromine from their compounds. Chlorine serves moreover to effect the solution of certain metals (gold, platinum), to decompose metallic sulphides, to convert sulphurous acid into sulphuric acid, ferrous oxide into ferric oxide, &c.; and also to destroy organic substances, as in presence of these it withdraws hydrogen from the water, whilst the liberated oxygen combines with the vegetable matters and decomposes them. For the latter purpose, it is better to produce the chlorine in the liquid which contains the organic substance; this may be done by adding hydrochloric acid to the solution, heating the mixture, and then adding chlorate of potassa. This gives rise to the formation of chloride of potassium, water, free chlorine, and hypochlorous acid which acts like chlorine.

§ 30.

3. Nitro-Hydrochloric Acid. *Aqua regia.*

Preparation.—1 part of pure nitric acid is mixed with from 3 to 4 parts of pure hydrochloric acid.

Uses.—Nitric acid and hydrochloric acid decompose each other, forming free chlorine water and nitrosyl chloride (chloronitrous acid, oxychloride of nitrogen);

$$HO,NO_5 + 3HCl = 2Cl + NO_2Cl + 4HO$$

$$[HNO_3 + 3HCl = Cl_2 + NOCl + 2H_2O].$$

This decomposition ceases as soon as the liquid is saturated with the gas; but it recommences the instant this state of saturation is disturbed by the application of heat or by decomposition of the acid. The presence of the free chlorine, and also, but in a very subordinate degree, that of the nitrosyl chloride, makes aqua regia the most powerful solvent for metals (with the exception of those which form insoluble compounds with chlorine). Nitro-hydrochloric acid is principally used to dissolve gold and platinum, which are insoluble both in hydrochloric and in nitric acid, and also to decompose various metallic sulphides, such as cinnabar, pyrites, &c.

§ 31.

4. Hydrofluosilicic Acid, HF,SiF_2 $[H_2SiF_6]$.

Preparation.—An intimate mixture is made of 1 part of perfectly dry fluor spar in powder * with 1¼ part of powdered glass, or 1 part of powdered ignited flint, or 1 part of quartz sand which has been carefully freed from dust by washing and then ignited; 6 parts of concentrated sulphuric acid free from arsenic are poured on to the mixture in a retort, and carefully mixed by shaking the vessel. As the mixture froths up when it gets warm, the retort should not be more than one-third filled. The neck of the retort must be connected air-tight with a small tubulated receiver, and the tubulus of the latter again, by means of india-rubber, with a wide glass tube twice bent at a right angle. To the descending limb of the glass tube a funnel is attached by means of

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* If the fluor spar contains organic matter or metallic sulphides, it must be ignited with free access of air before use.

india-rubber; this funnel is lowered into a beaker containing 4 parts of water. The disengagement of the gaseous fluoride of silicon, which commences even in the cold, is assisted by moderately heating the retort; towards the end of the process, a pretty strong heat should be applied. Every gas bubble produces in the water a precipitate of hydrated silicic acid, with simultaneous formation of hydrofluosilicic acid, $3SiF_2 + 2HO = 2(HF,SiF_2) + SiO_2$ [$SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$]. The precipitated hydrate of silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the descending limb of the tube cannot be allowed to dip directly into the water, as in that case it would soon be choked. It sometimes happens in the course of the operation, especially towards the end, that complete channels of silica are formed in the gelatinous liquid, through which the gas passes to the surface without undergoing decomposition if the liquid is not occasionally stirred. When the evolution of gas has entirely ceased, the gelatinous paste is thrown on to a linen cloth, the liquid squeezed out, and subsequently filtered. The filtrate is kept for use.

Tests.—Hydrofluosilicic acid should not produce any precipitate in solutions of salts of strontia (sulphate of strontia).

Uses.—With hydrofluosilicic acid, bases yield water and metallic silicofluorides. Many of these are insoluble, whilst others are soluble; the latter, therefore, may be distinguished from the former by means of this reagent. In the course of analysis, hydrofluosilicic acid is applied simply for the detection and separation of baryta.

c. SULPHUR ACIDS.

§ 32.

1. **Sulphuretted Hydrogen** (*Hydrosulphuric Acid*), HS [H_2S].

Preparation.—Sulphuretted hydrogen gas is evolved best from sulphide of iron, which is broken into small lumps and then treated with dilute sulphuric or hydrochloric acid.* Fused sulphide of iron may be procured so cheaply in commerce that it is hardly worth while to take the trouble of preparing it. However, if you wish to prepare it yourself, this may be done by heating iron turnings, or 1 to 1½ inch iron nails, in a covered Hessian crucible to a white heat, and then adding small lumps of roll-sulphur until the entire contents of the crucible are in fusion. As soon as this takes place, the fused mass is poured on to sand, or into an old Hessian crucible. Or a hole may be made in the bottom of the crucible in which the mass is fused, when the sulphide of iron will run through this hole as fast as it is formed, and may be received in a coal-shovel placed in the ash-pit. Or an intimate mixture of 30 parts of iron filings with 21 parts of flowers of sulphur may be projected in small portions into a red-hot crucible, awaiting always the incandescence of the portion last introduced before a fresh one is added. When the whole of the mixture has been thus introduced into the crucible, the latter is closely covered, and exposed to a more intense heat, sufficient to cause the sulphide of iron to fuse more or less.

The gas is evolved in the apparatus illustrated by fig. 31. Water is poured on to the sulphide of iron in *a*, concentrated sulphuric acid introduced through the thistle funnel *b*, and the mixture shaken; the

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* In respect of the preparation of sulphuretted hydrogen for medico-legal purposes, see § 225.

evolved gas is washed in *c*. When a sufficient quantity of gas is evolved, the acid liquid should be poured off the still undecomposed sulphide of iron, the bottle repeatedly rinsed with water, again charged with water, and the apparatus kept for the next operation. If this be neglected, the apparatus will soon become incrusted with crystals of sulphate of protoxide of iron, which is apt to interfere when the apparatus is again required for the evolution of gas.

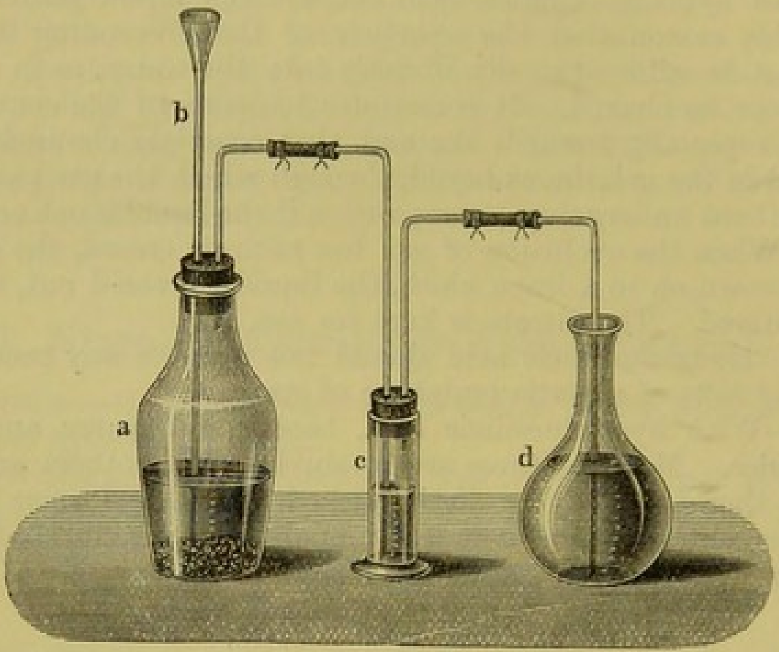

Fig. 31.

For larger laboratories, or for a chemist who has frequently to use large quantities of sulphuretted hydrogen, a gasometer may be used, or the following apparatus, devised by Brugnatelli, and modified as shown in fig. 32. The flask, B, is provided with a tubulure at *a*;[*] the neck is filled with broken glass, and the body with sulphide of iron in small pieces. The india-rubber stopper in the neck contains two tubes—*s* (which may sometimes be omitted, see next page), and the short tube *c*, which must have *a bore of* 1 cm. *at least;* the latter is connected with the tube *d* of the same size by means of indiarubber. The tube *e* extends almost to the bottom of A, and is connected on the other side with the bottle M by means of the india-rubber tube *f*. M is closed with a cork or india-rubber stopper, containing a small tube open at both ends. The stopper in the tubulure *a* of the flask B contains a glass tube, which is in connection with a leaden pipe *q;* the latter conducts the gas, and is supplied with the brass cocks *h*, *b*, *i i*.

To set the apparatus going, open *h*, and fill M with common hydrochloric acid, as free from arsenic as possible, and diluted with twice its volume of water. The liquid will pass into A, fill the bottle, and rise through *d* and *c* into the flask B. As soon as the neck of the latter is nearly full, close the cock *h*, and take care that M is not more than half full. If now *b* is opened, and also *i*, the acid rises up to the sul-

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[*] Flasks with a lateral tubulure, such as are generally used for receivers, are also applicable, and indeed one of these will be found in Brugnatelli's original drawing (Zeit. anal. Chem., 6, 390). But it is certainly better to have the tubulure at the top.

phide, the evolution of gas commences and proceeds with great regularity, since the wide tubes *c* and *d* allow the constant descent of the solution of protochloride of iron and ascent of fresh acid. If the acid does not rise in B as high as is wished, one or two blocks of wood should be placed under M. The current of gas may be entirely regulated by raising or lowering M, as Brugnatelli recommends, but the cocks will be found necessary in large laboratories where the gas has to be passed into several different solutions at the same time. If the apparatus is not required for some time, M should be placed lower; the liquid will thus sink in B, and ceasing to be in contact with the sulphide of iron, the evolution of gas will cease. In this case, if the evolution of gas in B is not rapid enough to fill the space vacated by the liquid, air will enter through the tube *s*. If the tube *s* is present at all, it should be sufficiently long to prevent the exit of liquid when there is a pressure of gas. After the acid has flowed from B the still moist sulphide of iron may continue evolving gas, but this will merely occasion more acid to pass from A to M. The tube *s* may be left out when cocks are used. Under these circumstances, the liquid in B will descend more slowly on lowering M, since the space filled by the descending acid has to be occupied by sulphuretted hydrogen.

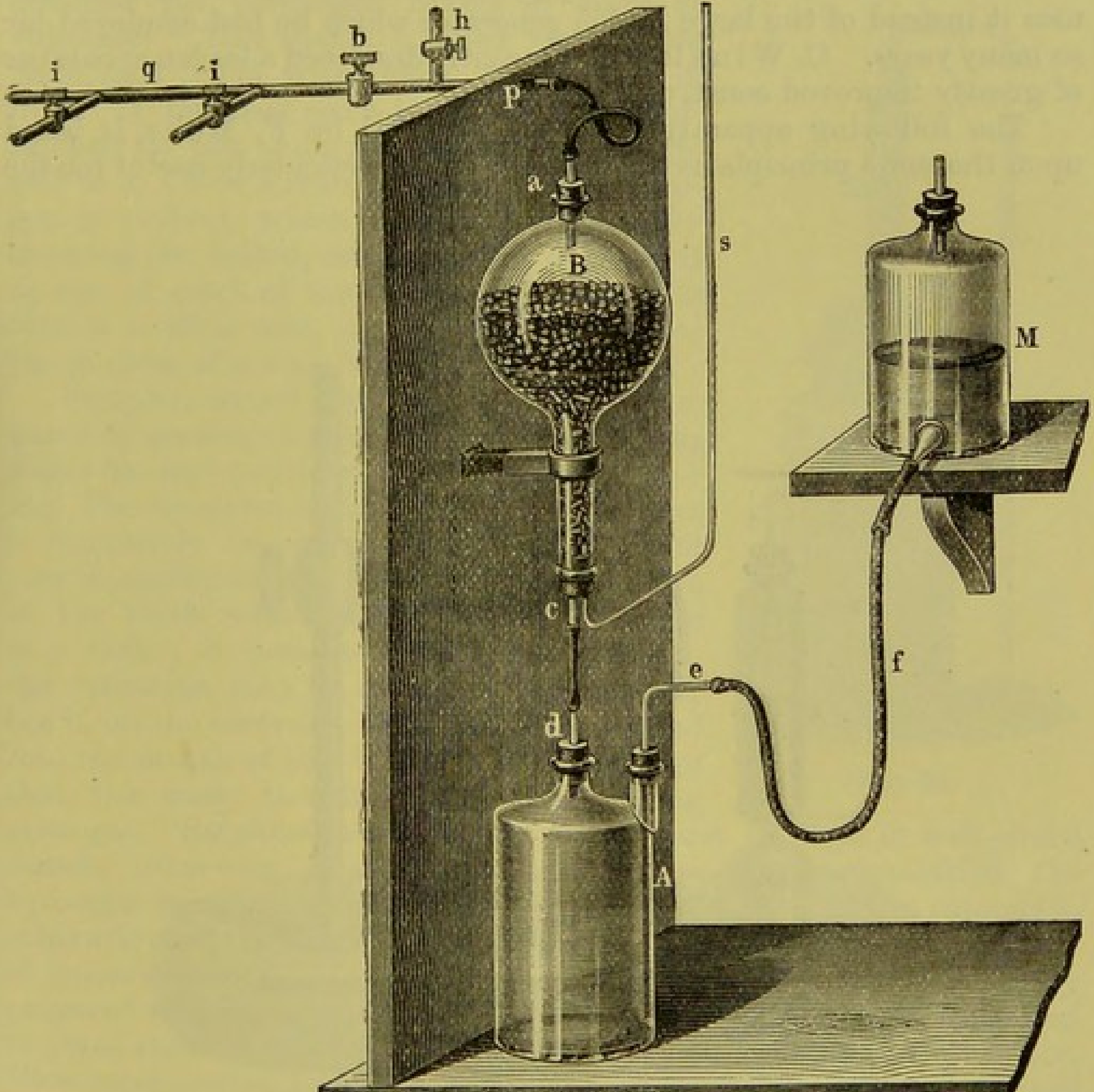

Fig. 32.

When there are no cocks, however, *s* is essential: otherwise on lowering M, the liquid through which the gas is passing might recede into the apparatus. This inconvenience may be easily prevented where cocks are provided, simply by closing *b* before lowering M. The gas from *i i* is led through wash-bottles, or in winter through U tubes filled with wool before being used.

When the acid is finally exhausted, M is placed lower than A, and the air-cock *h* is opened, if the tube *s* is not present. All the liquid then passes into M, and can be poured away.

The author found that this apparatus worked so well that he now uses it instead of the large leaden generator which he had employed for so many years. C. Winkler* has recently described a leaden apparatus of greatly improved construction.

The following apparatus (fig. 33), devised by F. Mohr, is based upon the same principle as the above; it is particularly useful for the evolution of small quantities of the gas. A is an eprouvette, a well-known piece of apparatus, used for drying large quantities of gas with chloride of calcium; at *b* is a perforated disk of lead, and above it lumps of sulphide of iron. To the end of *d* is fixed, by means of india-rubber *a*, a small piece of wide glass tube, which is filled with cotton wool, and is intended to stop any particles of protochloride of iron which may be spirted up. *c* is a glass cock with a long wooden handle, which may be replaced by a clip; *e* contains a solution of carbonate of soda, to prevent the escape of the sulphuretted hydrogen from the solution of proto-

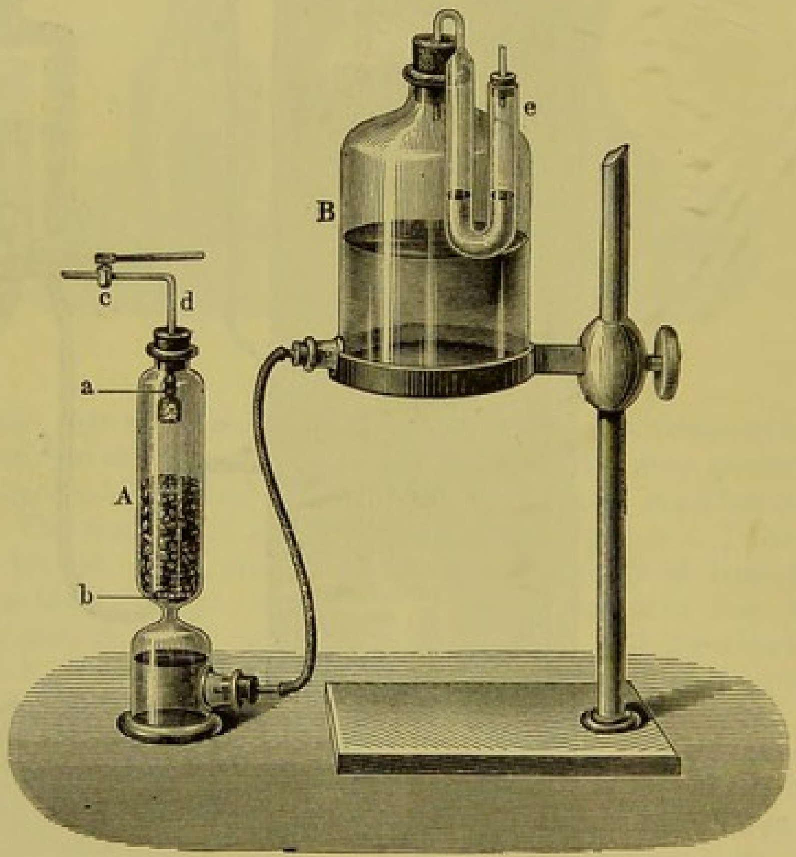

Fig. 33.

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* Zeit. anal. Chem., 21, 386.

chloride of iron, and to protect the latter from the action of the air. The acid used here is a mixture of common hydrochloric acid with one or two measures of water.

There are many other forms of apparatus used for the same purpose. That devised by Pohl is simple and convenient to use. It is shown in fig. 34. The bottle A, which contains dilute sulphuric acid, should hold from 2 to 2½ litres. The solid glass rod G, measuring at least 9 mm. in diameter, and with the upper end ground, fits pretty tightly into the india-rubber stopper B, so that it requires a certain degree of force to move it upwards or downwards. To the lower end of this rod is attached the perforated basket K, made of vulcanite. This basket is lined with coarse linen, and filled with lumps of sulphide of iron. If the glass rod G is pushed down sufficiently far just to dip into the dilute sulphuric acid in A, a slow stream of sulphuretted hydrogen is evolved, which may be increased by lowering the basket, or stopped by drawing it up out of reach of the fluid in A. The wide tube R is filled with cotton wool, and serves the purpose of a wash-bottle.

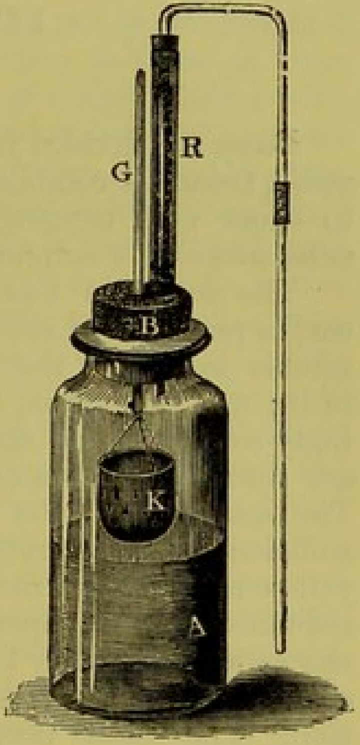

Fig. 34.

Sulphuretted hydrogen water is prepared by passing the gas into very cold water, which has been previously freed from air by boiling. The operation is continued until the water is completely saturated with the gas, which may be readily ascertained by closing the mouth of the bottle with the thumb, and shaking it a little; if pressure is felt from within, the operation may be considered at an end; but if, on the contrary, the thumb feels sucked into the mouth of the bottle, it is a sure sign that the water is still capable of absorbing more gas. Sulphuretted hydrogen water must be kept in well-closed vessels, otherwise it will soon suffer complete decomposition, the hydrogen being oxidized to water, and a small portion of the sulphur to sulphuric acid, the rest of the sulphur separating as such. The best way of preserving it unaltered for a very long time is to pour the freshly prepared solution immediately into small phials, to cork these well, and to place them in an inverted position in small jars filled with water. Pure sulphuretted hydrogen water should be perfectly clear and smell strongly of the gas; when treated with ferric chloride, it should yield a copious precipitate of sulphur. Addition of ammonia should not cause it to blacken, and when evaporated on platinum it should leave no residue.

Uses.—Sulphuretted hydrogen has a strong tendency to react with metallic oxides, forming water and metallic sulphides, and as the latter are mostly insoluble in water they are precipitated. The conditions under which the precipitation of these sulphides takes place differ materially; by altering or modifying the conditions we may therefore divide the whole of the precipitable metals into groups, as will be explained in Section III. On this account, sulphuretted hydrogen is an invaluable agent for effecting the separation of metals into groups. Some of the precipitated sulphides exhibit a characteristic colour indicative of the individual metals which they respectively contain. The great facility with which sulphuretted hydrogen is decomposed renders this substance also a useful reducing agent for many compounds; thus it serves, for instance, to reduce salts of sesquioxide of iron to salts of protoxide, chromic acid to the state of sesquioxide of chromium, &c. In these processes of reduction, the sulphur becomes separated in the form of a fine white powder. Special circumstances determine as to whether it is better to employ the sulphuretted hydrogen in the gaseous form or in aqueous solution.

III. Bases and Metals.

§ 33.

Bases are divided into oxygen bases and sulphur bases. The former result from the combination of metals or of compound radicals analogous to them with oxygen, the latter from the combination of the same substances with sulphur.

The oxygen bases may be classified as alkalies, alkaline earths, earths proper, and oxides of the heavy metals. The alkalies are readily soluble in water; the alkaline earths dissolve with greater difficulty in it; and magnesia, the last member of the class, is only very sparingly soluble. The earths proper and the oxides of the heavy metals are insoluble in water or nearly so (except protoxide of thallium). The solutions of the alkalies and alkaline earths are caustic when sufficiently concentrated; they have an alkaline taste, change the yellow colour of turmeric paper to brown, and restore the blue tint of reddened litmus paper; they saturate acids completely, so that even the salts which they form with strong acids do not change vegetable colours, whilst those with weak acids generally have an alkaline reaction. The earths proper and the oxides of the heavy metals likewise combine with acids to form salts, but, as a rule, they do not entirely take away the acid reaction of the latter.

The sulphur bases formed by the combination of the metals of the alkalies and alkaline earths with sulphur are soluble in water. The solutions have a strongly alkaline reaction. The other sulphur bases are insoluble in water. With sulphur acids, all sulphur bases form sulphur salts.

a. Oxygen Bases.

α. Alkalies.

§ 34.

1. Hydrate of Potassa, KO,HO [KHO], and Hydrate of Soda, NaO,HO [$NaHO$].

The preparation of perfectly pure potassa or soda is a difficult operation. It is advisable therefore to prepare, besides perfectly pure caustic alkali, also some which is not quite pure, and some which being free from certain impurities may in many cases be safely substituted for the pure substance.

a. Common solution of soda.—3 parts of crystallized carbonate of soda of commerce and 15 parts of water are put into a clean cast-iron pan provided with a lid, and heated to boiling; to this solution is added, in small portions at a time, thick milk of lime prepared by pouring 3 parts of warm water on to 1 part of quicklime, and allowing the mixture to remain in a covered vessel until the lime is reduced to a uniform pulpy mass. The liquid in the pan should be kept boiling while the milk of lime is being added, and for a quarter of an hour longer; a small portion is then filtered off, and tested to see whether the filtrate still effervesces with hydrochloric acid. If this is the case, the boiling must be continued, and if necessary some more milk of lime is added to the fluid. When the solution is perfectly free from carbonic acid, the pan is covered, and the liquid allowed to cool a little; the nearly clear solution is then drawn off from the residuary sediment, by means of a siphon filled with water, and transferred to a glass carboy. The residue is boiled a second and a third time with water, and the clear liquid drawn off in the same way. The carboy is carefully closed, and the lime suspended in the liquid is allowed to subside completely; the clear solution is then poured back into the iron pan, which in the meantime has been scoured clean, and is evaporated to 6 or 7 parts. The solution so prepared contains from 9 to 10 per cent. of soda, and has a sp. gr. of from 1·13 to 1·15. If it is wished to filter a solution of soda which is not quite clear, a covered funnel should be used, which has been charged first with lumps of white marble and then with powdered marble, the fine dust being rinsed out with water before the filter is used (Gräger). Solution of soda should be clear, colourless, and as free as possible from carbonic acid; sulphide of ammonium should not blacken it. Traces of silicic acid, alumina, and phosphoric acid, and small quantities of chloride of sodium and sulphate of soda are usually found in a solution of soda prepared in this manner, and render it unfit for use in very accurate experiments. Soda solution is kept best in bottles closed with ground glass caps. In default of capped bottles, common ones with well-ground stoppers may be used, in which case the neck must be wiped perfectly dry and clean inside, and the stopper coated with paraffin; if this precaution is neglected, it will be found impossible after a time to remove the stopper, particularly if the bottle is only rarely opened.

b. Hydrate of potassa purified with alcohol.—Some caustic potassa of commerce is dissolved in rectified spirit of wine in a stoppered bottle by digestion and shaking; the solution is allowed to remain until clear, decanted, or filtered if necessary, and the clear solution evaporated in a silver dish over the gas burner or spirit lamp until no more vapours escape; adding some water from time to time, during the evaporation, to prevent blackening of the mass. The silver dish is then placed in cold water until it has sufficiently cooled, the cake of caustic potash removed from the dish, broken into coarse lumps in a hot mortar, and kept in a well-closed glass bottle. When required for use, a small lump of it is dissolved in water.

The hydrate of potassa so prepared is sufficiently pure for most purposes; it contains, indeed, a minute trace of alumina, but is usually free from phosphoric acid, sulphuric acid, and silicic acid. The solution should remain clear on the addition of sulphide of ammonium; hydrochloric acid should only produce a barely perceptible effervescence in it. When the solution is acidified with hydrochloric acid and evaporated to dryness, it should leave a residue which yields a clear solution when dissolved in water. The solution acidified with hydrochloric acid, and then mixed with ammonia in the least possible excess, should not show any flocks of alumina, at least until it has stood in a warm place for several hours. The solution after being acidified with nitric acid should not give any precipitate with a nitric acid solution of molybdate of ammonia.

c. Hydrate of potassa prepared with baryta.—Pure crystals of baryta (§ 36) are dissolved in hot water, and pure sulphate of potassa added to the solution until a portion of the filtered liquid, acidified with hydrochloric acid and diluted, no longer gives a precipitate on the addition of a further quantity of the sulphate (16 parts of crystals of baryta require 9 parts of sulphate of potassa). When the turbid solution becomes clear, it is decanted from the sulphate of baryta, and evaporated in a silver dish as in *b*. The hydrate of potassa so prepared is perfectly pure, except that it contains a trifling admixture of sulphate of potassa, which is left behind on dissolving the hydrate in a little water. This hydrate is but rarely required, its use being in fact exclusively confined to the detection of minute traces of alumina.

Uses.—The great affinity which the fixed alkalies have for acids renders these substances powerful agents in effecting the decomposition of the salts of most bases, and consequently precipitates those bases which are insoluble in water. Many of the oxides thus precipitated redissolve in an excess of the precipitant, as, for instance, alumina, sesquioxide of chromium, and oxide of lead; whilst others remain undissolved, such as ferric oxide, oxide of bismuth, &c. The fixed alkalies serve therefore to separate the former from the latter. Potassa and soda likewise dissolve many salts (such as chromate of lead), sulphur compounds, &c., and are useful for separating and distinguishing them from other substances. Many of the oxides precipitated by the action of potassa or soda exhibit peculiar colours, or possess other characteristic properties which may serve to detect the individual metals which they respectively contain; such, for instance, are the precipitates of hydrate of protoxide of manganese, hydrate of protoxide of iron, mercurous oxide, &c. As fixed alkalies expel ammonia from its salts, we are by this means enabled to detect that compound by its odour, its action on vegetable colours, &c.

§ 35.

2. Ammonia, NH_3 [NH_3].

Preparation.—Ammonia is generally prepared in cast-iron vessels on a large scale, and it will be found more economical to buy it.* For preparing it on a small scale, the following method answers well. 4 parts of chloride of ammonium, either crystallized or in lumps, are introduced into a flask together with the dry hydrate of lime prepared from 5 parts of quicklime, the two mixed by shaking, and enough water is added cautiously to make the powder agglomerate into lumps. The flask is then placed on a sand bath and connected with a rather large wash-bottle and delivery tube. A small quantity of water is put in the wash-bottle, and about 10 parts of water in the flask destined to absorb

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* An excellent method for preparing ammonia in rather large quantities will be found in Zeit. anal. Chem., 1, 186.

the gas; the latter being placed in cold water. On applying heat, the evolution of gas begins; the heating is continued until no more bubbles appear, when the cork of the flask must be taken out to prevent the liquid from receding. The solution of ammonia contained in the washing bottle is impure, but that contained in the receiver is quite pure. It should be diluted with water until the sp. gr. is about 0·96 = 10 per cent. of ammonia, and kept in bottles closed with ground stoppers.

Tests.—Solution of ammonia should be colourless, and ought not to leave the least residue on evaporation in a platinum dish. When heated with an equal volume of lime water, it should cause no turbidity, at least not to a marked extent (carbonic acid). After supersaturation with nitric acid, no turbidity should be produced either by solution of nitrate of baryta or by nitrate of silver, and sulphuretted hydrogen should not impart to it the slightest colour. On neutralizing the ammonia with dilute hydrochloric acid, it should remain colourless, and should not emit any empyreumatic odour.

Uses.—Solution of ammonia, *liquor ammon.*, is really only a solution of ammonia in water, but it is sometimes convenient to consider it as a solution of oxide of ammonium,

$$NH_3 + HO = NH_4O \qquad [2NH_3 + H_2O = (NH_4)_2O].$$

On this assumption, solution of ammonia may be regarded as analogous to solution of potassa or soda; this greatly simplifies the explanation of all its reactions, the oxygen salts resulting from the neutralization of oxygen acids by solution of ammonia being also assumed to contain oxide of ammonium NH_4O, instead of ammonia, NH_3. Ammonia is one of the most frequently used reagents. It is especially useful for saturating acid liquids, and also for the precipitation of a great many metallic oxides and earths; many of these precipitates redissolve in excess of ammonia, as, for instance, the oxides of zinc, cadmium, silver, copper, &c., whilst others are insoluble in free ammonia. This reagent serves therefore to separate and distinguish the former from the latter. As some of these precipitates, as well as their solutions in ammonia, exhibit peculiar colours, they at once serve to detect the metals which they respectively contain.

Many of the oxides which are precipitated by ammonia from neutral solutions are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the ammonia salt formed in the process. Compare § 53.

β. Alkaline Earths.

§ 36.

1. Hydrate of Baryta, BaO,HO [BaH_2O_2].

Preparation.—There are a great many ways of preparing hydrate of baryta; but as witherite is easily and cheaply procurable, the following method is preferable to all others: 100 parts of finely pulverized witherite are intimately mixed with 10 parts of powdered charcoal and 5 parts of resin, the mixture is introduced into an earthenware pot, the lid is luted on with clay, and the vessel is then heated in a tile-kiln. The baked mass is powdered, boiled repeatedly with water in an iron pot, and filtered into flasks which are closed and allowed to remain until cold, when large quantities of crystals of hydrate of baryta, $BaO,HO + 8aq$ [$BaH_2O_2,8H_2O$], make their appearance. The crystals are drained in properly covered funnels, dried rapidly between sheets of blotting paper, and kept in well-closed bottles. For use, 1 part of the crystals is dissolved in 20 parts of water, with the aid of heat, and the solution filtered. The baryta water so prepared is purer than the mother liquor running off from the crystals. The residue, which is insoluble in water, and consists of undecomposed witherite and charcoal, is turned to account in the preparation of chloride of barium.

Tests.—Baryta water, after precipitation of the baryta by pure sulphuric acid, should give a filtrate which will remain clear when mixed with spirit of wine, and leave no fixed residue when evaporated in a platinum crucible.

Uses.—Caustic baryta, being a strong base, throws down the earths and metallic oxides insoluble in water from the solutions of their salts. In the course of analysis, it is used merely to precipitate magnesia. Baryta water may also be used to precipitate those acids which form insoluble compounds with this base; with this object, it is used to detect carbonic acid, to remove sulphuric acid, phosphoric acid, &c.

§ 37.

2. Hydrate of Lime, CaO,HO [CaH_2O_2].

a. Hydrate of lime in powder, and *b.* Lime water, are required.

The former is obtained by slacking pure calcined lime in lumps, in a porcelain dish, with half its weight of water. The heat developed by the combination of the lime with the water is sufficient to evaporate the excess of water. The hydrate of lime should be kept in a well-stoppered bottle.

To prepare lime water, hydrate of lime is digested for some time with cold distilled water, the mixture being shaken occasionally; the undissolved portion of lime is allowed to subside, the clear liquid decanted, and kept in well-stoppered bottles. If the lime water is required quite free from all traces of alkalies, baryta and strontia, which are almost invariably present in hydrate of lime prepared from calcined limestone, the lime is washed two or three times by decantation and the pure lime water is made from the residual lime.

Tests.—Lime water should impart a strongly-marked brown tint to turmeric paper, and give a fair precipitate with carbonate of soda. It speedily loses these properties on exposure to the atmosphere, and is thereby rendered unfit for analytical purposes.

Uses.—Lime forms insoluble salts with many acids and with other soluble salts. Lime water therefore serves to distinguish the former acids, which it precipitates from their solutions, from the latter, which it does not precipitate. Many of the precipitable acids are thrown down only under certain conditions, for instance, on boiling (citric acid); so that by altering these conditions we have a ready means of distinguishing between them. Lime water is used in analysis principally for detecting carbonic acid, and also to distinguish between citric acid and tartaric acid. Hydrate of lime is used chiefly to liberate ammonia from ammonia salts.

γ. Heavy Metals and their Oxides.

§ 38.

1. Zinc, Zn [Zn].

Zinc of good quality is selected, which should leave but little residue when dissolved in dilute sulphuric acid, and, above all, must be perfectly free from arsenic. The method described in § 132, 10, will serve to detect the presence of the slightest trace of the latter. The metal is fused and poured from a height of 4 or 5 feet, in a thin stream, into a large vessel of water. Zinc which contains arsenic must be rejected, as there is no simple process of purification known which will remove every trace of arsenic (Eliot and Storer).*

Uses.—In qualitative analysis zinc is used for preparing hydrogen, also arseniuretted and antimoniuretted hydrogen gases (compare § 131, 10, and § 132, 10); it is also employed to precipitate some metals from their solutions; the zinc simply displacing the other metal,

$$CuO,SO_3 + Zn = ZnO,SO_3 + Cu \qquad [CuSO_4 + Zn = ZnSO_4 + Cu].$$

Zinc is sometimes used in the detection of sulphurous acid and phosphorous acid; before being used for this purpose, it must be tested for sulphide of zinc or phosphide of zinc, as the case may be, see §§ 139 and 148.

2. Iron, Fe [Fe].

Iron reduces many metals and precipitates them from their solutions in the metallic state. It is used especially for the detection of copper, which is precipitated upon it with its characteristic colour. Any clean surface of iron, such as a knife-blade, a needle, a piece of wire, &c., will serve for this purpose.

3. Copper, Cu [Cu].

Copper is used to effect the reduction of mercury, and sometimes of arsenic; any clean surface of copper, such as copper foil or copper wire, may be employed for this purpose.

§ 39.

4. Hydrate of Oxide of Bismuth, BiO_3,HO [$BiHO_2$].

Preparation.—Bismuth, freed from arsenic by fusion with *hepar sulphuris*, is dissolved in dilute nitric acid, the solution diluted until a slight permanent precipitate is produced, and then filtered and evaporated until it crystallizes. The crystals are washed with water containing nitric acid, and triturated with water, ammonia in excess is then added, and the mixture allowed to digest for some time; the white precipitate thus produced is collected, washed, and dried.

Tests.—The hydrate of bismuth (commercial basic nitrate of bismuth

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* According to Gunning (Scheikundige Bijdragen, Deel I. Nr. 1, p. 113), the purification may be effected by repeated fusion with a mixture of carbonate of soda and sulphur, whilst Selmi (Zeit. anal. Chem., 22, 76) states that the arsenic may be removed by treating the melted zinc with chloride of ammonium.

may also be used if it is free from arsenic and antimony) dissolved in dilute nitric acid is precipitated with sulphuretted hydrogen, and a part of the precipitated sulphide is treated with ammonia and filtered, the remainder is treated with sulphide of ammonium and filtered. The filtrates are then mixed with hydrochloric acid in excess; the first should give no precipitate, the second only a white precipitate of sulphur.

Uses.—When teroxide of bismuth is boiled with alkaline solutions of metallic sulphides, it reacts with them forming metallic oxides and sulphide of bismuth. It is also used to convert tersulphide and pentasulphide of arsenic into arsenious and arsenic acids.

b. SULPHUR BASES.

§ 40.

1. Sulphide of Ammonium, NH_4S [$(NH_4)_2S$].

a. Colourless protosulphide of ammonium, and
b. Yellow polysulphide of ammonium, are employed.

Preparation.—*a.* Sulphuretted hydrogen gas is passed through 3 parts of solution of ammonia until no further absorption takes place; 2 parts more of the same solution of ammonia are then added. The action of sulphuretted hydrogen on ammonia gives rise to the formation, first, of NH_4S [$(NH_4)_2S$], then of NH_4S,HS [NH_4,HS]; on adding to the product solution of ammonia equal in volume to that which has been saturated, the ammonia reacts with the hydrosulphide of sulphide of ammonium, and protosulphide of ammonium is formed. Only two-thirds of this quantity of solution of ammonia should be added, however, as it is better that the reagent should contain a little hydrosulphide of sulphide of ammonium than that free ammonia should be present. Hydrosulphide of sulphide of ammonium has usually been employed hitherto, instead of the simple protosulphide; this is unnecessary, and tends to increase the smell of sulphuretted hydrogen in the laboratory, as the hydrosulphide gives off that gas in contact with metallic sulphur acids.

Sulphide of ammonium should be kept in well-corked bottles. It is colourless at first, and deposits no sulphur on the addition of an acid. On exposure to the air, however, it acquires a yellow tint, due to the formation of bisulphide of ammonium, ammonia and water, thus:

$$2NH_4S+O=NH_4S_2+NH_3+HO \quad [4(NH_4)_2S+O_2=2(NH_4)_2S_2+4NH_3+2H_2O].$$

By the continued action of the oxygen of the air, still higher sulphides are formed at first, but afterwards sulphur is deposited, and nothing remains in solution but ammonia and hyposulphite of ammonia. The hyposulphite is formed in the manner shown in the equation:

$$NH_4S_2+O_3=NH_4O,S_2O_2 \quad [2(NH_4)_2S_2+3O_2=2(NH_4)_2S_2O_3].$$

b. Sulphide of ammonium which has turned yellow by moderate exposure to the air may be used for all the purposes requiring the employment of yellow sulphide of ammonium. The yellow sulphide may also be expeditiously prepared by digesting the protosulphide with sulphur. All kinds of yellow sulphide of ammonium deposit sulphur and become turbid and milky on being mixed with acids.

Tests.—Sulphide of ammonium should strongly emit the odour peculiar to it; with acids it should evolve abundance of sulphuretted hydrogen; the evolution of gas may be attended by the separation of a pure white precipitate, but no other precipitate should be formed. It should leave no residue when evaporated and heated to redness in a platinum dish. It should not precipitate or render turbid solution of magnesia or solution of lime even on heating (carbonate of ammonia or free ammonia).

Uses.—Sulphide of ammonium is one of the reagents most frequently employed. It is used (*a*) to precipitate those heavy metals which sulphuretted hydrogen fails to throw down from acid solutions, such as iron, cobalt, &c.,

$NH_4S + FeO,SO_3 = FeS + NH_4O,SO_3$ [$(NH_4)_2S + FeSO_4 = FeS + (NH_4)_2SO_4$];

(*b*) to separate the metallic sulphides thrown down from acid solutions by sulphuretted hydrogen into two groups, as it dissolves some of them to sulphur salts, as, for instance, the sulphides of arsenic and antimony, &c., whilst others remain undissolved, such as sulphide of lead, sulphide of cadmium, &c. The sulphide of ammonium used for this purpose must contain an excess of sulphur if the metallic sulphide to be dissolved will dissolve only as a higher sulphide, as, for instance, SnS [SnS], which dissolves with ease only as SnS_2 [SnS_2].

From solutions of salts of alumina and sesquioxide of chromium, sulphide of ammonium precipitates hydrates of these oxides, with escape of sulphuretted hydrogen, as the sulphur compounds corresponding with these oxides cannot be formed in the wet way:

$$Al_2O_3,3SO_3 + 3NH_4S + 6HO = Al_2O_3,3HO + 3(NH_4O,SO_3) + 3HS$$

$$[Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S].$$

Salts insoluble in water are thrown down unaltered by sulphide of ammonium from their solutions in acids; for example, phosphate of lime is precipitated unaltered from its solution in hydrochloric acid.

§ 41.

2. Sulphide of Sodium, NaS [Na_2S].

Preparation.—The same as sulphide of ammonium, except that solution of soda is substituted for solution of ammonia. It is filtered, if necessary, and the solution kept in well-stoppered bottles. If required to contain some higher sulphide of sodium it must be digested with powdered sulphur.

Uses.—Sulphide of sodium must be substituted for sulphide of ammonium in the separation of sulphide of copper from sulphur compounds soluble in alkaline sulphides (*e.g.*, from stannous sulphide), as sulphide of copper is not quite insoluble in sulphide of ammonium.

IV. SALTS.

Of the many salts employed as reagents, those of potassa, soda, and ammonia are used principally on account of their acids; a salt of soda may therefore often be substituted for the corresponding potassa salt. Thus it is almost always a matter of indifference whether carbonate of soda or carbonate of potassa is used, ferrocyanide of potassium or ferrocyanide of sodium, &c. On this account, the salts of the alkalies are here classified *by their acids*. With the salts of the alkaline earths and those of the oxides of the heavy metals the case is different; these are not used for their acid, but for their base; we may therefore often substitute for one salt of a base another similar one, as nitrate or acetate of baryta for chloride of barium, &c. For this reason the salts of the alkaline earths and of the heavy metals are classified *by their bases*.

a. SALTS OF THE ALKALIES.

§ 42.

1. **Sulphate of Potassa,** KO,SO_3 [K_2SO_4].

Preparation.—Sulphate of potassa of commerce is purified by recrystallization, and a solution is made of 1 part of the pure salt in 12 parts of water.

Uses.—Sulphate of potassa serves to detect and separate baryta and strontia. It is in many cases used in preference to dilute sulphuric acid, which is employed for the same purpose, as it does not, like the latter reagent, disturb the neutrality of the solution.

§ 43.

2. **Phosphate of Soda,** $2NaO,HO,PO_5$ [Na_2HPO_4].

Crystallized, $2NaO,HO,PO_5 + 24aq$ $Na_2HPO_4,12H_2O$].

Preparation.—Commercial phosphate of soda is purified by recrystallization, and 1 part of the pure salt is dissolved in 10 parts of water for use.

Tests.—Solution of phosphate of soda should not become turbid when heated with ammonia. The precipitates which solution of nitrate of baryta and solution of nitrate of silver produce in it must redissolve completely, and without effervescence, on addition of dilute nitric acid. Sulphuretted hydrogen should not precipitate or colour the solution either as it is or when acidified, nor yet on warming it.

Uses.—Phosphate of soda precipitates the alkaline earths and all heavy metallic oxides by double affinity. In analysis, after the separation of the oxides of the heavy metals, it serves as a test for alkaline earths in general; and, after the separation of baryta, strontia, and lime, as a special test for the detection of magnesia; for the latter purpose, it is used in conjunction with ammonia, the magnesia being precipitated as basic phosphate of magnesia and ammonia. Instead of phosphate of soda, phosphate of soda and ammonia (§ 84) may also be used.

§ 44.

3. **Oxalate of Ammonia,** $2NH_4O,C_4O_6$ [$(NH_4)_2C_2O_4$].

Crystallized, $2NH_4O,C_4O_6 + 2aq$ [$(NH_4)_2C_2O_4,H_2O$].

Preparation.—1 part of commercial oxalic acid (which usually contains potassa or soda) is dissolved in 6 parts of boiling water, allowed to cool, and the solution poured off or filtered from the crystals of oxalic acid, which generally contain quadroxalate of potassa; it is then evaporated and again allowed to cool. The second crop of crystals is practically free from potassa. A third crop equally pure may also be obtained. The mother liquor together with the first crop may be used in the preparation of oxalate of potassa or soda. The purified oxalic acid is dissolved in 2 parts of distilled water, with the aid of heat, solution of ammonia added until the reaction is distinctly alkaline, and the vessel put aside in a cold place; the crystals which form are allowed to drain from the mother liquor, which, on evaporation, will give another crop of crystals. All the crystals are then purified by recrystallization: 1 part of the pure salt is dissolved in 24 parts of water for use.

Tests.—The solution of oxalate of ammonia should not be precipitated or rendered turbid by sulphuretted hydrogen, or by sulphide of ammonium. When ignited on platinum, the salt must volatilize without leaving any residue.

Uses.—Oxalic acid forms insoluble or very sparingly soluble compounds with lime, strontia, baryta, oxide of lead, and other metallic oxides; oxalate of ammonia, therefore, produces precipitates of the corresponding oxalates when added to the aqueous solutions of the salts of these bases. In analysis, it serves principally for the detection and separation of lime.

§ 45.

4. **Acetate of Soda,** $NaO,C_4H_3O_3 = NaO,\bar{A}$ [$NaC_2H_3O_2$].

Crystallized, $NaO,\bar{A} + 6aq$ [$NaC_2H_3O_2,3H_2O$].

Preparation.—Crystallized carbonate of soda is dissolved in a little water, acetic acid added to slight excess, the solution evaporated until it crystallizes, and the salt purified by recrystallization. For use, 1 part of the salt is dissolved in 10 parts of water.

Tests.—Acetate of soda should be colourless and free from empyreumatic matter and inorganic acids.

Uses.—The stronger acids in the free state decompose acetate of soda, combining with the base, and setting the acetic acid free. In the course of analysis, acetate of soda is used principally to precipitate ferric phosphate (which is insoluble in acetic acid) from its solution in hydrochloric acid. It serves also to effect the separation of ferric oxide and alumina, which are precipitated on adding acetate of soda to solutions of their salts and boiling.

§ 46.

5. **Carbonate of Soda,** NaO,CO_2 [Na_2CO_3].

Crystallized, $NaO,CO_2 + 10aq$ [$Na_2CO_3,10H_2O$].

Preparation.—Commercial bicarbonate of soda in powder is put into a funnel stopped loosely with cotton wool, the surface made level and covered with a disk of difficultly permeable paper with turned-up edges; it is then washed by pouring small quantities of water on the paper disk, until the filtrate, acidified with nitric acid, is no longer rendered turbid by nitrate of silver solution, or by solution of chloride of barium. The salt is then dried and converted into carbonate by gentle ignition. This is best effected in a silver or platinum crucible or dish; but it may be done also in a perfectly clean vessel of cast iron, or, on a small scale, in a porcelain dish. Pure carbonate of soda may be obtained also by the repeated recrystallization of commercial carbonate of soda. For use, 1 part of the anhydrous salt or 2·7 parts of the crystallized salt is dissolved in 5 parts of water.

Tests.—Carbonate of soda should be perfectly white. Its solution, after supersaturation with nitric acid, should not be rendered turbid by chloride of barium or nitrate of silver; neither should sulphocyanate of potassium impart a red, nor warming with molybdate of ammonia and nitric acid a yellow, tint to it, or give a yellow precipitate; the residue which remains on evaporating its solution to dryness, after previous supersaturation with hydrochloric acid, should leave no residue (silicic acid) when redissolved in water. When fused in a glass tube with cyanide of potassium for a long time in a current of carbonic acid, it should give no trace of a dark sublimate (arsenic). See § 132, 12.

Uses.—With the exception of the alkalies, carbonate of soda precipitates the whole of the bases in the form of neutral or basic carbonates. Those bases which are soluble in water as bicarbonates require boiling for their complete precipitation from acid solutions. Many of the precipitates produced by the action of carbonate of soda exhibit a characteristic colour, which may lead to the detection of the metals which produce them. Solution of carbonate of soda serves also to decompose many of the insoluble salts of the alkaline earths or of the metals, more particularly those containing organic acids. These salts when boiled with carbonate of soda are converted into insoluble carbonates, while the acids combine with the soda and are thus obtained in solution. Carbonate of soda is also frequently used to saturate free acids.

§ 47.

6. **Carbonate of Ammonia,** NH_4O,CO_2 $[(NH_4)_2CO_3]$.

Preparation.—Purified sesquicarbonate of ammonia is employed, such as is prepared on a large scale from a mixture of chloride of ammonium and carbonate of lime by sublimation; it should be entirely free from any smell of animal oil. The outer and the inner surface of the mass should be carefully scraped off. One part of the salt is dissolved by digestion with 4 parts of water to which 1 part of solution of caustic ammonia has been added.

Tests.—Pure carbonate of ammonia should volatilize completely. Neither solution of nitrate of baryta nor of nitrate of silver, nor sulphuretted hydrogen, should give any colour or precipitate with it, after it has been supersaturated with nitric acid.

Uses.—Carbonate of ammonia, like carbonate of soda, precipitates most metallic oxides and earths; it is generally employed in preference to the sodium salt, because it does not introduce a non-volatile substance into the solution. Complete precipitation of many of the oxides takes place only on boiling. Several of the precipitates redissolve again in an excess of the precipitant. In like manner, carbonate of ammonia dissolves many hydrated oxides and sulphides, and thus enables us to distinguish and separate them from others which are insoluble in this reagent.

Carbonate of ammonia, like caustic ammonia, and for the same reason, fails to precipitate from acid solutions many oxides, which it precipitates from neutral solutions. (Compare § 53.) Carbonate of ammonia is used in analysis principally to effect the precipitation of baryta, strontia, and lime, and the separation of these substances from magnesia; also to separate sulphide of arsenic, which is soluble in it, from sulphide of antimony, which is insoluble.

§ 48.

7. Bisulphite of Soda, $NaO,HO,2SO_2$ [$NaHSO_3$].

Preparation.—5 parts of copper clippings and 20 parts of concentrated sulphuric acid are heated together in a flask, and the sulphurous acid gas evolved is passed first through a wash-bottle containing some water, then into a flask containing 4 parts of purified bicarbonate of soda (§ 46), or 7 parts of pure crystallized carbonate of soda, and from 20 to 30 parts of water: it should not be much more than half full. The current of gas is passed until carbonic acid no longer escapes from the solution with effervescence. The solution, which smells strongly of sulphurous acid, should be kept in a well-stoppered bottle.

Tests.—Sulphite of soda, when evaporated to dryness with pure sulphuric acid, should leave a residue,* the aqueous solution of which is not altered by sulphuretted hydrogen, and does not yield a yellow precipitate when heated with a solution of molybdate of ammonia mixed with nitric acid.

Uses.—Sulphurous acid has a great tendency to absorb oxygen and pass to the state of sulphuric acid; it is therefore a very powerful reducing agent. Sulphite of soda, which has the advantage of being less readily decomposed than sulphurous acid, acts in an analogous manner on adding an acid to it. It is used principally to reduce arsenic acid to arsenious acid, chromic acid to sesquioxide of chromium, and sesquioxide of iron to protoxide.

§ 49.

8. Nitrite of Potassa, KO,NO_3 [KNO_2].

Preparation.—1 part of nitre is fused in an iron pan, 2 parts of lead are added, and the mixture is kept stirred with an iron rod. Even at a low red heat the lead becomes for the most part oxidized and converted into a yellow powder. To oxidize the remainder, the heat is increased to visible redness and maintained at that for half an hour. When cold, the product is treated with cold water, filtered, and carbonic acid passed through the filtrate; this precipitates almost the whole of the lead in solution, and the remainder may be removed with a little sulphuretted hydrogen. The clear solution is evaporated to dryness, finally with stirring, and then fused in order to destroy any hyposulphite of potassa which may have been formed (A. Stromeyer). When required, 1 part is dissolved in 2 parts of water, neutralized cautiously with acetic acid, and filtered.†

Tests.—On adding dilute sulphuric acid to nitrite of potassa, it should copiously evolve nitric oxide gas.

Uses.—Nitrite of potassa is an excellent reagent for detecting and separating cobalt, in the solutions of which metal it produces a precipitate of the nitrite of potassa and cobalt oxide. It serves also in presence of free acid to liberate iodine from its compounds.

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* Sulphurous acid is copiously evolved during the evaporation.

† For most purposes nitrite of soda may be employed instead of the potassa salt. The commercial article, which is now made in immense quantities for the manufacture of coal-tar dyes, is almost chemically pure.—[Editor.]

§ 50.

9. Dichromate of Potassa, $KO,2CrO_3$ [$K_2Cr_2O_7$].

Preparation.—The commercial salt is purified by recrystallization, and 1 part of the pure salt dissolved in 10 of water for use.

Tests.—The solution of the salt acidified with hydrochloric acid and boiled with alcohol, should yield a green solution which is not rendered turbid by chloride of barium.

Uses.—Chromate of potassa decomposes most of the soluble salts of metallic oxides by double affinity. Most of the precipitated chromates are but sparingly soluble, and many of them exhibit characteristic colours which lead readily to the detection of the particular metal which they contain. Dichromate of potassa is used principally as a test for lead, and also for separating and distinguishing bartya from strontia.

§ 51.

10. Acid Metantimonate of Potassa,

$KO,HO,SbO_5 + 6aq$ [$K_2H_2Sb_2O_7,6H_2O$].

Preparation.—A mixture of equal parts of pulverized tartar-emetic and nitrate of potassa is projected into a red-hot crucible in small portions at a time. After the mass has deflagrated it is kept at a moderate red heat for a quarter of an hour longer, which causes it to froth at first, but after some time it passes to a state of calm fusion. The crucible is now removed from the fire, and when sufficiently cold the mass is extracted with warm water; the product can now be easily washed out, and on standing deposits a heavy white powder from which the supernatant liquid is decanted (Brunner). It is washed with cold water, boiled for a short time with 200 parts of water, and filtered when cold.

Tests and *Uses.*—Acid metantimonate of potassa is very sparingly soluble in water, requiring 90 parts of boiling and 250 parts of cold water for solution. The solution prepared in the way described can be kept unaltered for a considerable time. It should be clear and of neutral reaction; it should give no precipitate with solution of chloride of potassium, or with solution of chloride of ammonium; but solution of chloride of sodium should yield a crystalline precipitate with it. Metantimonate of potassa is a valuable reagent for soda, but its employment requires great caution, see § 90.

§ 52.

11. Molybdate of Ammonia, NH_4O,MoO_3 [$(NH_4)_2MoO_4$], dissolved in Nitric Acid.

Preparation.—Sulphide of molybdenum is mixed with about an equal bulk of coarse quartz sand previously washed with hydrochloric acid, and triturated until it is reduced to a moderately fine powder; the powder is then heated to faint redness, with repeated stirring, until the mass has acquired a lemon-yellow colour (which after cooling turns whitish). With small quantities, this operation may be conducted in a flat platinum dish, with large quantities in a muffle. The residue is extracted with solution of ammonia, filtered, evaporated, and the product heated to faint redness until the mass appears yellow or white;

it is then digested for several days with nitric acid in the water bath, in order to convert the phosphoric acid which is almost invariably present in the ore to the tribasic state. When the nitric acid is evaporated, the residue (or commercial pure molybdic acid) is dissolved in 4 parts of solution of ammonia, filtered rapidly, and the filtrate poured into 15 parts by weight of nitric acid of sp. gr. 1·20. The mixture is allowed to remain several days in a moderately warm place, which will cause the separation of any remaining traces of phosphoric acid as phospho-molybdate of ammonia. The colourless solution is decanted from the precipitate, and kept for use. If heated to 40°, no white precipitate (molybdic acid or an acid salt of the same) will separate; but if the temperature is raised beyond that point this will at once take place unless more nitric acid be added (Eggertz).

Uses.—Phosphoric acid and arsenic acid form with molybdic acid and ammonia peculiar yellow compounds which are almost absolutely insoluble in the nitric acid solution of molybdate of ammonia. The phosphoric acid compound is formed in the cold, the arsenic acid compound requires heat. Molybdate of ammonia affords therefore an excellent means for detecting these acids, and more especially very minute quantities of phosphoric acid in acid solutions containing ferric oxide, alumina, and alkaline earths.

§ 53.

12. Chloride of Ammonium, NH_4Cl [NH_4Cl].

Preparation.—The white sublimed sal ammoniac of commerce is selected; if it contains iron, it must be purified. For this purpose, some chlorine water is added to the boiling solution, to convert the ferrous to ferric chloride, and then ammonia to alkaline reaction, the boiling being continued until the alkaline reaction has almost disappeared; the precipitate is then allowed to subside, and the solution filtered and evaporated until it crystallizes. For use, 1 part of the salt is dissolved in 8 parts of water.

Tests.—Solution of chloride of ammonium should leave no fixed residue when evaporated on a platinum spatula. Sulphide of ammonium should have no action on it, and it must be perfectly neutral to test paper.

Uses.—Chloride of ammonium serves principally to retain in solution certain oxides (such as protoxide of manganese, magnesia) or salts (such as tartrate of lime) when other oxides or salts are to be precipitated by ammonia or some other reagent. This application of chloride of ammonium is based upon the tendency of ammonia salts to form double compounds with other salts. Chloride of ammonium serves also to distinguish between precipitates possessed of similar properties; for instance, to distinguish the basic phosphate of magnesia and ammonia, which is insoluble in chloride of ammonium, from other precipitates of magnesia. It is used also to precipitate from their solutions in potassa various substances which are soluble in that alkali, but insoluble in ammonia; such as alumina, sesquioxide of chromium, &c. In this process, the elements of the chloride of ammonium react with those of the potassa, chloride of potassium, water, and ammonia being formed. Chloride of ammonium is used also as a special reagent in the precipitation of platinum as platinochloride of ammonium.

§ 54.

13. Cyanide of Potassium, $KC_2N = KCy$ [KCN].

Preparation.—Commercial ferrocyanide of potassium (perfectly free from sulphate of potassa) is gently heated, with stirring, until the water of crystallization is completely expelled; it is then powdered, and 8 parts mixed with 3 parts of perfectly dry carbonate of potassa; the mixture is fused in a covered Hessian crucible or, better still, in a covered iron pot, until the mass is in a faint glow, appears clear, and a sample of it, taken out with a heated glass or iron rod, looks perfectly white. The crucible is then removed from the fire, tapped gently, and allowed to cool a little until the evolution of gas has ceased; the fused cyanide of potassium is poured into a heated tall, crucible-shaped vessel of clean iron or silver, or into a moderately hot Hessian crucible, with care, so as to prevent any of the minute particles of iron which have separated in the process of fusion and have subsided to the bottom of the crucible from running out with the cyanide. The product is allowed to cool slowly in a somewhat warm place. The cyanide of potassium prepared in this way is well adapted for analytical purposes, although it contains carbonate and cyanate of potassa; when dissolved in water, the latter is converted into carbonate of ammonia and carbonate of potassa;

$$KO,C_2NO + 4HO = KO,CO_2 + NH_4O,CO_2$$

$$[2KCNO + 4H_2O = K_2CO_3 + (NH_4)_2CO_3].$$

The cyanide should be kept in the solid form in a well-stoppered bottle, and when required for use 1 part of it is dissolved in 4 parts of water, without application of heat. The mixture of the cyanides of potassium and sodium obtained by substituting 2 parts of dry carbonate of soda for the 3 parts of carbonate of potassa may also be employed.

Tests.—Cyanide of potassium should be milk-white and quite free from particles of iron or charcoal. It should dissolve completely in water to a clear liquid. It must be free from silicic acid and sulphide of potassium; the precipitate which salts of lead produce in its solution should therefore be white, and the residue which its solution leaves on being supersaturated with hydrochloric acid and evaporated,* should dissolve completely in water to a clear solution. If fused with pure carbonate of soda in a gentle current of dry carbonic acid in a tube of glass free from arsenic, it should not give the slightest indication of an arsenical mirror (see § 132, 12).

Uses.—Cyanide of potassium prepared in the manner described produces in the solutions of most of the salts of metallic oxides precipitates of cyanides of the metals, or of oxides or carbonates. The precipitated cyanides are soluble in cyanide of potassium, and may therefore by further addition of the reagent be separated from the oxides or carbonates which are insoluble in cyanide of potassium. Some of the metallic cyanides redissolve invariably in the cyanide of potassium as double cyanides, even in presence of free hydrocyanic acid and on boiling; whilst others combine with cyanogen to form new radicles, which remain in solution in combination with the potassium. The most common compounds of the latter kind are cobalticyanide of potassium and ferro- and ferricyanide of potassium. These differ from

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* This supersaturation with hydrochloric acid is attended with disengagement of hydrocyanic acid.

the double cyanides particularly in that dilute acids fail to precipitate the metallic cyanides which they contain. Cyanide of potassium may accordingly be used to separate the metals which form compound-radicles, from others the cyanides of which are precipitated on adding an acid to their solution in cyanide of potassium. In the course of analysis, this reagent is of great importance, as it serves to separate cobalt from nickel; also copper from cadmium, the sulphide of the former being soluble in it, whilst that of the latter is insoluble.

§ 55.

14. Ferrocyanide of Potassium,

$2K,C_6N_3Fe = 2K,Cfy$ $[K_4Fe(CN)_6]$.

Crystallized, $2K,Cfy + 3aq$ $[K_4Cfy,3H_2O]$.

Preparation.—Commercial ferrocyanide of potassium is sufficiently pure. 1 part of the salt is dissolved in 12 parts of water for use.

Uses.—With most metals, ferrocyanogen forms compounds insoluble in water, which frequently exhibit highly characteristic colours. These ferrocyanides are formed when ferrocyanide of potassium is brought into contact with soluble salts of metallic oxides, with chlorides, &c., the potassium changing places with the metals. Ferrocyanide of copper and ferrocyanide of iron exhibit the most characteristic colours of all: ferrocyanide of potassium serves therefore particularly as a test for oxide of copper and ferric oxide.

§ 56.

15. Ferricyanide of Potassium,

$3K,C_{12}N_6Fe_2 = 3K,Cfdy$ $[K_6Fe_2(CN)_{12}]$.

Preparation.—Chlorine gas is passed slowly into a solution of 1 part of ferrocyanide of potassium in 10 parts of water, with frequent stirring, until the solution exhibits a fine deep red colour by transmitted light (a candle-light is best), and a sample of the solution no longer yields a blue precipitate with a solution of ferric chloride, but imparts a brownish tint to it. The solution is then concentrated in an evaporating dish to $\frac{1}{4}$ of its weight, and put aside to crystallize. On further evaporation, the mother liquor will yield a second crop of crystals. The whole of the crystals obtained are dissolved in 3 parts of water, filtered if necessary, the solution evaporated quickly to half its volume, and again allowed to crystallize. Whenever required for use, a few of the crystals, which are of a splendid red colour, are dissolved in a little water. The solution, if exposed to light, is decomposed, ferrocyanide of potassium is formed and a blue precipitate is deposited; as already observed, the solution should not give either a blue precipitate or a blue colour with a solution of ferric chloride.

Uses.—Ferricyanide of potassium reacts with solutions of metallic oxides in the same manner as ferrocyanide of potassium. Of the metallic ferricyanides, ferrous ferricyanide is more particularly characterized by its colour, and ferricyanide of potassium therefore is used principally as a test for ferrous oxide.

§ 57.

16. Sulphocyanate or Thiocyanate of Potassium,

K,C_2NS_2 or K,CyS_2 [KCNS].

Preparation.—46 parts of anhydrous ferrocyanide of potassium are mixed with 17 parts of carbonate of potassa and 32 parts of sulphur: the mixture is introduced into an iron pot provided with a lid, and fused over a gentle fire; the same temperature is maintained until the swelling of the mass which occurs at first has completely subsided and the whole is in a state of tranquil fusion; the temperature is now increased, towards the end of the operation, to low redness, in order to decompose the hyposulphite of potassa which is formed in the process. The product is poured out on to a clean iron plate, broken up, and boiled repeatedly with alcohol of from 80 to 90 per cent. On cooling, part of the sulphocyanide of potassium separates in colourless crystals; and the remainder may be obtained by distilling off the alcohol from the mother liquor. 1 part of the salt is dissolved in 10 parts of water for use.

Tests.—Solution of sulphocyanate of potassium must remain perfectly colourless when mixed with perfectly pure dilute hydrochloric acid.

Uses.—Sulphocyanate of potassium is used for the detection of ferric oxide, for which it is a most characteristic and delicate test, surpassing all others in this respect. It is also useful for detecting and separating copper, which it throws down as white cuprous sulphocyanate from cupric solutions to which sulphurous acid has been added.

b. SALTS OF THE ALKALINE EARTHS.

§ 58.

1. Chloride of Barium, $BaCl$ [$BaCl_2$].

Crystallized, $BaCl + 2aq$ [$BaCl_2,2H_2O$].

Preparation.—*a*. From heavy spar. Crude sulphide of barium is prepared by the long-continued heating of a mixture of 8 parts of pulverized sulphate of baryta, 2 parts of charcoal in powder, and 1 part of common resin. About $\frac{9}{10}$ of the crude sulphide is boiled with 4 times its weight of water, and hydrochloric acid added until the effervescence due to the escape of sulphuretted hydrogen has ceased, and the solution has a slightly acid reaction: the remaining $\frac{1}{10}$ part of the sulphide of barium is now added, the whole boiled some time longer, filtered, the filtrate acidified with hydrochloric acid, heated for some time, again filtered, and put aside to crystallize. The dried crystals are dissolved in water, and recrystallized.

b. From witherite. 10 parts of water are poured on to 1 part of pulverized witherite, and crude hydrochloric acid gradually added until the witherite is almost entirely dissolved; a little more finely pulverized witherite is now added, and the solution heated with frequent stirring, until it has entirely or very nearly lost its acid reaction; solution of sulphide of barium is added as long as a precipitate forms, the latter is separated by filtration and the clear liquid evaporated to crystallization. After the chloride of barium has been purified by recrystallization, 1 part of it is dissolved in 10 parts of water.

Tests.—Pure chloride of barium should not alter vegetable colours; its solution should not be coloured or precipitated by sulphuretted hydrogen, or by sulphide of ammonium. Pure sulphuric acid must precipitate the whole of the fixed matter in it, so that the filtrate from the precipitate formed should not leave the slightest residue when evaporated on platinum foil and heated to low redness. If it does (sulphate of strontia or lime), it may be purified by dissolving it in 2 parts of hot water, adding twice the volume of spirit, washing the crystalline precipitate with spirit, and drying it.

Uses.—Baryta forms soluble compounds with many acids, and with others insoluble compounds. This property affords a means of distinguishing the former acids, which are not precipitated by chloride of barium, from the latter, which yield a precipitate with this reagent. The precipitated salts of baryta vary in their behaviour with acids. By treating these salts with acids, therefore, we are enabled to subdivide the group of precipitable acids and even to detect certain individual acids. This makes chloride of barium one of the most important reagents not only for distinguishing between certain groups of acids, but especially for the detection of sulphuric acid.

§ 59.

2. **Nitrate of Baryta,** BaO,NO_5 [$Ba(NO_3)_2$].

Preparation.—Carbonate of baryta, either witherite or that precipitated by carbonate of soda from solution of sulphide of barium, is dissolved with dilute nitric acid free from chlorine, and the solution treated exactly as described in the preparation of chloride of barium from witherite. For use, 1 part of the salt is dissolved in 15 parts of water.

Tests.—Solution of nitrate of baryta should not be rendered turbid by solution of nitrate of silver. The other tests are the same as for chloride of barium.

Uses.—Nitrate of baryta is used instead of chloride of barium in cases where it is desirable to avoid the introduction of a chloride into the solution.

§ 60.

3. **Carbonate of Baryta,** BaO,CO_2 [$BaCO_3$].

Preparation.—Crystallized chloride of barium is dissolved in water, heated to boiling, and a solution of carbonate of ammonia mixed with some caustic ammonia is added as long as a precipitate is formed; when the precipitate has subsided, it is washed by decantation five or six times, transferred to a filter, and then washed until the washing water is no longer rendered turbid by solution of nitrate of silver. The precipitate is made into a cream with water, and the mixture kept in a stoppered bottle; it must, of course, be well shaken up immediately before using it.

Tests.—Pure sulphuric acid should precipitate the whole of the fixed matter from a solution of carbonate of baryta in hydrochloric acid (compare § 36).

Uses.—Carbonate of baryta completely decomposes the solutions of certain metallic oxides, such as sesquioxide of iron, or alumina, precipitating from them the whole of the oxide as hydrate and basic salt; there is another class of metallic salts which is not precipitated by it. It serves, therefore, to separate the former from the latter, and affords an excellent means of effecting the separation of ferric oxide and alumina from protoxide of manganese, oxide of zinc, lime, magnesia, &c. It must be borne in mind, however, that these oxides must not be present as sulphates, for in that case carbonate of baryta would also precipitate the latter bases from the solution.

§ 61.

4. Sulphate of Lime, CaO,SO_3 [$CaSO_4$].

Crystallized, $CaO,SO_3 + 2aq$ [$CaSO_4,2H_2O$].

Preparation.—Powdered crystallized gypsum (selenite) is digested and shaken with water for some time; the undissolved portion is allowed to subside, and the clear solution is decanted and kept for use.

Uses.—Sulphate of lime, being a sparingly soluble salt, is a convenient agent in cases where it is wished to apply a solution of a lime salt or of a sulphate of a definite degree of dilution. As a dilute solution of a lime salt, it is used for the detection of oxalic acid; whilst as a dilute solution of a sulphate it affords an excellent means of distinguishing between baryta, strontia, and lime.

§ 62.

5. Chloride of Calcium, $CaCl$ [$CaCl_2$].

Crystallized, $CaCl + 6aq$ [$CaCl_2,6H_2O$].

Preparation.—1 part of crude hydrochloric acid is diluted with 6 parts of water, and marble or chalk is added to the dilute acid as long as it is dissolved; some hydrate of lime is now added, and then sulphuretted hydrogen water until a filtered portion of the mixture is no longer altered by sulphide of ammonium. The vessel is covered and allowed to remain at a gentle heat for 12 hours; it is then filtered, the filtrate exactly neutralized, concentrated by evaporation, and left to crystallize. The crystals are put to drain, and 1 part of the salt is dissolved in 5 parts of water for use.

Tests.—Solution of chloride of calcium should be perfectly neutral, and neither be coloured nor precipitated by sulphuretted hydrogen or by sulphide of ammonium; it ought not to evolve ammonia when mixed with hydrate of potassa or hydrate of lime.

Uses.—In its action and application, chloride of calcium is analogous to chloride of barium. As the latter reagent is used to separate the inorganic acids into groups, in like manner chloride of calcium serves to effect the separation of the organic acids into groups, since it precipitates some of them, whilst it forms soluble compounds with others.

And, as is the case with the baryta precipitates, the different conditions under which the various insoluble lime salts are thrown down enables us to subdivide the group of precipitable acids.

§ 63.

6. Sulphate of Magnesia, MgO,SO_3 [$MgSO_4$].

Crystallized, $MgO,SO_3 + 7aq$ [$MgSO_4,7H_2O$].

Preparation.—1 part of commercial sulphate of magnesia is dissolved in 10 parts of water; if the salt is not perfectly pure, it should be recrystallized.

Tests.—Sulphate of magnesia should have a neutral reaction. Its solution, mixed with a sufficient quantity of chloride of ammonium, should not appear clouded or tinged by pure ammonia, or by carbonate or oxalate of ammonia, or by sulphide of ammonium, even after the lapse of half an hour.

Uses.—Sulphate of magnesia is used almost exclusively for the detection of phosphoric acid and arsenic acid, which it precipitates from aqueous solutions of phosphates and arsenates, in presence of ammonia and chloride of ammonium, in the form of almost absolutely insoluble, highly characteristic double salts (basic phosphate or basic arsenate of magnesia and ammonia). Sulphate of magnesia is also employed to test sulphide of ammonium (see § 40).

c. SALTS OF THE OXIDES OF THE HEAVY METALS.

§ 64.

1. Ferrous Sulphate or Sulphate of Protoxide of Iron,

FeO,SO_3 [$FeSO_4$]. Crystallized, $FeO,SO_3 + 7aq$ [$FeSO_4,7H_2O$].

Preparation.—Iron in the form of nails free from rust, or clean iron wire, is heated with dilute sulphuric acid until the evolution of hydrogen ceases, taking care to keep the iron in excess; the solution is concentrated, filtered, a few drops of dilute sulphuric acid added to the filtrate, and it is then allowed to cool. The crystals which are deposited are washed with water very slightly acidified with sulphuric acid, dried and kept for use. Ferrous sulphate may also be prepared from the solution obtained when sulphide of iron is dissolved in dilute sulphuric acid, as in the process of evolving sulphuretted hydrogen.

Tests.—The crystals of ferrous sulphate should be of a fine pale-green colour. Crystals that have been more or less oxidized by the action of the air, and give a brownish-yellow solution when treated with water, leaving basic ferric sulphate undissolved, must be rejected. Sulphuretted hydrogen should not precipitate solution of ferrous sulphate after it has been acidified with hydrochloric acid, or even impart a blackish tint to it.

Uses.—Ferrous sulphate has a great tendency to absorb oxygen, and to be converted into the ferric sulphate; it acts therefore as a powerful reducing agent. It is employed principally for the reduction of nitric acid, from which it separates nitric oxide by withdrawing three atoms of oxygen from it; the decomposition of the nitric acid being attended in this case with the formation of a very deep brownish-black compound of nitric oxide with a portion of the undecomposed salt of the protoxide of iron: this reaction affords a particularly characteristic and delicate test for the detection of nitric acid. Ferrous sulphate is also used to detect hydroferricyanic acid, with which it produces a kind of Prussian blue, and also to precipitate metallic gold from solutions of the salts of that metal.

§ 65.

2. Ferric Chloride or Sequichloride of Iron,

Fe_2Cl_3 [Fe_2Cl_6].

Preparation.—A mixture of 10 parts of water and 1 part of pure hydrochloric acid is heated in a flask with small iron nails until no further evolution of hydrogen is observed, even after adding the nails in excess; the solution is filtered into another flask, and chlorine gas passed into it with frequent shaking, until the solution no longer produces a blue precipitate with ferricyanide of potassium; it is then heated until the excess of chlorine is expelled. The solution is diluted until it is twenty times the weight of the iron dissolved, and kept for use.

Tests.—Solution of ferric chloride should not contain an excess of acid; this may be readily ascertained by stirring a diluted sample of it with a glass rod dipped in ammonia, when the absence of any excess of acid will be proved by the formation of a precipitate which shaking the vessel or agitating the liquid fails to redissolve. Ferricyanide of potassium should not impart a blue colour to it.

Uses.—Ferric chloride is used for subdividing the group of organic acids which chloride of calcium fails to precipitate, as it produces precipitates in solutions of benzoates and succinates, but not in cold solutions of acetates and formates. The aqueous solutions of the neutral acetate and formate of sesquioxide of iron exhibit an intense red colour; ferric chloride is therefore a useful agent for detecting acetic acid and formic acid. Ferric chloride is exceedingly useful for effecting the decomposition of phosphates of the alkaline earths (see § 142, 9); and it serves also for the detection of hydroferrocyanic acid, with which it produces Prussian blue.

§ 66.

3. Nitrate of Silver, AgO,NO_5 [$AgNO_3$].

Preparation.—1 part of the pure commercial salt is dissolved in 20 parts of water.

Tests.—Dilute hydrochloric acid should completely precipitate all the fixed matter from solution of nitrate of silver; the filtrate from the precipitated chloride of silver therefore must leave no residue when evaporated on a watch-glass, and should be neither precipitated nor coloured by sulphuretted hydrogen. Solution of nitrate of silver should have a neutral reaction.

Uses.—Oxide of silver forms soluble compounds with some acids, and with others insoluble compounds. Nitrate of silver, therefore, like chloride of barium, is useful in effecting the separation and classification of acids into groups.

Most of the insoluble compounds of silver dissolve in dilute nitric acid; chloride, bromide, iodide, and cyanide, ferrocyanide, ferricyanide, and sulphide of silver, however, are insoluble in that menstruum. Nitrate of silver is therefore an excellent reagent for distinguishing and separating the hydracids corresponding with the last enumerated compounds of silver from all other acids. Many of the insoluble salts of silver are of a peculiar colour (chromate of silver, arsenate of silver), or exhibit a characteristic behaviour with other reagents or on the application of heat (formate of silver); nitrate of silver is therefore an important agent for the detection of certain acids.

§ 67.

4. Acetate of Lead, $PbO,C_4H_3O_3 = PbO,\bar{A}$ [$Pb(C_2H_3O_2)_2$].

Crystallized, $PbO,C_4H_3O_3 + 3aq$ [$Pb(C_2H_3O_2)_2,3H_2O$].

The best commercial acetate of lead (sugar of lead) is sufficiently pure; for use, 1 part of the salt is dissolved in 10 parts of water.

Tests.—Acetate of lead should dissolve completely in water acidified with one or two drops of acetic acid; the solution should be quite clear and colourless; sulphuretted hydrogen should throw down all the fixed matter from it. On mixing a solution of acetate of lead with carbonate of ammonia in excess, and filtering the mixture, the filtrate should be quite free from any bluish tint (copper).

Uses.—With a great many acids, oxide of lead forms compounds insoluble in water, which are marked either by peculiarity of colour or characteristic behaviour; acetate of lead therefore yields precipitates with the solutions of these acids or of their salts, and materially contributes to the detection of several of them. Chromate of lead, for instance, is characterized by its yellow colour, phosphate of lead by its peculiar behaviour before the blowpipe, and malate of lead by its ready fusibility.

§ 68.

5. Mercurous Nitrate or Nitrate of Suboxide of Mercury, Hg_2O,NO_5 [$Hg_2(NO_3)_2$].

Crystallized, $Hg_2O,NO_5 + 2aq$ [$Hg_2(NO_3)_2,2H_2O$].

Preparation.—1 part of pure nitric acid of 1·2 sp. gr. is poured on to 1 part of pure mercury in a porcelain dish, and the vessel allowed to remain for twenty-four hours in a cool place; the crystals which are formed are separated from the undissolved mercury and the mother liquor, and dissolved by grinding them up in a mortar with water which has been previously mixed with one-sixteenth part of nitric acid. The solution is filtered and kept in a bottle with some metallic mercury sufficient to cover the bottom of the vessel.

Tests.—With dilute hydrochloric acid, the solution of mercurous nitrate should give a copious white precipitate of mercurous chloride; sulphuretted hydrogen should produce no precipitate in the filtrate from this, or at most only a trifling black precipitate (sulphide of mercury).

Uses.—Mercurous nitrate acts in a manner analogous to the corresponding silver salt. In the first place, it precipitates many acids, especially the hydracids; and, in the second place, it serves for the detection of several readily oxidizable bodies, such as formic acid, as the oxidation of such bodies, which takes place at the expense of the oxygen of the suboxide of mercury, is attended with the highly characteristic separation of metallic mercury.

§ 69.

6. Mercuric Chloride or Chloride of Mercury,

$HgCl$ [$HgCl_2$].

Commercial mercuric chloride is sufficiently pure. For use, 1 part of the salt is dissolved in 16 parts of water.

Uses.—Mercuric chloride gives with several acids, for example, hydriodic acid, characteristic coloured precipitates, and may, therefore, be used for the detection of these acids. It is an important agent in the detection of tin where that metal is in solution in the state of protochloride; if the smallest quantity of that compound be present the addition of excess of mercuric chloride to the solution will be followed by separation of mercurous chloride insoluble in water. In like manner, mercuric chloride may be used to detect formic acid.

§ 70.

7. Sulphate of Copper, CuO,SO_3 [$CuSO_4$].

Crystallized, $CuO,SO_3 + 5aq$ [$CuSO_4,5H_2O$].

Preparation.—This reagent may be obtained in a state of great purity from the residue remaining in the flask in the process of preparing bisulphite of soda (§ 48), by treating it with water, applying heat, filtering, adding a few drops of nitric acid, boiling the solution for some time, allowing it to crystallize, and purifying the salt by recrystallization. For use, 1 part of the salt is dissolved in 10 parts of water.

Tests.—After precipitation by sulphuretted hydrogen, ammonia and sulphide of ammonium must leave the filtrate unaltered.

Uses.—Sulphate of copper is employed in qualitative analysis to precipitate hydriodic acid as subiodide of copper. For this purpose the solution of 1 part of sulphate of copper is mixed with 2½ parts of ferrous sulphate, otherwise half of the iodide would be separated in the free state. The protoxide of iron during the reaction is changed to sesquioxide, at the expense of the oxygen of the oxide of copper, the latter being reduced to the state of suboxide. Sulphate of copper is used also for the detection of arsenious and arsenic acids; it serves likewise as a test for the soluble ferrocyanides.

§ 71.

8. Stannous Chloride or Protochloride of Tin,

$SnCl$ [$SnCl_2$]. Crystallized, $SnCl + 2aq$ [$SnCl_2,2H_2O$].

Preparation.—Grain tin is reduced to powder by means of a file, or by fusing it in a small porcelain dish, removing it from the fire, and triturating with a pestle until the tin again becomes solid.* The granulated or powdered tin is boiled for some time with concentrated hydrochloric acid in a flask (taking care always to have an excess of tin in the vessel) until the evolution of hydrogen ceases almost entirely; the solution is then diluted with 4 times the quantity of water slightly acidified with hydrochloric acid, and filtered. The filtrate is kept for use in a well-stoppered bottle containing some small pieces of granulated tin, or some pure tin-foil. If these precautions are neglected, the protochloride will soon change to bichloride, with separation of white oxychloride of tin, and the reagent will be unfit for use.

Tests.—When solution of stannous chloride is added to excess of solution of chloride of mercury, it should immediately produce a white precipitate of mercurous chloride; when treated with sulphuretted hydrogen, it should give a dark brown precipitate; it should not be precipitated or rendered turbid by sulphuric acid. If the stannous chloride solution is heated with 10 times its volume of pure fuming hydrochloric acid, it should not turn brown (arsenic).

Uses.—The great tendency of stannous chloride to absorb oxygen, and thus to form binoxide, or rather stannic chloride—as the binoxide in the moment of its formation reacts with the free hydrochloric acid present—makes this substance a most powerful reducing agent. It is more particularly suited to remove the part or the whole of the chlorine from chlorides. It is employed in the course of analysis as a test for mercury; also for the detection of gold.

§ 72.

9. Hydrochloride of Platinum, $HCl,PtCl_2$ [H_2PtCl_6].

Crystallized, $HCl,PtCl_2 + 6aq$ [$H_2PtCl_6,6H_2O$].

Preparation.—Platinum clippings, purified by boiling with nitric acid, are treated with concentrated hydrochloric acid and some nitric acid in a narrow-necked flask, applying a very gentle heat, and adding fresh portions of nitric acid occasionally, until the platinum is entirely dissolved. The solution is evaporated on the water-bath, with addition of hydrochloric acid, and the semifluid residue dissolved in 10 parts of water for use.

Tests.—Chloride of platinum, when evaporated to dryness in the water-bath, should leave a residue which dissolves completely in spirit of wine.

Uses.—Chloride of platinum forms very sparingly soluble double salts with chloride of potassium and chloride of ammonium, but not with chloride of sodium; it serves therefore to detect ammonia and potassa, and may, indeed, be looked upon as the most delicate reagent for the latter substance in the wet way.

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* It is far more convenient to use granulated tin, which may be readily obtained by melting the metal in a crucible or dish, and pouring it into a basin of water from the height of a foot or so.—[Editor.]

§ 73.

10. Palladiochloride of Sodium, $NaCl,PdCl$ [Na_2PldCl_4].

Five parts of palladium are dissolved in nitrohydrochloric acid (comp. § 72), 6 parts of pure chloride of sodium added, and the mixture evaporated to dryness on the water-bath. 1 part of the double salt is dissolved in 12 parts of water for use. The brownish solution affords an excellent means for detecting and separating iodine.

§ 74.

11. Hydrochloride of Gold, $HCl,AuCl_3$ [$HAuCl_4$].

Crystallized, $HCl,AuCl_3 + 6aq$ [$HAuCl_4,3H_2O$].

Preparation.—Fine gold cuttings, either pure or an alloy with silver or copper, are treated in a flask with nitrohydrochloric acid in excess, a gentle heat being applied until no more of the metal dissolves: the solution is diluted with 10 parts of water. If the gold was alloyed with copper—which is known by the brownish-red precipitate produced by ferrocyanide of potassium in a portion of the solution diluted with water—the solution must be mixed with solution of ferrous sulphate in excess; this reduces the terchloride to metallic gold, which separates in the form of a fine brownish-black powder. The powder thus obtained is washed with water in a small flask, and then redissolved in nitrohydrochloric acid; the solution is evaporated on the water-bath, and the crystalline residue dissolved in 30 parts of water. If the gold was alloyed with silver, the latter remains as chloride when the alloy is treated with nitrohydrochloric acid; under these circumstances, the whole is evaporated on the water-bath with repeated addition of hydrochloric acid, and the residue dissolved in water for use.

Uses.—Chloride of gold has a great tendency to yield up its chlorine; it therefore readily converts protochlorides into higher chlorides, and protoxides, with the simultaneous action of water, into higher oxides. These oxidations are usually indicated by the precipitation of pure metallic gold in the form of a brownish-black powder. In the course of analysis, this reagent is used only for the detection of protoxide of tin, in the solutions of which it produces a brownish-red or purple colour or precipitate.

V. COLOURING MATTERS AND INDIFFERENT VEGETABLE SUBSTANCES.

§ 75.

1. TEST PAPERS.

a. Blue Litmus Paper.

Preparation.—1 part of litmus is digested with 6 parts of water, and the solution filtered; the intensely blue filtrate is divided into 2 equal parts; the free alkali in the one half is saturated by repeatedly stirring the solution with a glass rod dipped in very dilute sulphuric acid, until the colour of the fluid just appears red; the other half of the blue filtrate is then added, and the whole poured into a dish; slips of fine unsized paper (white blotting-paper) are passed through this solution, and then hung on threads to dry. The colour of the litmus paper should be uniform, and neither too light nor too dark. It must be readily wetted by aqueous fluids.

Uses.—The red colouring matters contained in litmus appear blue in the commercial article, in the aqueous extract of the same, and in the paper coloured with it, only from the presence of alkaline bases. If any one of the blue preparations comes in contact with free acid, the latter combines with the bases, and in consequence the colour proper to the natural litmus appears. Litmus paper is therefore an excellent means for the detection of free acids. The power of weak volatile acids to bind the alkaline bases is but temporary; so that when they volatilize the blue colour again appears. It must be borne in mind that the soluble neutral salts of most of the heavy metals also cause the blue colour to change to red.

β. Reddened Litmus Paper.

Preparation.—Blue solution of litmus is stirred with a glass rod dipped in dilute sulphuric acid, and the process repeated until the solution has just turned distinctly red. Slips of paper are dipped in the solution, and dried as in α. The dried slips should be distinctly red.

Uses.—Alkalies and alkaline earths, and also the sulphides of their metals, alkaline carbonates, and the soluble salts of some other weak acids, especially of boric acid, all afford bases which combine with the red colouring matters of litmus forming blue compounds similar to those contained in blue litmus. Reddened litmus, therefore, is coloured blue by the solutions of these substances, and it serves for their detection in general. Ammonia does not colour litmus paper permanently blue, so that the natural red colour of the litmus reappears as the alkali volatilizes.

γ. Turmeric Paper.

Preparation.—1 part of ground turmeric root is warmed and digested with 6 parts of weak spirit of wine, the tincture filtered, and slips of fine unsized paper are dipped in the filtrate. The dried slips should be of a fine yellow tint; they must be readily wetted by aqueous fluids.

Uses.—Turmeric paper is used for the same purpose as red litmus paper for the detection of free alkalies, &c., as they change its yellow colour to brown. It is not so delicate as litmus paper; but the change of colour is highly characteristic, and is very distinctly perceptible with many coloured liquids; it cannot, therefore, well be dispensed with. When testing with turmeric paper, it is to be borne in mind that, besides the substances mentioned in β, other compounds (boric acid, for instance) possess the property of turning its yellow colour to red, especially on drying. It affords an excellent means for the detection of boric acid.

All test papers should be cut into slips and kept in small well-closed boxes, or in bottles covered with black paper, as the continued action of light destroys the colour.

2. Solution of Indigo.

Preparation.—1 part of finely pulverized indigo is added slowly and in small portions at a time to 4–6 parts of fuming sulphuric acid, taking care to keep the mixture well stirred. The acid at first becomes of a brownish tint from impurities in the indigo blue, but it subsequently turns deep blue. Any great elevation of temperature is to be avoided, as part of the indigo blue may be thereby destroyed; it is advisable, therefore, when dissolving large quantities of the substance to place the vessel in cold water. When the whole of the indigo has been added to the acid, the vessel is covered and allowed to remain forty-eight hours, when the contents are poured into 20 times the quantity of water, and the whole mixed, filtered, and the blue solution kept for use.

Uses.—Indigo is decomposed by boiling with nitric acid, yellow-coloured oxidation products being formed. It serves, therefore, for the detection of nitric acid. Solution of indigo is also useful for detecting chloric acid and free chlorine.

B. REAGENTS IN THE DRY WAY.

I. Fluxes and Decomposing Agents.

§ 76.

1. Mixture of Carbonate of Soda and Carbonate of Potassa (Fusion Mixture),

$NaO,CO_2 + KO,CO_2$ $[Na_2CO_3 + K_2CO_3]$.

Preparation.—10 parts of purified bitartrate of potassa in powder are digested with 10 parts of water and 1 part of hydrochloric acid for several hours on the water-bath, with frequent stirring; the mass is then put into a funnel with a small filter in the point, and allowed to drain; the crystalline mass is then covered with a disk of rather difficultly permeable filtering paper with upturned edges, and washed by repeatedly pouring small quantities of cold water on to the filter paper; the washing being continued in this way until the liquid which runs through is no longer rendered turbid by solution of nitrate of silver, after addition of nitric acid. The bitartrate of potassa which has been freed from lime (and phosphoric acid) by this treatment is now dried.

The next thing is to prepare pure nitrate of potassa. This is done by dissolving commercial nitrate of potassa in half its weight of boiling water, filtering the solution into a porcelain or stoneware dish—a hot funnel should be used—and stirring it well with a clean wooden or porcelain spatula until cold. The crystalline powder is transferred to a funnel loosely stopped with cotton wool, allowed to drain, pressed down tightly, made even at the top, and covered with a double disk of difficultly permeable filtering paper with upturned edges; on to this, at intervals, water is poured in small portions at a time until the washings are no longer rendered turbid by solution of nitrate of silver. The contents of the funnel are emptied into a porcelain dish, dried, and the mass reduced to a fine powder.

Two parts of the purified bitartrate of potassa are now mixed with 1 part of the pure nitrate of potassa, and the perfectly dry mixture is projected in small portions at a time into a clean scoured cast-iron pot heated to low redness; after the mixture has deflagrated, it is heated strongly until a sample yields a perfectly colourless solution when treated with water. The charred mass is triturated with water, filtered, washed slightly, and the filtrate evaporated in a porcelain, or, better still, in a silver dish, until the liquid becomes covered with a persistent pellicle. The mixture is now cooled with constant stirring; and the crystals of carbonate of potassa which form are put into a funnel, allowed to drain well, washed slightly, dried thoroughly in a silver or platinum dish, and kept in a well-stoppered bottle. On evaporation, the mother liquor leaves a salt which, although containing traces of alumina and silicic acid, is still available for many purposes.

Pure carbonate of potassa may also readily be prepared from commercial bicarbonate of potassa; this is powdered, and washed with small quantities of water until the washings, acidified with nitric acid, no longer give the slightest precipitate with nitrate of silver or nitrate of baryta. The powder is then dried, and converted into the monocarbonate by heating it in a platinum or silver dish.

Thirteen parts of the pure carbonate of potassa prepared in the manner just described are mixed with 10 parts of pure anhydrous carbonate of soda, and the mixture kept in a well-stoppered bottle. The mixture of carbonate of potassa and carbonate of soda may also be prepared by deflagrating 20 parts of pure bitartrate of potassa with 9 parts of pure nitrate of soda, treating with water, and evaporating the solution to dryness; or by igniting pure tartrate of potassa and soda, extracting the carbonaceous mass with water, and evaporating the clear solution to dryness.

Tests.—The purity of the mixed salt is tested as directed in § 46. To detect any trace of cyanide of potassium that may happen to be present, a little solution of proto-sesquioxide of iron is added, and then hydrochloric acid in excess; a bluish-green coloration of the solution and the formation of a blue precipitate after a time will indicate the presence of cyanide of potassium.

Uses.—If silicic acid or a silicate is fused with about 4 parts (consequently with an excess) of carbonate of potassa or soda, carbonic acid escapes with effervescence, and a basic alkaline silicate is formed, which, being soluble in water, may be readily separated from such metallic oxides as it may contain in admixture; from this basic alkaline silicate, hydrochloric acid separates the silicic acid as hydrate. If a fixed alkaline carbonate is fused with sulphate of baryta, strontia, or lime, carbonates of the alkaline earths and sulphate of the alkali are formed; in these new compounds, both the base and the acid of the originally insoluble salt may be readily detected. However, neither carbonate of potassa nor carbonate of soda is used separately to effect the decomposition of the insoluble silicates and sulphates, but the above-described mixture of both, because this mixture requires a far lower degree of heat for fusion than either of its two components; this renders it possible to do the fusion over a Berzelius spirit lamp, or over a simple bunsen burner. The fusion with alkaline carbonates is always done in a platinum crucible, provided no reducible metallic oxides are present.

§ 77.

2. Hydrate of Baryta, BaO,HO [BaH_2O_2].

Preparation.—The crystals of baryta prepared in the manner directed in § 36 are heated gently in a silver or platinum dish, until the water of crystallization is completely expelled. The residuary white mass is pulverized, and kept for use in a well-closed bottle.

Uses.—Hydrate of baryta fuses at a gentle red heat without losing its water. When silicates which resist decomposition by acids are fused with about 4 times their weight of hydrate of baryta, basic silicates are formed which acids will decompose. If, therefore, the fused mass is treated with water and hydrochloric acid, the solution evaporated to dryness, and the residue digested with dilute hydrochloric acid, the silicic acid is left behind, and the oxides are obtained in solution in the form of chlorides. Hydrate of baryta is used as a flux when we wish to test silicates for alkalies. This reagent is preferable as a flux to carbonate or nitrate of baryta, as it neither requires a very high temperature for its fusion, as is the case with the carbonate, nor does it cause any spirting in the fusing mass, arising from disengagement of gas, as is the case with the nitrate. The fusion with hydrate of baryta is done in silver or platinum crucibles.

§ 78.

3. Fluoride of Calcium, CaF [CaF_2].

Fluor-spar as pure as can be procured and, more particularly, free from alkalies, is reduced to fine powder, and kept for use.

Uses.—Fluoride of calcium in conjunction with sulphuric acid is used to decompose silicates insoluble in acids, and more especially to detect the alkalies which they contain. If pure aqueous hydrofluoric acid (which must volatilize completely when heated in a platinum dish) or pure fluoride of ammonium is to be had, they are preferable to fluoride of calcium for decomposing silicates. Compare Section III. *Silicic acid,* § 150.

§ 79.

4. Nitrate of Soda, NaO,NO_5 [$NaNO_3$].

Preparation.—Pure nitric acid is exactly neutralized with pure carbonate of soda, and evaporated to crystallization. The crystals are dried thoroughly, powdered, and kept for use.

Tests.—A solution of nitrate of soda should not give any turbidity with solution of nitrate of silver or nitrate of baryta, nor be precipitated by carbonate of soda.

Uses.—Nitrate of soda is a very powerful oxidizing agent, yielding oxygen to combustible substances when heated with them. This reagent is used chiefly to convert various metallic sulphides, more particularly the sulphides of tin, antimony, and arsenic, into oxides or acids; also to effect the rapid and complete combustion of organic substances. For the latter purpose, however, nitrate of ammonia is sometimes preferable; it is prepared by saturating nitric acid with carbonate of ammonia.

§ 80.

5. Acid Sulphate of Potassa, $KO,HO,2SO_3$ [$KHSO_4$].

Preparation.—87 parts of neutral sulphate of potassa (§ 42) is mixed with 49 parts of pure concentrated sulphuric acid in a platinum dish or large platinum crucible, and heated to low redness until the whole is in a state of calm fusion; it is then poured out into a platinum dish placed in cold water, or on to a piece of porcelain, and the cake broken up into smaller pieces and kept for use.

Tests.—Acid sulphate of potassa should dissolve in water with ease to a clear liquid with a strongly acid reaction. The solution should not be rendered turbid or precipitated by sulphuretted hydrogen or by ammonia and sulphide of ammonium.

Uses.—Acid sulphate of potassa at the temperature of fusion dissolves and decomposes many compounds, which cannot be dissolved and decomposed by acids in the wet way without considerable difficulty, such as ignited alumina, titanic acid, chrome iron ore, &c. This reagent, therefore, is useful for dissolving or decomposing such substances. It is better to do the fusion in platinum vessels.

II. Blowpipe Reagents.

§ 81.

6. Carbonate of Soda, NaO,CO_2 [Na_2CO_3].

Preparation.—See § 46.

Uses.—Carbonate of soda is useful, in the first place, to promote the reduction of oxidized substances in the inner flame of the blowpipe. In fusing, it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the substance under examination. With salts of the heavy metals the reduction is preceded by separation of the base. It co-operates in this process also chemically by the transposition of its constituents (according to R. Wagner, in consequence of the formation of cyanide of sodium). Where the quantity operated on is very minute, the reduced metal is often found in the pores of the charcoal. In such cases, the parts surrounding the cavity which contains the substance are scooped out with a knife, and triturated in a small mortar; the charcoal is then washed off from the metallic particles, which now become visible either in the form of powder or as small spangles, as the case may be.

Carbonate of soda serves, in the second place, as a solvent. Platinum wire is the most convenient support for testing the solubility of substances in melted carbonate of soda. A few only of the bases dissolve in fused carbonate of soda, but acids dissolve in it with facility. Carbonate of soda is also applied as a decomposing agent and flux, more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, the newly-formed sulphate of soda being reduced at the same time to sulphide of sodium; also to effect the decomposition of sulphide of arsenic, with which it forms a double sulphide of arsenic and sodium, and arsenite or arsenate of soda, thus converting it to a state which permits of its subsequent reduction by hydrogen. Carbonate of soda also is the most sensitive reagent in the dry way for the detection of manganese, as, when fused in the outer flame with a substance containing manganese, it yields a green opaque bead, owing to the formation of manganate of soda.

§ 82.

2. Cyanide of Potassium, $HC_2N = KCy$ [KCN].

Preparation.—See § 54.

Uses.—Cyanide of potassium is an exceedingly powerful reducing agent in the dry way; indeed it excels in its action almost all other reagents of the same class, and separates the metals not only from most oxygen compounds, but also from many sulphur compounds. This reduction is attended in the former case with formation of cyanate of potassa, by the absorption of oxygen, and in the latter case with formation of the sulphocyanate, by the taking up of sulphur. By means of this reagent, we may effect the reduction of metals from their compounds with the greatest possible facility; for instance, we may obtain metallic antimony from antimonious acid or from sulphide of antimony, metallic iron from sesquioxide of iron, &c. The readiness with which cyanide of potassium enters into fusion facilitates the reduction of the metals greatly; the process may usually be conducted even in a porcelain crucible over a spirit or gas-lamp. Cyanide of potassium is a most valuable and important agent for reducing binoxide of tin, antimonic acid, and more particularly tersulphide of arsenic. Cyanide of potassium is equally important as a blowpipe reagent. Its action is exceedingly energetic; substances like binoxide of tin, the reduction of which by means of carbonate of soda requires a tolerably strong flame, are reduced by cyanide of potassium with the greatest facility. In blowpipe experiments, we invariably use a mixture of equal parts of carbonate of soda and cyanide of potassium; the admixture of carbonate of soda is intended here to check in some measure the excessive fusibility of the cyanide of potassium. This mixture of cyanide of potassium with carbonate of soda, besides being a far more powerful reducing agent than the simple carbonate of soda, has moreover this great advantage over the latter, that it is absorbed by the pores of the charcoal with extreme facility, and thus permits the production of the metallic globules in a state of the greatest purity.

§ 83.

3. Biborate of Soda or Borax, $NaO,2BO_3$ [$Na_2B_4O_7$].

Crystallized, $NaO,2BO_3 + 10aq$ [$Na_2B_4O_7,10H_2O$].

The purity of commercial borax may be tested by adding to its solution carbonate of soda, or, after previous addition of nitric acid, solution of nitrate of baryta or of nitrate of silver. The borax may be considered pure if these reagents do not produce any alteration in the solution; but if either of them causes the formation of a precipitate, or renders the liquid turbid, recrystallization is necessary. The pure crystallized borax is exposed to a gentle heat, in a platinum crucible, until it ceases to swell up; when cold it is pulverized and kept for use.

Uses.—Boric acid manifests a great affinity for oxides when brought into contact with them in a state of fusion. This affinity enables it, in the first place, to combine directly with oxides; secondly, to expel weaker acids from their salts; and, thirdly, to predispose metals, sulphides, and haloïd compounds to oxidize in the outer flame of the blowpipe, that it may combine with the oxides. Most of the borates thus produced fuse readily, even without the aid of a flux, but far more so in conjunction with borate of soda; the latter salt acts in this operation either as a mere flux, or by the formation of double salts. Now we may regard biborate of soda as containing both free boric acid and borate of soda; the union of these two substances renders it one of our most important blowpipe reagents. In fusing with borax, we usually employ platinum wire for a support; the loop of the wire is moistened or heated to redness, then dipped into the powder and exposed to the outer flame; a colourless bead of fused borax is thus produced. A small portion of the substance is then attached to the bead, by bringing the latter into contact with it whilst still hot or after having previously moistened it. The bead with the substance adhering to it is now exposed to the gas or blowpipe flame, and the reactions are observed. The following points ought to be more particularly watched:—(1) Whether or not the substance dissolves to a transparent bead, and whether or not the bead retains its transparency on cooling; (2) whether the bead exhibits a distinct colour, which in many cases at once clearly indicates the individual metal which the substance contains; as is the case, for instance, with cobalt; and (3) whether the bead behaves in the same or a different way in the outer and in the inner flame. Reactions of the latter kind arise from the reduction of higher to lower oxides, or even to the metallic state, and are particularly characteristic for some substances.

§ 84.

4. Phosphate of Soda and Ammonia. Microcosmic Salt.

NaO,NH_4O,HO,PO_5 $[Na(NH_4)HPO_4]$.

Crystallized, NaO,NH_4O,HO,PO_5+8aq $[Na(NH_4)HPO_4,4H_2O]$.

Preparation.—*a.* 6 parts of phosphate of soda and 1 of pure chloride of ammonium are dissolved by boiling in 2 parts of water, and the solution is allowed to cool; the crystals of double phosphate of soda and ammonia which separate are freed from the chloride of sodium which adheres to them by recrystallization, after addition of some solution of ammonia. The purified crystals are then dried, pulverized, and kept for use.

b. Two equal portions of a solution of pure tribasic phosphoric acid are taken, and solution of soda is added to the one, and solution of ammonia to the other, until both mixtures have a distinctly alkaline reaction; the two are then mixed, and the solution allowed to crystallize.

Tests.—Phosphate of soda and ammonia dissolves in water yielding a feebly alkaline solution. The yellow precipitate produced in this solution by nitrate of silver should dissolve completely in nitric acid. Microcosmic salt should give a clear and colourless bead when fused on a loop of platinum wire.

Uses.—On heating phosphate of soda and ammonia, the ammonia escapes with the water of crystallization, leaving acid pyrophosphate of soda, NaO,HO,PO_5 [$Na_2H_2P_2O_7$]; when this is heated more strongly, the last equivalent of water escapes likewise, and the readily fusible metaphosphate of soda, NaO,PO_5 [$NaPO_3$], is left. The action of microcosmic salt is analogous to that of biborate of soda. In some cases, however, it is preferable to use borax as a solvent or flux, the beads which it forms with many substances being more beautifully and distinctly coloured than those of borax. Platinum wire is also used for a support in the process of fluxing with microcosmic salt; the loop must be made small and narrow, otherwise the bead will not adhere to it. The operation is conducted as directed for borax on p. 81.

§ 85.

5. Nitrate of Protoxide of Cobalt, CoO,NO_5 [$Co(NO_3)_2$].

Crystallized, $CoO,NO_5 + 6aq$ [$Co(NO_3)_2,6H_2O$].

Preparation.—Commercial oxide of cobalt is dissolved in hydrochloric acid, the solution evaporated to dryness on the water-bath, and the residue dissolved in water; carbonate of baryta made into a cream with water (§ 60) is then added in excess, the mixture allowed to remain for some hours, with frequent stirring, filtered, and the residue washed. More carbonate of baryta is now added to the filtrate, chlorine passed in, and the whole allowed to remain for a considerable time, shaking repeatedly; the precipitate, consisting of peroxide of cobalt and the excess of carbonate of baryta, is separated from the solution which contains the nickel, thoroughly washed, dissolved in hydrochloric acid, sulphuric acid added in slight excess to precipitate the baryta, and sulphuretted hydrogen passed into the mixture (without filtering) heated to 70°. The product is filtered, ammonia added to the filtrate to alkaline reaction, then sulphide of ammonium in excess, and lastly acetic acid to acid reaction; the sulphide of cobalt thus precipitated is collected, washed, dissolved in nitro-hydrochloric acid, and the excess of acid removed by evaporation. The residue is next dissolved in water, and the hot solution precipitated with carbonate of soda; the precipitate is well-washed, and treated while still moist with oxalic acid in excess. The rose-red oxalate of protoxide of cobalt is thoroughly washed, dried, and heated to redness in a glass tube, in a current of hydrogen; this decomposes the oxalate into carbonic acid, which escapes, and metallic cobalt, which is left behind. The metal is washed, first with water containing acetic acid, then with pure water, dissolved in dilute nitric acid, and evaporated to dryness on the water bath. 1 part of the residue is dissolved in 10 parts of water for use.

Tests.—Solution of nitrate of protoxide of cobalt should be free from other metals, and especially from salts of the alkalies; no fixed residue should be left when the solution is precipitated with sulphide of ammonium, filtered, and the filtrate evaporated on platinum. When treated with cyanide of potassium in excess, adding soda if necessary, it should not give the slightest black precipitate of hydrated oxide of nickel even after remaining for an hour.

Uses.—When protoxide of cobalt is ignited with certain infusible compounds (oxide of zinc, alumina), it forms characteristically coloured compounds, and may accordingly serve for their detection.

SECTION III.

REACTIONS,

OR

Behaviour of Compounds with Reagents.

§ 86.

In the introductory remarks, it was stated that the operations and experiments of qualitative analysis have for their object the conversion of the unknown constituents of any given compound into forms of which we know the behaviour, relations, and properties, affording us information from which we may draw correct inferences regarding the several constituents of which the analysed compound consists. The greater or less value of such analytical experiments, like that of all other inquiries and investigations, depends on the greater or less degree of certainty with which they lead to definite results, no matter whether these are positive or negative. But as a question does not render us any the wiser if we do not know the language in which the answer is given, so, in like manner, analytical investigations will be of no use if we do not understand the mode of expression in which the desired information is conveyed to us; in other words, if we do not know how to interpret the phenomena produced by the action of the reagents on the substance examined.

Before we can proceed, therefore, to enter on the practical investigations in analytical chemistry, it is indispensable that we should really have a very accurate knowledge of the behaviour, relations, and properties of the new forms into which we intend to convert the substances we wish to analyse. Now this accurate knowledge consists, in the first place, in a clear conception and comprehension of the conditions necessary for the formation of the new compounds, and the manifestation of the various reactions; and in the second place, in a distinct impression of the colour, form, and physical properties which characterize the new compound. This section of the work demands therefore not only the most careful and attentive study, but requires moreover that the student should examine and verify by actual experiment every fact stated in it.

The method usually adopted in elementary works on chemistry is to treat of the various substances and their behaviour with reagents individually and separately, and to point out their characteristic reactions. The author, however, in the present work has considered it to be more judicious and better adapted to the use of the student, to arrange those substances which are in many respects analogous in groups, and thus, by comparing their analogies with their differences, to place the latter in the clearest possible light.

A.—BEHAVIOUR OF THE METALLIC OXIDES AND OF THEIR RADICLES.

§ 87.

Before proceeding to the special study of the several metallic oxides, it will be advisable to give a general view of the whole of them classified in groups, and showing the oxides belonging to each group. The grounds on which the classification has been arranged will appear when the several groups are specially considered.

First group—

Potassa, soda, ammonia, (oxide of cæsium, oxide of rubidium, lithia).

Second group—

Baryta, strontia, lime, magnesia.

Third group—

Alumina, sesquioxide of chromium (beryllia, thoria, zirconia, yttria, oxide of erbium, oxides of cerium, lanthanum, didymium, titanium, tantalum, niobium).

Fourth group—

Oxides of zinc, manganese, nickel, cobalt, iron (of uranium, thallium, indium, vanadium).

Fifth group—

Oxides of silver, mercury, lead, bismuth, copper, cadmium (of palladium, rhodium, osmium, ruthenium).

Sixth group—

Oxides and acids of gold, platinum, tin, antimony, arsenic (of iridium, molybdenum, tellurium, tungsten, selenium).

Of the metallic oxides, only those the names of which are spaced (like potassa) are found distributed extensively and in large quantities in that portion of the earth's crust which is accessible to our investigations; these are the most important to chemistry, arts and manufactures, agriculture, pharmacy, &c., and we shall therefore consider them at greater length. The remainder are more briefly noticed in paragraphs printed in smaller type, and may be passed over by the younger class of students of analytical chemistry. The properties and reactions of the metals themselves are given only in the case of those which are more frequently met with in the metallic state in analytical operations.

§ 88.

First Group.

More common oxides:—Potassa, Soda, Ammonia.

Rarer oxides:—Oxide of Cæsium, Oxide of Rubidium, Lithia.

Properties of the group.—The alkalies are readily soluble in water, as well in the pure or caustic state as in the form of sulphides, carbonates, and phosphates. (The salts of lithia, however, dissolve with difficulty.) Accordingly, the alkalies do not precipitate one another in the pure state, nor as carbonates or phosphates (which in the case of lithia, however, presupposes a higher degree of dilution of the solutions), nor are they precipitated by suphuretted hydrogen under any condition whatever. The solutions of the pure alkalies as well as of their sulphides and carbonates restore the blue colour of reddened litmus-paper, and impart an intensely brown tint to turmeric paper.

Special Reactions of the more common Oxides of the first group.

§ 89.

a. **Potassa,** KO [K_2O].

1. Potassa and its hydrate and salts are not volatile at a low red-heat. Potassa and its hydrate deliquesce in the air; the oily liquids thereby formed absorb carbonic acid rapidly from the air, but without solidifying.

2. Nearly all the salts of potassa are soluble in water. Those with colourless acids are colourless. The neutral salts of potassa with strong acids do not alter vegetable colours. Carbonate of potassa crystallizes (in combination with water of crystallization) with difficulty, and deliquesces in the air. Sulphate of potassa is anhydrous and suffers no alteration in the air.

3. **Chloride of platinum** produces in the neutral and acid solutions of potassa a yellow, crystalline, heavy precipitate of chloride of platinum and chloride of potassium (platinochloride of potassium), $KCl,PtCl_2$ [K_2PtCl_6]. In concentrated solutions, this precipitate separates immediately on adding the reagent: in dilute solutions it is formed only after some time, often after a *considerable* time. Very dilute solutions are not precipitated by the reagent. The precipitate consists of octahedrons discernible under the microscope. Alkaline solutions must be acidified with hydrochloric acid before the chloride of platinum is added. The precipitate is very sparingly soluble in water; the presence of free acids does not greatly increase its solubility; it is insoluble in alcohol. Chloride of platinum is therefore a particularly delicate test for salts of potassa dissolved in spirit of wine. The best method of applying this reagent is to evaporate the aqueous solution of the potassa salt with chloride of platinum nearly to dryness on the water-bath, and to pour a little water over the residue (or, better still, some spirit of wine, provided no substances insoluble in that menstruum be present), when the platinochloride of potassium will be left undissolved. Care must be taken not to confound this double salt with platinochloride of ammonium, which greatly resembles it (see § 91, 4).

4. **Tartaric acid** produces in neutral or alkaline[*] solutions—a white, quickly subsiding, *granular* crystalline precipitate of acid tartrate of potassa, $KO,HO,C_8H_4O_{10}$ [$KHC_4H_4O_6$]. In concentrated solutions, this precipitate separates immediately; in dilute solutions often only after the lapse of a *considerable* time. Vigorous shaking or stirring of the liquid greatly promotes its formation. Very dilute solutions are not precipitated by this reagent. Free alkalies and free mineral acids dissolve the precipitate; it is sparingly soluble in cold, but pretty readily soluble in hot water. In acid solutions, the free acid must, if practicable, first be expelled by evaporation and ignition, or the solution must be neutralized with soda or carbonate of soda.

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[*] If the solution is alkaline, the reagent must be added until the liquid shows a strongly acid reaction.

Acid tartrate of soda answers as a test for potassa still better than free tartaric acid. The reaction is the same in kind, but different in degree, being much more delicate with the salt than with the free acid, since where the former is used the soda salt of the acid combined with the potassa is formed, whereas with free tartaric acid the hydrate of the acid combined with the potassa is formed, and this tends to increase the solvent action of the water present on the acid tartrate of potassa, and consequently checks the separation of the latter,

$$KO,NO_5 + NaO,HO,C_8H_4O_{10} = KO,HO,C_8H_4O_{10} + NaO,NO_5$$

$$[KNO_3 + NaHC_4H_4O_6 = KHC_4H_4O_6 + NaNO_3].$$

5. If a potassa salt which is volatile at an intense red heat is held on the loop of a fine platinum wire in the fusing zone of the Bunsen **gas-lamp** (p. 23), the salt volatilizes, and imparts a blue violet tint to the part of the flame above the sample. Chloride of potassium and nitrate of potassa volatilize rapidly, the carbonate and sulphate less rapidly, and the phosphate still more slowly; but they all distinctly show the reaction, although decreasing in degree. If a more uniform manifestation of the reaction is desired, that is, a manifestation independent of the nature of the acid that may chance to be combined with the potassa, the sample need simply be moistened with sulphuric acid, dried at the border of the flame, and then introduced into the fusing zone. With silicates, and other compounds of potassa which volatilize with difficulty, the reaction may be ensured by fusing the sample first with pure gypsum, as in this way silicate of lime and sulphate of potassa are formed, and the latter then readily colours the flame. Decrepitating salts should be ignited in a platinum spoon before they are attached to the loop. The sample of the potassa salt may also be held before the apex of the inner **blow-pipe flame** produced with a spirit-lamp. It should be noted that the presence of a salt of soda completely obscures the potassa coloration of the flame.

The spectrum of the potassa flame as observed by the **spectroscope** (p. 28, or p. 29) is shown in the coloured plate of spectra. It contains two characteristic lines, the red line α and the indigo blue line β. If the potassa flame is observed through the **indigo prism** (p. 27) the coloration appears sky-blue, violet, and at last intensely crimson, even through the thickest layers of the solution. Admixtures of lime, soda, and lithia compounds do not alter this reaction, as the yellow rays cannot penetrate the indigo solution, and the rays of the lithia flame also are only able to pass through the thinner layers of that solution, but not through the thicker layers; the exact spot where the penetrating power of the rays of the lithia flame ceases has to be marked by the operator on his indigo prism. But organic substances which impart luminosity to the flame might lead to mistakes, and must therefore, if present, first be removed by combustion. Instead of the indigo prism, Cornwall's permanganate prism (p. 27) or a blue glass may be used; if lithia is present, the absorbent medium must be sufficiently thick to keep out the red lithia rays.

6. If a salt of potassa (chloride of potassium answers best) is heated with a small quantity of water, **alcohol** (burning with colourless flame) added, the mixture heated, and then kindled, the flame appears violet. The presence of soda obscures this reaction, which is altogether much less delicate than the one described in 5.

§ 90.

b. **Soda,** NaO [Na_2O].

1. Soda and its hydrate and salts have in general the same properties and reactions as potassa and its corresponding compounds. The oily liquid which soda forms by deliquescence on exposure to the air resolidifies speedily by absorption of carbonic acid. Carbonate of soda crystallizes readily; the crystals, $NaO,CO_2 + 10aq$ [$Na_2CO_3,10H_2O$], effloresce rapidly when exposed to the air; the same applies to the crystals of sulphate of soda, $NaO,SO_3 + 10aq$ [$Na_2SO_4,10H_2O$].

2. If a sufficiently concentrated solution of a soda salt with neutral or alkaline reaction is mixed, for greater convenience, in a watch-glass, with a solution of **metantimonate of potassa** prepared according to the directions given in § 51, the mixture remains clear at first, or appears only slightly turbid; but upon rubbing the part of the glass wetted by the liquid with a glass rod, a crystalline precipitate of metantimonate of soda, $NaO,HO,SbO_5 + 6aq$ [$Na_2H_2Sb_2O_7,6H_2O$], speedily separates; this makes its appearance first along the lines rubbed with the rod, and ultimately subsides as a heavy, sandy precipitate. The precipitate does not separate from dilute solutions of soda salts until after the lapse of some time, occasionally as long as twelve hours. From very dilute solutions, it does not separate at all. The precipitated antimonate of soda is *invariably* crystalline. Where it has separated slowly, it occasionally consists of well-formed microscopic cubic octahedrons, but more frequently of four-sided prisms with pyramidal summits; if it has separated quickly, it appears in the form of small boat-shaped crystals. The presence of large quantities of salts of potassa interferes very considerably with the reaction. Acid solutions cannot be tested with metantimonate of potassa, as free acids will separate from the latter substance hydrated metantimonic acid. It is indispensable, therefore, before adding the reagent, to remove, if possible, the free acid by evaporation or ignition, or where this is not practicable, by neutralizing the acid solution with a little carbonate of potassa until the reaction is feebly alkaline. It should also be borne in mind that solutions cannot be tested with metantimonate of potassa if they contain any other bases besides soda and potassa.

3. If salts of soda are held in the fusing zone of the Bunsen **gas-lamp** or in the inner **spirit blowpipe flame,** they show, with regard to their relative volatility and the action of decomposing agents on them, a similar behaviour to the salts of potassa; the soda salts, are, however, a little less volatile than the corresponding potassa salts. But the most characteristic sign of the presence of soda salts is the intense yellow coloration which they impart to the flame. This reaction will effect the detection of even the minutest quantities of soda, and is not obscured even by the presence of large quantities of potassa.

The spectrum (see coloured plate) shows only a single yellow line *a* in an ordinary **spectroscope,** but with a more powerful apparatus two lines will be visible distinctly, although they are exceedingly close to each other. The reaction is so delicate that the chloride of sodium contained in atmospheric dust generally suffices to give a soda spectrum, although a faint one.

It is characteristic of the soda flame, that a crystal of dichromate of potassa appears colourless in its light, and that a slip of paper coated with iodide of mercury appears white with a faint shade of yellow (Bunsen); also that it looks orange yellow when observed through a **green glass** (Merz). These reactions are not obscured by the presence of salts of potassa, lithia, or lime.

4. If salts of soda (chloride of sodium answers best) are treated as stated on p. 86, 6, the **alcohol flame** is coloured intensely yellow. The presence of a potassa salt does not affect the distinctness of this reaction.

5. **Chloride of platinum** produces no precipitate in neutral or acid solutions of soda salts, as platinochloride of sodium is readily soluble both in water and in spirit of wine; it crystallizes in yellowish-red prisms.

6. **Tartaric acid** and **acid tartrate of soda** fail to precipitate even concentrated neutral solutions of soda salts.

§ 91.

c. **Ammonia,** NH_4O [$(NH_4)_2O$].

1. Anhydrous ammonia, NH_3 [NH_3], is gaseous at the ordinary temperature, but is generally employed in aqueous solution, in which it betrays its presence at once by its penetrating odour. It is expelled from this solution by the application of heat. It is sometimes convenient to assume that the solution contains it as oxide of ammonium, NH_4O [$(NH_4)_2O$] (see § 35).

2. All the salts of ammonia are volatile at a low heat, either with or without decomposition. Most of them are readily soluble in water. The solutions are colourless. The neutral compounds of ammonia with strong acids do not alter vegetable colours.

3. If salts of ammonia are triturated with **hydrate of lime,** best with the addition of a few drops of water, or are, either in the solid state or in solution, heated with solution of **potassa** or of **soda,** the ammonia is liberated in the gaseous state, and its presence may be recognized—1, by its characteristic odour; 2, by its action on moistened test-papers; and 3, by giving rise to the formation of white fumes when any object, such as a glass rod, moistened with hydrochloric acid, nitric acid, acetic acid, or any of the volatile acids, is brought in contact with it. These fumes are produced by the finely divided solid ammoniacal salts formed by the vapour of the acid and the ammonia. Hydrochloric acid is the most delicate test in this respect; acetic acid, however, is less liable to give rise to a mistake. If the expulsion of the ammonia is effected in a small beaker, best with hydrate of lime, with addition of a very little water, and the beaker is covered with a watch-glass having a slip of moistened turmeric or reddened litmus paper attached to the centre of the convex side, the reaction will show the presence of even very minute quantities of ammonia; only the action is not immediate in such cases, but requires some time for its manifestation. It is promoted and accelerated by the application of a gentle heat.

4. **Chloride of platinum** behaves in the same manner with salts of ammonia as it does with salts of potassa; the yellow precipitate of platinochloride of ammonium, $NH_4Cl,PtCl_2$ [$(NH_4)_2PtCl_6$], consists,

like the corresponding potassium compound, of octahedrons discernible under the microscope.

5. **Tartaric acid** in highly concentrated solutions of neutral ammonium salts after some time throws down part of the ammonia as acid tartrate of ammonia, $NH_4O,HO,C_8H_4O_{10}$ [$(NH_4)HC_4H_4O_6$]. Less concentrated solutions are not precipitated. **Acid tartrate of soda** precipitates concentrated solutions more completely, and produces a precipitate even in more dilute solutions. The precipitate is white and crystalline. Its separation may be promoted by shaking the mixture, or by rubbing the inside of the vessel with a glass rod. It is acted on by solvents like the corresponding potassa salt, except that it is somewhat more readily soluble in water and in acids.

§ 92.

Recapitulation and Remarks.

The salts of potassa and soda are not volatile at a moderate red heat, whilst the salts of ammonia volatilize readily; the latter may therefore be easily separated from the former by ignition. The expulsion of **ammonia** from its compounds by hydrate of lime affords the surest means of ascertaining its presence. Salts of potassa can be detected in the wet way only after the removal of the ammoniacal salts which may be present, since both classes of salts behave in the same or a similar way with chloride of platinum and tartaric acid. After the removal of the ammonia, the **potassa** is clearly and positively characterized by either of these two reagents; it should be borne in mind, however, that the reactions will only take place in concentrated solutions, so that dilute solutions must first be concentrated. A single drop of a *concentrated* solution will give a positive result, which cannot be obtained with a large quantity of a dilute solution. The most simple way of detecting the potassa in the two sparingly soluble compounds that have come under our consideration here—namely, the platinochloride of potassium and the acid tartrate of potassa—is to decompose these salts by gentle ignition; the former thereupon yields the potassa in the form of chloride of potassium, the latter in the form of carbonate of potassa. For the direct detection of potassium in iodide of potassium, tartaric acid or acid tartrate of soda is better suited than chloride of platinum; as with the latter reagent the separation of the platinochloride of potassium is interfered with in consequence of the formation of a dark red liquid containing iodide of platinum and free iodine. As regards **soda**, this alkali may be detected with positive certainty in the wet way by metantimonate of potassa, provided the reagent be properly prepared and freshly dissolved, and the soda salt solution be concentrated, neutral, or feebly alkaline, and free from other bases; moreover, it must be borne in mind that metantimonate of soda invariably separates in the crystalline form, and never in a flocculent state. To detect in this way very minute quantities of soda in presence of a large proportion of potassa, the latter should be first precipitated with chloride of platinum, the platinochloride of potassium filtered off, and the platinum removed from the filtrate by sulphuretted hydrogen (§ 127); it is again filtered, the filtrate evaporated to dryness, ignited gently, the residue dissolved in a very little water, and the solution finally tested with metantimonate of potassa.

Potassa and soda may be detected much more readily and speedily than in the wet way, and also with far greater delicacy, by the flame coloration. We have seen, indeed, that the soda coloration completely obscures the potassa coloration, even when the potassa salt contains but a trifling admixture of soda salt. With the aid of the spectrum apparatus, however, the spectra of the two are obtained so distinct and beautiful that a mistake is altogether impossible. And even without a spectrum apparatus the potassa coloration can always be distinctly recognized through the indigo or permanganate prism, or through a blue glass, even in a flame coloured strongly yellow by soda; the soda coloration again may be placed beyond doubt, if necessary, by the aid of iodide of mercury paper, or green glass, in the manner already described.

The following methods serve for the detection of **ammonia in exceedingly minute quantities,** as for instance in natural waters; they depend on the separation of certain mercury compounds which are insoluble in water, and which contain the nitrogen, or the nitrogen and part of the hydrogen of the ammonia.

a. If water containing a trace of ammonia or carbonate of ammonia is mixed with a few drops of solution of mercuric chloride, a white precipitate is formed, even in very dilute solution; the precipitate consists of NH_2Hg_2Cl [NH_2HgCl], and may be considered as a double amide and chloride of mercury, or as chloride of dimercurammonium:
$2NH_3 + 2HgCl = NH_2Hg_2Cl + NH_4Cl$ [$2NH_3 + HgCl_2 = NH_2HgCl + NH_4Cl$].
If the solution is extraordinarily dilute, no turbidity occurs, but on the addition of a few drops of solution of carbonate of potassa or carbonate of soda, the liquid will become turbid or opalescent after a few minutes. This reaction takes place when water containing a trace of a neutral salt of ammonia is mixed with a few drops of solution of mercuric chloride and a few drops of solution of carbonate of potassa or carbonate of soda. The precipitate which separates on the addition of carbonate of soda consists of 1 equivalent of the previously mentioned precipitate with 2 equivalents of oxide of mercury:

$$NH_3 + 4HgCl + 3(KO,CO_2) = NH_2Hg_2Cl,2HgO + HO + 3KCl + 3CO_2$$
$$[2NH_3 + 4HgCl_2 + 3K_2CO_3 = 2(NH_2HgCl,HgO) + H_2O + 6KCl + 3CO_2].$$

Too much mercuric chloride and carbonate of soda must not be added, otherwise a yellow precipitate of oxychloride of mercury would be formed. (Bohlig, Schöyen.)

b. On adding to a solution of mercuric iodide and potassium containing potassa* a liquid containing ammonia, or an ammonia salt, a reddish-brown precipitate is formed if the ammonia is present in some quantity; and even if only the most minute trace of ammonia is present, there is always a yellow coloration produced. The precipitate consists of tetramercurammonium iodide $NHg_4I,2HO$ [NHg_2I,H_2O]. The reaction is:

$$4(HgI,KI) + 3(KO,HO) + NH_3 = NHg_4I,2HO + 7KI + 4HO$$
$$[2(HgI_2,2KI) + 3KHO + NH_3 = NHg_2I,H_2O + 7KI + 2H_2O].$$

The application of heat promotes the separation of the precipitate.

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* Prepared as follows:—Two grams of iodide of potassium are dissolved in 5 c.c. water, the solution is heated and iodide of mercury added until the last portions remain undissolved. The mixture is then allowed to cool, and diluted with 20 c.c. water. This solution is allowed to remain for some time, filtered, and 20 c.c. of the filtrate mixed with 30 c.c. of a concentrated solution of potassa. Should the liquid turn turbid, it is allowed to stand for a time and the clear portion poured off for use.

Presence of chlorides of the alkali metals, or of salts of the alkalies with oxygen acids does not interfere with the reaction; but the presence of cyanide of potassium, or of sulphide of potassium, will prevent it (J. Nessler).

§ 93.

Special Reactions of the rarer Oxides of the first group.

1. Cæsia (Oxide of Cæsium), CsO [Cs_2O], and

2. Rubidia (Oxide of Rubidium), RbO [Rb_2O.]

The cæsium and rubidium compounds are, it would appear, found pretty widely distributed in nature, but in very minute quantities only. They have hitherto been found chiefly in the mother liquors of mineral waters, and in a few minerals (lepidolite, melaphyr, carnallite). Cæsium has been found in considerable quantities in pollux, and rubidium has been found in beetroot molasses and in the ashes of plants. The cæsium and rubidium compounds bear in general a great resemblance to the potassium compounds, more particularly in this, that their concentrated aqueous solutions are precipitated by **tartaric acid** and by **chloride of platinum,** and also that those of them that are volatile at a red heat tinge the **flame** violet. The most notable characteristic differences, on the other hand, are that the precipitates produced by chloride of platinum are far more insoluble in water than the platinochloride of potassium; 100 grams water at 10° will dissolve 900 mgrm. of platinochloride of potassium, but only 154 mgrm. of the platinochloride of rubidium, and as little as 50 mgrm. of the platinochloride of cæsium. Again, the alums show great differences as regards their solubility in cold water; thus 100 parts of water at 17° dissolve 13·5 parts of potassium alum, 2·27 parts of rubidium alum, and 0·619 parts of cæsium alum. But above all, the flames coloured by cæsium and rubidium compounds give **spectra** quite different from the potassium spectrum (see plate of spectra). The cæsium spectrum is especially characterized by the two blue lines α and β, which are remarkable for their wonderful intensity and sharp outline; also by the line γ, which, however, is less strongly marked. Amongst the lines in the rubidium spectrum, the splendid indigo-blue lines marked α and β strike the eye by their extreme brilliancy. Less brilliant, but still very characteristic, are the lines δ and γ. To detect both alkalies in presence of each other by the spectroscope, the chlorides should be taken and not the carbonates, as with the latter salts the rubidium spectrum is not always distinct in the presence of the cæsium spectrum. (Allen, Heintz.) Lastly, we have still to mention that carbonate of cæsia is soluble in absolute alcohol, whilst carbonate of rubidia is insoluble in that menstruum; a separation of the two oxides, however, is effected only with difficulty by this means, as they seem to form a double salt which is not absolutely insoluble in alcohol. It is more easy to separate them when they are in the form of acid tartrates; the acid tartrate of rubidia dissolves in 8·5 parts of boiling water, and 84·57 parts of water at 25°, while the corresponding salt of cæsia dissolves in 1·02 parts of boiling water, and 10·32 parts of water at 25° (Allen). (The acid tartrate of potassa requires 15 parts of boiling water, and 89 parts of water at 25°.)

A separation may also be effected by adding stannic chloride to a hot solution of the salts containing a rather large excess of hydrochloric acid; under these circumstances cæsium stannichloride separates as a sparingly soluble precipitate whilst the rubidium and potassium remain in solution. Care must be taken not to mistake the sparingly soluble ammonium stannichloride for cæsium stannichloride (Stolba).

3. Lithia, LiO [Li_2O].

Lithia is also found pretty widely distributed in nature, but in minute quantities only. It is often met with in the analysis of mineral waters and ashes of plants, less frequently in the analysis of minerals, and only rarely in that of technical and pharmaceutical products. Lithia forms the transition from the first to the second group. It is only sparingly soluble in water; it does not attract moisture from the air. Most of its salts are soluble in water; some of them are deliquescent (chloride of lithium). Carbonate of lithia is sparingly soluble, particularly in cold water. On adding phosphate of soda to solutions of salts of lithia, and boiling, a white crystalline precipitate of tribasic phosphate of lithia, $3(LiO,PO_5)+aq$ [$2Li_3PO_4,H_2O$], is produced if the solution is not too dilute; this precipitate quickly subsides to the bottom of the vessel. This reaction, which is characteristic of lithia, is rendered much more delicate by adding at the same time as the phosphate of soda, a little solution of soda, just sufficient to leave the reaction alkaline, evaporating the mixture to dryness, treating the residue with water, and adding an equal volume of liquid ammonia; in this way even very minute quantities of lithia will be separated as tribasic phosphate. The precipitate fuses before the blowpipe, and on fusion with carbonate of soda gives a clear bead; when fused upon charcoal it is absorbed. It dissolves in hydrochloric acid yielding a solution which, when diluted and supersaturated with ammonia, remains clear in the cold, but on boiling gives a heavy crystalline precipitate of the phosphate. (Reactions by which phosphate of lithia differs from the phosphates of the alkaline earths.) **Tartaric acid** and **chloride of platinum** fail to precipitate even concentrated solutions of salts of lithia. If salts of lithia are exposed to the **gas** or **blowpipe flame,** in the manner described in § 89, 5, they tinge the flame carmine-red. With silicates containing lithia, it is necessary to add gypsum to produce this reaction, or, better still, a mixture of gypsum with pure fluor-spar in the proportions 2 : 1. Phosphate of lithia will tinge the flame carmine-red, if the fused bead is moistened with hydrochloric acid. The soda coloration conceals the lithia coloration; in presence of soda, therefore, the lithia tint must be viewed through a blue glass, or through a thin layer of indigo solution. The presence of a small proportion of potassa will not conceal the lithia coloration; in presence of a large proportion of potassa, the lithia may be identified by placing the substance in the fusing zone, viewing the coloured flame through the indigo prism and comparing it with a pure potassa flame produced in the opposite part of the fusing zone. Viewed through a thin layer of indigo solution, the lithia-coloured flame appears redder than the pure potassa flame; viewed through somewhat thicker layers, the flames appear at last equally red, if the proportion of the lithia to the potassa is only trifling; but when lithia predominates in the sample examined the intensity of the red coloration imparted by lithia decreases perceptibly when viewed through thicker layers, whilst that due to the pure potassa-flame is scarcely impaired. By this means, lithia may be detected in potassa salts, even though present only in the proportion of one part in several thousand parts of the latter. Soda, unless present in very large quantities, interferes but little with these reactions (Cartmell, Bunsen).

The **lithium spectrum** (see coloured plate) is most brilliantly characterized by the splendid carmine-red line α, and the orange-yellow very faint line β. The flame of a Bunsen burner yields only these two lines, but if chloride of lithium is introduced into a hydrogen flame, a dull blue line is perceptible, which becomes brilliant if the oxyhydrogen flame is used. Its position almost coincides with the weaker of the two blue lines of cæsium (Tyndall, Frankland). If alcohol be poured over chloride of lithium, and then ignited, the flame shows also a carmine-red tint. Presence of salts of soda will mask this reaction.

To detect small quantities of cæsia, rubidia, and lithia in presence of very large quantities of soda or potassa, extract the dry chlorides of the metals, after adding a few drops of hydrochloric acid, with alcohol of 90 per cent.; this leaves behind by far the larger portion of the chloride of sodium and chloride of potassium. The alcoholic solution is then evaporated to dryness, the residue dissolved in a little water, and precipitated with chloride of platinum. The precipitate is collected and boiled repeatedly with small quantities of water, to remove the platinochloride of potassium present, examining the progress of the purification by means of the spectroscope. For this purpose a small quantity of the precipitate is rolled up in a piece of moistened filter-paper, a thin platinum wire wound round it, and the paper charred in the point of the flame at as low a temperature as possible; it is then transferred to the fusing zone, and the flame examined by the spectroscope. The potassium spectrum will be found to grow fainter and fainter, whilst the spectra of rubidium and cæsium will become visible, if these metals are present. The solution filtered off from the original platinum precipitate is evaporated to dryness, the residue heated to low redness in a current of hydrogen, in order to decompose the platinochloride of sodium and the excess of chloride of platinum; it is then moistened with hydrochloric acid, the acid driven off again, and the chloride of lithium finally extracted with a mixture of absolute alcohol and ether. The evaporation of the solution obtained leaves the chloride of lithium behind in a state of almost perfect purity; it may then be further examined and tested. Before drawing from the simple coloration of the flame the conclusion that lithia is present, it is advisable, in order to guard against the chance of error, to test a portion of the residue, dissolved in water, with sulphuric acid and alcohol, to make quite sure that neither strontia nor lime is present. The addition of hydrochloric acid, which is repeatedly prescribed in the above process to precede the extraction of the chloride of lithium with alcohol, is necessary as chloride of lithium, even at a moderate red heat, is converted by the action of aqueous vapour into caustic lithia, this then attracts carbonic acid, and forms carbonate of lithia, which is insoluble in alcohol.

§ 94.

Second Group.

BARYTA, STRONTIA, LIME, MAGNESIA.

Properties of the Group.—The alkaline earths are soluble in water in the pure (caustic) state; magnesia, however, is only very sparingly soluble in water. The solutions have an alkaline reaction; the alkaline reaction of magnesia is best observed when it is laid upon moistened test-paper. The neutral carbonates and phosphates of the alkaline earths are insoluble in water, and the solutions of the salts of the alkaline earths are therefore precipitated by carbonates and phosphates of the alkalies; this reaction distinguishes the oxides of the second group from those of the first. From the oxides of the other groups, they are distinguished by their solutions not being precipitated either by sulphuretted hydrogen, or by sulphide of ammonium. The alkaline earths and their salts are white or colourless, and not volatile at a moderate red heat. The solutions of their nitrates and chlorides are not precipitated by carbonate of baryta.

Special Reactions.

§ 95.

a. **Baryta,** BaO [BaO].

1. Baryta is pretty readily soluble in hot water, but rather sparingly so in cold water; it dissolves freely in dilute hydrochloric or nitric acid. Hydrate of baryta fuses at a red heat, without losing its water, but this is given off at a very high temperature (Brügelmann).

2. Most of the salts of baryta are insoluble in water. The

soluble salts do not affect vegetable colours; they are decomposed when ignited in a glass tube, with the exception of the chloride, bromide, and iodide of barium. The insoluble salts dissolve in dilute hydrochloric acid, except sulphate of baryta and silicofluoride of barium. Nitrate of baryta and chloride of barium are insoluble in alcohol, and do not deliquesce in the air. Concentrated solutions of baryta are precipitated by concentrated hydrochloric or nitric acid if the acid is added in large proportion, chloride of barium and nitrate of baryta being insoluble in the concentrated aqueous solutions of the said acids.

3. **Ammonia** produces no precipitate in aqueous solutions of salts of baryta; **potassa** or **soda** (free from carbonic acid) only in highly concentrated solutions. Water redissolves the bulky precipitate of crystals of hydrate of baryta, $BaO,HO + 8aq$ [$BaH_2O_2,8H_2O$], produced by potassa or soda.

4. **Carbonates of the alkalies** throw down carbonate of baryta, BaO,CO_2 [$BaCO_3$], in the form of a white precipitate. If the solution was previously acid, complete precipitation takes place only after heating the liquid. The precipitate is soluble in chloride of ammonium to a trifling yet clearly perceptible extent; carbonate of ammonia therefore produces no precipitate in very dilute solutions of baryta containing much chloride of ammonium.

5. **Sulphuric acid** and all the soluble **sulphates**, more particularly also solution of **sulphate of lime**, produce, even in very dilute solutions, a heavy, finely pulverulent, white precipitate of sulphate of baryta, BaO,SO_3 [$BaSO_4$], which is insoluble in alkalies, nearly so in dilute acids, but perceptibly soluble in boiling concentrated hydrochloric and nitric acids, as well as in concentrated solutions of ammonia salts; in the latter, however, only if there is no excess of sulphuric acid or a sulphate present. This precipitate is generally formed immediately the reagent is added; from highly dilute solutions, however, especially when strongly acid, it separates only after some time.

6. **Hydrofluosilicic acid** throws down silicofluoride of barium, BaF,SiF_2 [$BaSiF_6$], in the form of a colourless crystalline quickly subsiding precipitate. In dilute solutions, this precipitate is formed only after the lapse of some time: it is perceptibly soluble in hydrochloric and nitric acids. The addition of an equal volume of alcohol hastens the precipitation, and makes it so complete that the filtrate remains clear on the addition of sulphuric acid.

7. **Phosphate of soda** in neutral or alkaline solutions of baryta salts produces a white precipitate of phosphate of baryta, $2BaO,HO,PO_5$ [$BaHPO_4$], which is soluble in free acids. Addition of ammonia only slightly increases the quantity of this precipitate, a portion of which is converted into basic phosphate of baryta, $3BaO,PO_5$ [$Ba_3(PO_4)_2$], by this reagent. Chloride of ammonium dissolves the precipitate to a clearly perceptible extent.

8. **Oxalate of ammonia** in moderately dilute solutions produces a white pulverulent precipitate of oxalate of baryta,

$$2BaO,C_4O_6 + 2aq \quad [BaC_2O_4,H_2O],$$

which is soluble in hydrochloric and nitric acids. When recently thrown down, this precipitate dissolves also in oxalic and acetic acids; but the solutions speedily deposit acid oxalate of baryta,

$$BaO,HO,C_4O_6 + 2aq \quad [BaH_2C_4O_8,2H_2O],$$

in the form of a crystalline powder.

9. **Chromate of potassa,** and dichromate of potassa, produce a bright yellow precipitate of chromate of baryta, BaO,CrO_3 [$BaCrO_4$], even in very dilute solutions of salts of baryta. The precipitate dissolves readily in hydrochloric or nitric acid to a yellowish red solution, from which it is thrown down again by ammonia; it is insoluble in acetic acid and chromic acid.

10. If soluble salts of baryta in powder are heated with dilute **spirit of wine,** they impart to the flame a greenish-yellow colour.

11. If salts of baryta are held on the loop of a platinum wire in the fusing zone of the Bunsen **gas flame,** the part of the flame above the sample is coloured yellowish green; or if the baryta salts are held in the inner spirit **blowpipe flame,** the same coloration is imparted to the part of the flame before the sample. With soluble baryta salts, and also with carbonate and sulphate of baryta, the reaction takes place immediately or very quickly; but the phosphate must be previously moistened with sulphuric acid or hydrochloric acid; by similar treatment, baryta may be detected by the flame coloration also in silicates decomposable by acids. Silicates which are not decomposed by hydrochloric acid must be fused with carbonate of soda, when the carbonate of baryta produced will show the reaction. It is characteristic of the yellowish-green baryta coloration of the flame that it appears bluish-green when viewed through the green glass. If the sulphates are used for the experiment, the presence of lime and strontia will not interfere with the reaction. The baryta **spectrum** is shown in the coloured plate. The green lines, α and β are the most intense; γ is less marked, but still characteristic. Platinum wire sometimes contains barium (Kraut), so that it is well to see first whether it will give a barium spectrum by itself.

12. Cold solutions of **bicarbonates of the alkalies** or of **carbonate of ammonia** do not decompose sulphate of baryta, or more accurately, they decompose that salt only to an almost imperceptible extent; the same applies to a boiling solution of 1 **part of carbonate and 3 parts of sulphate of potassa.** The repeated action of boiling solutions of monocarbonates of the alkalies on sulphate of baryta, however, at last completely decomposes that salt, and it is also readily decomposed by fusion with carbonates of the alkalies; a sulphate of the alkali, soluble in water is formed, together with carbonate of baryta, insoluble in that menstruum.

§ 96.

b. **Strontia,** SrO [SrO].

1. Strontia, its hydrate and its salts have nearly the same general properties and reactions as baryta and its corresponding compounds. Hydrate of strontia is more sparingly soluble in water than hydrate of baryta. Chloride of strontium dissolves in absolute alcohol and deliquesces in moist air. Nitrate of strontia is insoluble in absolute alcohol and does not deliquesce in the air.

2. With **ammonia, potassa,** and **soda,** and also with the **carbonates of the alkalies** and with **phosphate of soda,** the salts of strontia give nearly the same reactions as the salts of baryta. Carbonate of strontia, however, is somewhat less soluble in chloride of ammonium than carbonate of baryta.

3. **Sulphuric acid** and **sulphates** throw down sulphate of strontia, SrO,SO_3 [$SrSO_4$] in the form of a white precipitate. Thrown down by dilute sulphuric acid from concentrated solutions, the sulphate is at first flocculent and amorphous, afterwards pulverulent and crystalline; precipitated by dilute sulphuric acid from dilute solutions, or produced by solutions of sulphates, it is immediately pulverulent and crystalline. The application of heat greatly promotes the precipitation. Sulphate of strontia is far more soluble in water than sulphate of baryta; owing to this readier solubility, the precipitated sulphate of strontia does not separate from rather dilute solutions until some time has elapsed; and this is invariably the case (even in concentrated solutions) if solution of **sulphate of lime** is used as the precipitant. Sulphate of strontia is insoluble in spirit of wine; the addition of alcohol, therefore, will promote the separation of the precipitate. As sulphate of strontia dissolves perceptibly in hydrochloric acid and in nitric acid, the presence of large quantities of these acids most seriously impair the delicacy of the reaction. If the solution of sulphate of strontia in hydrochloric acid be diluted with water, it will be rendered turbid by chloride of barium. Sulphate of strontia does not dissolve when boiled with a concentrated solution of sulphate of ammonia.

4. **Hydrofluosilicic acid** does not produce a precipitate even in concentrated solutions; even when an equal volume of alcohol is added no precipitation takes place, unless the solution is concentrated.

5. **Oxalate of ammonia**, even from rather dilute solutions, throws down oxalate of strontia, $2SrO,C_4O_6 + aq$ [$2SrC_2O_4,5H_2O$], in the form of a white precipitate which dissolves readily in hydrochloric and nitric acid, and perceptibly in salts of ammonia, but is only sparingly soluble in oxalic and acetic acids.

6. **Dichromate of potassa** does not precipitate solutions of salts of strontia, even when they are concentrated. **Neutral chromate of potassa** produces no precipitate at first; but on long standing, the bright yellow chromate of strontia separates in the crystalline form from neutral solutions, if not too dilute; it is not formed if free acetic acid is present. The chromate is only slightly soluble in water, but readily in hydrochloric, nitric, and chromic acids.

7. If salts of strontia soluble in water or alcohol are heated with dilute spirit of wine, and the spirit is ignited, the flame appears of a very intense carmine colour, more particularly on stirring the alcoholic mixture.

8. If a strontia salt is held in the fusing zone of the Bunsen **gas flame,** or in the inner spirit **blowpipe flame,** an intensely red colour is imparted to the flame. With chloride of strontium, the reaction is the most distinct, less clear with strontia and carbonate of strontia, fainter still with sulphate of strontia, and scarcely at all with strontia salts of fixed acids. The sample, therefore, after its first exposure to the flame, should be moistened with hydrochloric acid, and then again placed in the flame. If sulphate of strontia is likely to be present, the sample is first exposed for a short time to the reducing flame (to produce sulphide of strontium), before it is moistened with hydrochloric acid. Viewed through the **blue glass**, the strontia flame appears purple or rose (difference between strontia and lime, the latter exhibiting a faint greenish-gray colour when treated in this manner); this reaction is best seen if the sample moistened with hydrochloric acid

is allowed to spirt up in the flame. In presence of baryta, the strontia reaction is seen only when the sample moistened with hydrochloric acid is first introduced into the flame. The strontia **spectrum** is shown in the coloured plate. It contains a number of characteristic lines, more especially the orange line α, the red lines β and γ, and the blue line δ; the latter is more particularly suited for the detection of strontia in presence of baryta and lime.

9. Sulphate of strontia is completely decomposed by continued digestion with solutions of **carbonate of ammonia**, or of the **carbonates or bicarbonates of the alkalies**, but much more rapidly by boiling with a solution of 1 part of **carbonate of potassa and 3 parts of sulphate of potassa** (essential difference between sulphate of strontia and sulphate of baryta).

§ 97.

c. Lime, CaO [CaO].

1. Lime, its hydrate and its salts, in their general properties and reactions, bear a very close resemblance to baryta and strontia and their corresponding compounds. Hydrate of lime is far more sparingly soluble in water than the hydrates of baryta and strontia; it is also less soluble in hot than in cold water. Hydrate of lime loses its water on ignition. Chloride of calcium and nitrate of lime are soluble in absolute alcohol, and deliquesce when exposed to the air.

2. **Ammonia, potassa, soda, carbonates of the alkalies,** and **phosphate of soda** give nearly the same reactions with salts of lime as with salts of baryta. Recently precipitated carbonate of lime, CaO,CO_2 [$CaCO_3$], is bulky and amorphous, but after a time, and immediately when heated in the liquid, it falls down and assumes a crystalline form. Recently precipitated carbonate of lime dissolves pretty readily in solution of chloride of ammonium; but the solution speedily becomes turbid, and deposits the greater part of the dissolved salt in the form of crystals.

3. **Sulphuric acid** and **sulphate of soda**, in highly concentrated solutions of lime salts, immediately produce a white precipitate of sulphate of lime, $CaO,SO_3 + 2aq$ [$CaSO_4,2H_2O$], which redissolves completely in a large proportion of water, and is far more soluble in acids. Sulphate of lime dissolves readily when boiled with a concentrated solution of sulphate of ammonia. In less concentrated solutions of lime, the precipitates are formed only after the lapse of some time; and no precipitation whatever takes place in dilute solutions. Solution of sulphate of lime of course cannot produce a precipitate in salts of lime; but even a cold saturated solution of sulphate of potassa, mixed with 3 parts of water, does not produce a precipitate until the mixture has been allowed to stand from twelve to twenty-four hours. If two volumes of alcohol are added to solutions of lime which are so very dilute that sulphuric acid has no apparent action on them, a precipitate will form either immediately, or after the lapse of some time.

4. **Hydrofluosilicic acid** does not precipitate salts of lime, even when an equal volume of alcohol is added.

5. **Oxalate of ammonia** produces a white pulverulent precipitate of oxalate of lime. If the solutions are moderately concentrated or hot, the precipitate, $2CaO,C_4O_6 + 2aq$ [CaC_2O_4,H_2O], forms at once; but

if they are very dilute and cold, it forms only after some time; in the latter case it is more distinctly crystalline, and consists of a mixture of the above salt with $2CaO,C_4O_6 + 6aq$ [$CaC_2O_4,3H_2O$]. Oxalate of lime dissolves readily in hydrochloric and nitric acids, but not appreciably in acetic or oxalic acids.

6. Neither **chromate of potassa** nor dichromate of potassa precipitates solutions of salts of lime.

7. When soluble salts of lime are heated with dilute **spirit of wine,** they impart to the flame of the latter an orange-red colour, which is liable to be confounded with that communicated to the flame of alcohol by salts of strontia.

8. If salts of lime are held in the fusing zone of the Bunsen **gas flame,** or in the inner spirit **blowpipe flame,** they impart to the flame an orange-red colour. This reaction is the most distinct with chloride of calcium; sulphate of lime shows it only after its incipient decomposition, and carbonate of lime also most distinctly after the escape of the carbonic acid. Compounds of lime with fixed acids do not colour flame; those which are decomposed by hydrochloric acid will, however, show the reaction after moistening with that acid. The reaction is in such cases promoted by flattening the loop of the platinum wire, placing a small portion of the lime compound upon it, letting it frit, adding a drop of hydrochloric acid, which remains hanging to the loop, and then holding the latter in the fusing zone. The reaction is most distinctly seen at the instant the drop evaporates and disappears; this takes place, as in Leidenfrost's phenomenon, without ebullition (Bunsen). Viewed through the **green glass,** the lime coloration of the flame appears finch-green on letting the sample moistened with hydrochloric acid spirt in the flame (difference between lime and strontia; the latter, under similar circumstances, shows a very faint yellow. Merz). In presence of baryta, the lime reaction is only seen on the first introduction of the sample into the flame. The lime **spectrum** is shown in the plate of spectra. The intensely green line β is more particularly characteristic, also the intensely orange line α. It requires a very good apparatus to show the indigo-blue line to the right of G in the solar spectrum, as this is much less luminous than the other lines.

9. With monocarbonates and bicarbonates of the alkalies, as also with a solution of carbonate and sulphate of potassa, sulphate of lime shows the same reactions as sulphate of strontia.

§ 98.

d. **Magnesia,** MgO [MgO].

1. **Magnesium** is silver white, hard, malleable, of 1·74 sp. gr.; it melts at a moderate red heat, and volatilizes at a white heat. When ignited in the air, it burns with a dazzling white flame, forming magnesia. It preserves its lustre in dry air, but gradually becomes coated with hydrate of magnesia when exposed to moist air. Pure water is not decomposed by magnesium at the ordinary temperature, but in water acidified with hydrochloric or sulphuric acid, magnesium dissolves rapidly with evolution of hydrogen.

2. Magnesia and its hydrate are white powders far more bulky

than the other alkaline earths and their hydrates. Magnesia and hydrate of magnesia are almost insoluble in water whether cold or hot. Hydrate of magnesia loses its water when ignited.

3. Some of the salts of magnesia are soluble in water, others insoluble. The soluble salts of magnesia have a nauseous bitter taste; in the neutral state they do not alter vegetable colours; with the exception of sulphate of magnesia, they undergo decomposition when gently ignited, and the greater part of them even on merely evaporating their solutions. Sulphate of magnesia loses its acid at a white heat. Nearly all the salts of magnesia which are insoluble in water dissolve readily in hydrochloric acid.

4. **Ammonia** throws down from the solutions of neutral salts part of the magnesia as hydrate, MgO,HO [MgH_2O_2] in the form of a white bulky precipitate. The rest of the magnesia remains in solution as a double salt, that is, in combination with the ammonia salt which is formed by the decomposition of the salt of magnesia; these double salts are not decomposed by a small excess of ammonia. It is owing to this tendency of salts of magnesia to form such double salts with ammoniacal compounds that ammonia fails to precipitate them in presence of a sufficient proportion of an ammonia salt with neutral reaction; or, what is the same, that ammonia produces no precipitate in solutions of magnesia containing a sufficient quantity of free acid, and that precipitates produced by ammonia in neutral solutions of magnesia are redissolved on adding chloride of ammonium. It should be borne in mind, that in solutions containing only 1 equivalent of an ammonia salt (sulphate of ammonia or chloride of ammonium) to 1 equivalent of magnesia salt, although no precipitate is produced by the addition of a slight excess of ammonia, yet a portion of the magnesia is thrown down on adding a large excess of ammonia.

5. **Potassa, soda, baryta,** and **lime** throw down hydrate of magnesia; the separation of the precipitate is greatly promoted by boiling the mixture. Chloride of ammonium and similar salts of ammonia redissolve the washed precipitated hydrate of magnesia. If the salts of ammonia are added in sufficient quantity to the solution of magnesia before the addition of the precipitant, small quantities of the latter fail to produce a precipitate. However, on boiling the solution afterwards with an excess of potassa, the precipitate will of course make its appearance, as the ammonia salt is decomposed, and the agent which retains the hydrate of magnesia in solution is thereby removed. It should be remembered that hydrate of magnesia is more soluble in solutions of chloride of potassium, chloride of sodium, sulphate of potassa, and sulphate of soda, than in water, and that on this account its precipitation is less complete when these salts are present in large quantities. From such solutions the magnesia is, however, thrown down, for the most part, by an excess of solution of potassa or soda.

6. **Carbonate of potassa** and **carbonate of soda** produce, in neutral solutions, a white precipitate of basic carbonate of magnesia $4(MgO,CO_2) + MgO,HO + x\text{aq}$ [$4MgCO_3,MgH_2O_2,xH_2O$]. One-fifth of the carbonic acid of the decomposed alkaline carbonate is liberated in this reaction, and combines with a portion of the carbonate of magnesia to form bicarbonate, which remains in solution. This carbonic acid is expelled by boiling, and an additional precipitate is formed, $MgO,CO_2 + 3\text{aq}$ [$MgCO_3,3H_2O$]. The application of heat there-

fore promotes the separation and increases the quantity of the precipitate. Chloride of ammonium and similar salts of ammonia, when present in sufficient quantity, prevent this precipitation, and also readily redissolve the precipitates after they have been washed.

7. If solutions of magnesia are mixed with **carbonate of ammonia**, the liquid always remains clear at first; but after some time, it deposits a crystalline precipitate, more or less quickly according to the concentration of the solution. When a small quantity only of carbonate of ammonia is added, the precipitate consists of carbonate of magnesia, $MgO,CO_2 + 3aq$ [$MgCO_3,3H_2O$], but when the carbonate of ammonia is in large excess, it consists of carbonate of magnesia and ammonia, $MgO,CO_2 + NH_4O,CO_2 + 4aq$ [$Mg(HN_4)_2(CO_3)_2,4H_2O$]. This precipitate is not formed in very dilute solutions. The addition of ammonia and of excess of carbonate of ammonia promotes its separation, whilst chloride of ammonium hinders it; it does not, however, prevent the formation of the precipitate in very concentrated solutions.

8. **Phosphate of soda** added to solutions of magnesia, if they are not too dilute, precipitates phosphate of magnesia,

$$2MgO,HO,PO_5 + 14aq \ [MgHPO_4,7H_2O],$$

as a white powder. On boiling, basic phosphate of magnesia,

$$3MgO,PO_5 + 7aq \ [Mg_3(PO_4)_2,7H_2O],$$

separates, even from rather dilute solutions. If the addition of the precipitant is, however, preceded by that of **chloride of ammonium** and **ammonia** a white crystalline precipitate of basic phosphate of magnesia and ammonia,

$$2MgO,NH_4O,PO_5 + 12aq \ [Mg(NH_4)PO_4,6H_2O],$$

will be thrown down even from very dilute solutions of magnesia; its separation may be greatly promoted and accelerated by stirring with a glass rod; even should the solution be so extremely dilute that no precipitate is formed, yet the lines of direction in which the glass rod has moved along the side of the vessel will after the lapse of some time appear distinctly as white streaks (soluble in hydrochloric acid). Water and solutions of salts of ammonia dissolve the precipitate but very slightly; it is, however, readily soluble in acids, even in acetic acid. It may be considered as insoluble in water containing ammonia.

9. **Oxalate of ammonia** produces no precipitate in very dilute solutions of magnesia; in less dilute solutions no precipitate is formed at first, but after some time, crystalline crusts of various ammonia magnesia oxalates make their appearance. In highly concentrated solutions, oxalate of ammonia very speedily produces a precipitate of oxalate of magnesia, $2MgO,C_4O_6 + 4aq$ [$MgC_2O_4,2H_2O$], which contains small quantities of the above-named double salts. Chloride of ammonium, especially in presence of free ammonia, interferes with the formation of these precipitates, but does not usually entirely prevent it.

10. **Sulphuric acid, hydrofluosilicic acid,** and **chromate of potassa** do not precipitate salts of magnesia.

11. Salts of magnesia do not colour flame.

§ 99.

Recapitulation and Remarks.

The sparing solubility of hydrate of magnesia, the ready solubility of the sulphate (unless it is present in the natural form, either anhydrous or combined with 1 equivalent of water) and the disposition of salts of magnesia to form double salts with ammonia compounds, are the three principal points in which magnesia differs from the other alkaline earths. To detect magnesia in solutions containing all the alkaline earths, it is necessary first to remove the baryta, strontia, and lime. This is effected most conveniently by means of carbonate of ammonia, with addition of some ammonia and chloride of ammonium, heat being applied; in this way the baryta, strontia, and lime are obtained in a form of combination suited for further examination. If the solutions are somewhat dilute, and the precipitated fluid is quickly filtered, the carbonates of baryta, strontia, and lime are obtained on the filter, whilst the whole of the magnesia is found in the filtrate. But as chloride of ammonium dissolves a little carbonate of baryta, and also a little carbonate of lime, though much less of the latter than of the former, trifling quantities of these bases are found in the filtrate; nay, where only traces of them are present, they may altogether remain in solution. In accurate experiments, therefore, the separation is effected in the following way: the filtrate is divided into three portions, one portion is tested with dilute sulphuric acid for the trace of baryta which it may contain in solution, and another portion with oxalate of ammonia for the minute trace of lime which may have remained in solution. If the two reagents produce no turbidity even after some time, the third portion is tested for magnesia with phosphate of soda. But if one of the reagents causes turbidity, the solution is filtered from the gradually subsiding precipitate, and the filtrate tested for magnesia. Should both reagents produce precipitates, the two first portions are mixed together, filtered after some time, and the filtrate tested. To make sure that the precipitate thrown down by oxalate of ammonia is actually oxalate of lime, and not, as it may be, oxalate of magnesia and ammonia, it is dissolved in a little hydrochloric acid, dilute sulphuric acid is added, and then spirit of wine.

To show the presence of the baryta, strontia, and lime in the precipitate produced by carbonate of ammonia, the precipitate is dissolved in a little dilute hydrochloric acid and solution of gypsum is added to a small portion of this solution; the immediate formation of a precipitate will prove the presence of baryta. The remainder of the hydrochloric acid solution is evaporated to dryness on the water-bath, and the residue is treated with absolute alcohol, which will dissolve the chloride of strontium and the chloride of calcium, leaving the greater part of the chloride of barium. The alcoholic solution is mixed with an equal volume of water and a few drops of hydrofluosilicic acid, and allowed to remain at rest for several hours, when the last traces of the baryta present will be precipitated as silicofluoride of barium. The solution is then filtered, and sulphuric acid added to the alcoholic filtrate; this will throw down the strontia and the lime. The precipitate is collected on a filter, washed with weak spirit of wine, and the sulphates boiled for some time with a sufficient quantity of sulphate of ammonia in strong solution, renewing the water as it evaporates and adding ammonia, so as to keep the liquid slightly alkaline; sulphate of strontia remains undissolved, while the sulphate of lime dissolves. After the solution has been much diluted, the lime may be thrown down by oxalate of ammonia. The mixture of sulphate of strontia and sulphate of lime may also be treated as follows: it is first boiled with solution of carbonate of soda, by which means the sulphates are converted into carbonates. These are washed, dissolved in nitric acid, the solution evaporated to dryness, and the residue pulverized, and digested for a considerable time with absolute alcohol to which a little ether has been added; the nitrate of lime will then dissolve, leaving the nitrate of strontia undissolved. The latter may be readily examined, by dissolving it in a small quantity of water and adding solution of sulphate of lime. The lime in the alcoholic solution of nitrate of lime may be detected by the addition of sulphuric acid; the precipitate of sulphate of lime thus produced, when treated with water, should yield a solution which gives an immediate and considerable precipitate with oxalate of ammonia. The separation of baryta and strontia from lime may also be effected by means of chromate of potassa. For this purpose it is best to dissolve the carbonate in acetic acid and precipitate with neutral (yellow) chromate of potassa (Kämmerer). By this means the baryta is almost completely precipitated as chromate of baryta, whilst strontia and lime remain in solution; these may either be precipitated by means of dilute sulphuric acid with addition of alcohol, or by carbonate of ammonia, and then separated by the methods previously described. The best and most convenient method of detecting the alkaline earths in their phosphates is to decompose the latter by means of ferric chloride, with addition of acetate of soda (§ 142). The oxalates of the alkaline earths are converted into carbonates by ignition, preparatory to the detection of the several earths which they may contain. The following method will serve to analyse mixtures of the sulphates of the alkaline earths. The mixture under examination is extracted with small portions of boiling water; the solution contains the whole of the sulphate of magnesia, unless it is present in the native anhydrous state, besides a trifling quantity of sulphate of lime. The residue is digested, according to H. Rose's direction, in the cold for twelve hours, with a solution of carbonate of ammonia, or boiled for ten minutes with a solution of 1 part of carbonate and 3 parts of sulphate of potassa, collected on a filter, washed and then treated with dilute hydrochloric acid, which will dissolve the carbonates of strontia and lime formed, and if the anhydrous native sulphate of magnesia was present, the carbonate of magnesia or the carbonate of ammonia and magnesia, but always also a minute trace of baryta (Fresenius), leaving behind the undecomposed sulphate of baryta. The latter may then be decomposed by fusion with carbonates of the alkalies. The solutions obtained are to be examined further according to the above directions.

The detection of baryta, strontia, and lime in the moist way is very instructive, but also rather laborious and tedious. By means of the spectroscope, these alkaline earths are much more readily detected, even when present all three together. According to the nature of the acid, the sample is either introduced at once into the flame, or after previous ignition in the reducing flame and moistening with hydrochloric acid. To detect very minute quantities of baryta and strontia in presence of large quantities of lime, a few grams of the mixed carbonates are ignited for a few minutes in a platinum crucible strongly over the blast;[*] the ignited mass is extracted by boiling it with a little distilled water, the solution evaporated with hydrochloric acid to dryness, and the residue examined spectroscopically (Engelbach).

If traces of lime and strontia are to be tested for in baryta minerals, the bases present are converted into chlorides, extracted with a very small quantity of absolute alcohol, and the residue left after evaporation is examined spectroscopically. If strontia minerals are to be examined for traces of lime and baryta, the chlorides are repeatedly extracted, first with cold, and then with hot alcohol. The lime is found in the first extract and the strontia in the succeeding extract, whilst the baryta is found in the last extract or in the residue. The products thus obtained are heated to redness in the reducing flame, moistened with hydrochloric acid, and introduced into the flame (Bunsen). On the detection of magnesium by means of its absorption spectrum comp. H. W. Vogel and F. v. Lepel, Zeit. anal. Chem., **17**, 89.

§ 100.

Third Group.

More common oxides:—Alumina, Sesquioxide of Chromium.

Rarer oxides:—Beryllia, Thoria, Zirconia, Yttria, Oxide of Erbium, Oxides of Cerium, Oxide of Lanthanum, Oxide of Didymium, Titanic Acid, Tantalic Acid, Niobic Acid.

Properties of the group.—The oxides of the third group are insoluble in water, both in the pure state and as hydrates. Their sulphides cannot be produced in the moist way, sulphuretted hydrogen therefore fails to precipitate the solutions of their salts. From the solutions of the salts in which the oxides of the third group constitute the base,[†] sulphide of ammonium throws down the hydrated oxides in the same way that ammonia does. This reaction with sulphide of ammonium distinguishes the oxides of the third from those of the two preceding groups.

Special Reactions of the more common Oxides of the third group.

§ 101.

a. **Alumina,** Al_2O_3 [Al_2O_3].

1. Aluminium is nearly white. It is not oxidized by the action of the air, in compact masses not even when ignited. It may be filed, and is very malleable; its sp. gr. is only 2·67. It is fusible at a bright red heat. It does not decompose water at the boiling temperature.

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[*] The carbonates of baryta and strontia are much more readily reduced to the caustic state in this process than would be the case in the absence of carbonate of lime.

[†] The oxides of the third group may nearly all of them form saline compounds by combining with bases as well as with acids; alumina, for instance, combines with potassa yielding aluminate of potassa, with sulphuric acid to form sulphate of alumina. The oxides of the third group stand, accordingly, partly on the verge between bases and acids. Those which incline more to the latter, as is the case with the three last members of the group, are therefore also called acids.

Aluminium dissolves readily in hydrochloric acid, as well as in hot solution of potassa, with evolution of hydrogen. Nitric acid dissolves it only slowly, even with the aid of heat.

2. Alumina is non-volatile and colourless; the hydrate is also colourless. Alumina dissolves in dilute acids slowly and with very great difficulty, but more readily in concentrated hot hydrochloric acid. In fused bisulphate of potassa, it dissolves readily to a mass soluble in water. The hydrate in the amorphous condition is readily soluble in acids; in the crystalline state, it dissolves in them with very great difficulty. After ignition with alkalies, the alumina, or, more correctly speaking, the alkaline aluminate formed, is readily soluble in acids.

3. The salts of alumina are colourless and non-volatile; some of them are soluble, others insoluble. The anhydrous chloride is solid, colourless, crystalline, volatile. The soluble salts have a sweetish, astringent taste, redden litmus paper, and lose their acid when ignited. The insoluble salts are dissolved by hydrochloric acid, with the exception of certain native compounds of alumina; the compounds of alumina which are insoluble in hydrochloric acid, are decomposed and made soluble by ignition with carbonate of soda and potassa, or bisulphate of potassa. This decomposition and solution may, however, be effected also by heating them, in fine powder, with hydrochloric acid of 25 per cent., or with a mixture of 3 parts by weight of sulphuric acid, and 1 part by weight of water, in sealed glass tubes, at 200°–210° for two hours (A. Mitscherlich).

4. **Potassa** and **soda** throw down from solutions of alumina salts a bulky precipitate of hydrate of alumina, $Al_2O_3,3HO$ [$Al_2(OH)_6$], which contains alkali and generally also an admixture of basic salt; this precipitate redissolves readily and completely in an excess of the precipitant; this solution remains clear when boiled, but the hydrate of alumina is reprecipitated on adding chloride of ammonium, even in the cold, more completely on application of heat (compare § 53). The precipitate does not dissolve in excess of chloride of ammonium. The presence of salts of ammonia does not prevent the precipitation by potassa or soda.

5. **Ammonia** and also **sulphide of ammonium** produces a precipitate of hydrate of alumina, which contains ammonia and an admixture of basic salt; this precipitate redissolves in a large excess of ammonia, but only with difficulty, and this is the greater the larger the quantity of salts of ammonia contained in the solution. Boiling promotes precipitation, as it drives off the excess of ammonia. It is this behaviour which accounts for the complete precipitation of hydrate of alumina from the solution in potassa or soda by an excess of chloride of ammonium.

6. **Carbonates of the alkalies** precipitate basic carbonate of alumina, which is somewhat soluble in excess of fixed alkaline carbonate, but less soluble in excess of carbonate of ammonia. Boiling promotes precipitation by the latter.

7. If the solution of a salt of alumina is digested with finely divided **carbonate of baryta**, the greater part of the acid of the alumina salt combines with the baryta, the liberated carbonic acid escapes, and the alumina is completely precipitated as hydrate mixed with basic salt of alumina; even digestion in the cold suffices to produce this reaction.

Note to 4, 5, 6, and 7.—Tartaric, citric, and other non-volatile organic acids completely prevent the precipitation of alumina as hydrate or basic salt, when they are present in any notable quantity. The presence of sugar and similar organic substances interferes with the completeness of the precipitation.

8. **Phosphate of soda** precipitates phosphate of alumina, $Al_2O_3,PO_5 + 8aq$ [$Al_2P_2O_8,8H_2O$], from solutions of salts of alumina. The bulky white precipitate is readily soluble in potash or soda solution, with difficulty in ammonia, and scarcely at all in presence of ammonia salts; chloride of ammonium therefore precipitates it from its solution in potash or soda. The precipitate is readily soluble in hydrochloric or nitric acid, but not in acetic acid (difference from alumina); acetate of soda, therefore, precipitates it from its solution in hydrochloric acid, if the latter is not in too great excess. Tartaric acid, sugar, &c., do not prevent the precipitation of phosphate of alumina, but citric acid does prevent it (Grothe).

9. **Oxalic acid** and its salts do not precipitate the solutions of salts of alumina.

10. **Sulphate of potash**, added to very concentrated solutions of salts of alumina, occasions the gradual separation of sulphate of alumina and potash, alum, $KO,SO_3 + Al_2O_3,3SO_3 + 24aq$ [$KAl(SO_4)_2,12H_2O$], in the form of crystals, or of a crystalline powder.

11. If alumina or one of its compounds is ignited upon charcoal before the blowpipe, and afterwards moistened with a solution of **nitrate of cobalt**, and then again strongly ignited, an unfused mass of a deep sky-blue colour is produced, which consists of a compound of the two oxides. The blue colour becomes distinct only on cooling. By candlelight, it appears violet. This reaction is in a measure to be relied on only in the case of infusible or difficultly fusible compounds of alumina pretty free from other oxides; it is never quite decisive, since cobalt solution gives a blue colour under similar circumstances not only with readily fusible compounds, but also with certain infusible compounds free from alumina, such as the neutral phosphates of the alkaline earths.

§ 102.

b. Sesquioxide of Chromium, Cr_2O_3 [Cr_2O_3].

1. Sesquioxide of chromium is a green, its hydrate a bluish gray-green powder. The hydrate dissolves readily in acids; the non-ignited sesquioxide dissolves less readily, whilst the ignited sesquioxide is almost insoluble.

2. The salts of sesquioxide of chromium are of a green or violet colour. Many of them are soluble in water, and most of them dissolve in hydrochloric acid. The solutions are of a fine green or a dark violet colour; the latter, however, changes to green on heating. The salts of sesquioxide of chromium with volatile acids are decomposed by ignition, the acids being expelled. The salts of sesquioxide of chromium which are soluble in water redden litmus. Anhydrous sesquichloride of chromium is crystalline, violet-coloured, insoluble in water and in acids, and volatilizes with difficulty.

3. **Potassa and soda** produce in the green as well as in the violet solutions a bluish-green precipitate of hydrate of sesquioxide of

chromium, which dissolves readily and completely in an excess of the precipitant, imparting to the liquid an emerald-green tint. On **long-continued** ebullition of this solution, the whole of the hydrated sesquioxide separates again, and the supernatant liquid appears perfectly colourless. The same reprecipitation takes place if chloride of ammonium is added to the alkaline solution; the application of heat promotes the separation of the precipitate.

4. **Ammonia** and also **sulphide of ammonium** produces in green solutions a grayish-green, in violet solutions a grayish-blue precipitate of hydrate of sesquioxide of chromium. The former precipitate dissolves in cold hydrochloric acid to a green solution, the latter to a violet-coloured solution. Other circumstances (concentration, way of adding the ammonia, &c.) also exercise some influence on the composition and colour of these hydrates. A small portion of the hydrates redissolves in an excess of the precipitant in the cold, imparting to the solution a peach-blossom red tint; but if the mixture is heated after the addition of ammonia in excess, the precipitation is complete.

5. **Carbonates of the alkalies** precipitate basic carbonate of sesquioxide of chromium, which redissolves slowly and with difficulty in excess of the precipitant.

6. **Carbonate of baryta** precipitates the whole of the sesquioxide as a greenish hydrate mixed with basic salt. Precipitation takes place in the cold, but is complete only after long-continued digestion.

Note to 4, 5, and 6.—Tartaric and citric acids, sugar, and oxalic acid interfere more or less with the precipitation of violet or green solutions of oxide of chromium by ammonia, the first formed precipitates frequently redissolving entirely to violet or green liquids after long standing. The acids above-mentioned usually prevent the precipitation by carbonate of soda. In the presence of these acids, also, the precipitation by carbonate of baryta is incomplete.

7. If a solution of sesquioxide of chromium in solution of potassa or soda is mixed with some brown **peroxide of lead** in excess, and the mixture boiled for a short time, the sesquioxide of chromium is oxidized to chromic acid; on filtering, a yellow liquid is obtained, which contains chromate of oxide of lead dissolved in solution of potassa or soda. When this solution is acidified with acetic acid, the chromate of lead separates as a yellow precipitate (Chancel). Very minute traces of chromic acid may be detected in this solution with still greater certainty by acidifying with hydrochloric acid, and bringing it in contact with peroxide of hydrogen and ether. Compare § 138.

8. The fusion of sesquioxide of chromium or of any of its compounds with **nitrate of soda and carbonate of soda**, or still better, with **chlorate of potassa and carbonate of soda**, gives rise to the formation of a yellow alkaline chromate, which dissolves in water yielding an intensely yellow solution. For the reactions of chromic acid see § 138.

9. **Microcosmic salt** dissolves sesquioxide of chromium and its salts, both in the oxidizing and reducing flame of the blowpipe, to a clear bead of a faint yellowish-green tint, which on cooling changes to emerald-green. The sesquioxide of chromium and its salts show a similar reaction with **borax**. Either the Bunsen gas flame (§ 16) or the blowpipe flame may be used for the experiment.

§ 103.

Recapitulation and Remarks.

The solubility of hydrate of alumina in solutions of potassa and soda (or in baryta water, which is preferable, unless the potassa or soda is quite free from silica and alumina, Beckmann), and its reprecipitation from the alkaline solutions by chloride of ammonium, afford a safe means of detecting alumina in the absence of sesquioxide of chromium. If, however, the latter is present, which is seen either by the colour of the solution, or by the blowpipe reaction with microcosmic salt, it must be removed before alumina can be tested for. The most complete separation of sesquioxide of chromium from alumina is effected by fusing 1 part of the mixed oxides with 2 parts of carbonate and 2 parts of chlorate of potassa, which may be done in a platinum crucible. The yellow mass obtained is then boiled with water; in this way the whole of the chromium is dissolved as chromate of potassa, and part of the alumina as aluminate of potassa, the rest of the alumina remaining undissolved. If the solution is acidified with nitric acid, it acquires a reddish-yellow tint; and on adding ammonia to feebly alkaline reaction, the dissolved portion of the alumina separates.

The precipitation of sesquioxide of chromium effected by boiling its solution in solution of potassa or soda is also sufficiently exact if the ebullition is continued long enough; it is often liable to mislead, however, in cases where but little sesquioxide of chromium is present, or where the solution contains organic matter, even though in small proportion. It should be noted that the solubility of hydrated sesquioxide of chromium in an excess of cold solution of potassa or soda is considerably impaired by the presence of other oxides (protoxides of manganese, nickel, cobalt, and more particularly ferric oxide); if these oxides happen to be present in large excess the precipitation may even be altogether prevented. Lastly, the influence of non-volatile organic acids, sugar, &c., on the precipitation of alumina and sesquioxide of chromium by ammonia, &c., must be remembered. If organic substances are present, therefore, the sample should be ignited, the residue fused with carbonate and chlorate of potassa, and the treatment continued as above. With regard to the detection of minute traces of alumina by means of tincture of cochineal, see Luckow,[*] and for the use of an alcoholic solution of morin, and the fluorescence produced, compare Goppelsröder.[†] For the detection of alumina by means of its spectrum, compare H. W. Vogel[‡] and H. W. Vogel and F. v. Lepel.[§]

Special Reactions of the rarer Oxides of the third group.

§ 104.

1. **Beryllia**, Be_2O_3 [Be_2O_3].

Beryllia is a rare earth found in the form of a silicate in phenacite, and, with other silicates, in beryl, euclase, and some other rare minerals. It is a white, tasteless powder insoluble in water. The ignited earth dissolves slowly but completely in acids; it is readily soluble after fusion with bisul-

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[*] Zeit. anal. Chem., 3, 362.

[†] *Ibid.*, 7, 208.

[‡] *Ibid.*, 15, 332.

[§] *Ibid.*, 17, 89.

phate of potassa. The hydrate dissolves readily in acids. The compounds of beryllia very much resemble the alumina compounds; the soluble salts have an acid reaction and a sweet astringent taste. The native silicates of beryllia are completely decomposed by fusion with 4 parts of carbonate of soda and potassa. Anhydrous chloride of beryllium is volatile at a high temperature. **Potassa, soda, ammonia,** and **sulphide of ammonium** throw down from solutions of beryllia salts a white flocculent hydrate, which is sparingly soluble in ammonia, but dissolves readily in solution of potassa or soda, but is precipitated again on adding chloride of ammonium; the concentrated alkaline solutions remain clear on boiling, but from more dilute alkaline solutions almost the whole of the beryllia separates on continued ebullition (difference between beryllia and alumina). **Tartaric acid** interferes with the precipitation by alkalies. On continued ebullition with **chloride of ammonium,** the freshly precipitated hydrate dissolves as chloride of beryllium, with expulsion of ammonia (difference between beryllia and alumina). **Carbonates of the alkalies** precipitate white carbonate of beryllia, which redissolves in a great excess of the carbonates of the fixed alkalies, and in a much less considerable excess of carbonate of ammonia (most characteristic difference between beryllia and alumina; the two cannot be completely separated in this way, however, as in the presence of beryllia a certain quantity of alumina dissolves in carbonate of ammonia, Joy). On boiling these solutions, basic carbonate of beryllia separates readily and completely from the solution in carbonate of ammonia, but only after dilution and imperfectly from the solutions in carbonates of the fixed alkalies. On adding phosphate of ammonia in considerable excess to a solution of a salt of beryllia (phosphate of soda cannot be employed), dissolving the precipitate thus formed in hydrochloric acid, adding ammonia drop by drop to the warmed solution until the reaction is neutral—excess of ammonia must be avoided—and then heating to boiling for some time, the precipitate (phosphate of ammonia and beryllia), which is at first gelatinous, becomes crystalline and is readily deposited. The presence of citric acid does not affect the reaction (distinction from alumina, which never yields a crystalline precipitate under similar circumstances, and yields no precipitate at all in the presence of citric acid). The presence of much alumina and citric acid prevents the formation of the beryllia precipitate (C. Rössler). Beryllia is completely precipitated from its salts when boiled with **carbonate of baryta,** but not in the cold. **Oxalic acid** and **oxalates** do not precipitate beryllia (difference between beryllia and thoria, zirconia, yttria, protoxide of cerium, oxide of lanthanum, oxide of didymium). Beryllia, when fused with 2 parts of **acid fluoride of potassium,** dissolves in water acidified with hydrofluoric acid. (This reaction serves as a means of separating beryllia from alumina, for when alumina is similarly treated it remains insoluble as fluoride of aluminium and potassium.) In order to detect small quantities of beryllia in the presence of much alumina, the hydrates are dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue dissolved in a small quantity of water, with the addition, if necessary, of a very little hydrochloric acid; the solution thus obtained is transferred to a tube of strong Bohemian glass, sealed at one end, sulphate of potassa is added (about 12 parts to 1 of alumina), and sufficient water to dissolve all the sulphate on heating: the tube is then sealed, warmed until everything has dissolved, and then heated at 180° for half an hour. When cold, the tube is opened, the precipitated basic sulphate of potassa and alumina filtered off, the solution precipitated by ammonia, and the precipitate collected and dissolved in hydrochloric acid; sufficient citric acid is then added to prevent the formation of any precipitate on the addition of ammonia, and the beryllia is precipitated as the crystalline phosphate of ammonia and beryllia (C. Rössler). Beryllia compounds when moistened with a solution of **nitrate of cobalt,** and ignited, yield a gray mass.

2. Thoria, ThO_2 [ThO_2].

Thoria is a very rare earth found in thorite and monacite. It is white, or gray. If the earth has been ignited, it is soluble only on heating it with a mixture of 1 part of concentrated sulphuric acid and 1 part of water; but it is not soluble in other acids, even after fusion with alkalies. When thoria obtained by ignition of the oxalate is evaporated with hydrochloric or nitric acid, the corresponding salts are left in a varnish-like form, which dissolves easily in water to a clear solution. From such solutions hydrochloric and nitric acids precipitate the chloride or nitrate; even sulphuric acid may produce a precipitate in the solutions (Bahr). The moist hydrate dissolves readily in acids, the dried hydrate only with difficulty. Chloride of thorium is not volatile. Thorite (silicate of thoria) is decomposed by moderately concentrated sulphuric acid, and also by concentrated hydrochloric acid. From solutions of thoria salts, **potassa, ammonia,** and **sulphide of ammonium** precipitate the white hydrate, which is insoluble in an excess of the precipitant, even of potassa (difference between thoria and alumina and beryllia); tartaric acid prevents the precipitation. **Carbonate of potassa** and **carbonate of ammonia** precipitate basic carbonate of thoria, which readily dissolves in an excess of the precipitant in concentrated solutions; with difficulty, however, in dilute solutions (difference between thoria and alumina). From the solution in carbonate of ammonia, basic salt separates again even at 50°. **Carbonate of baryta** precipitates thoria completely. **Hydrofluoric acid** precipitates the fluoride, which at first appears gelatinous, but after a little while pulverulent; the precipitate is insoluble in water and hydrofluoric acid. (In this respect thoria differs from alumina, beryllia, zirconia, and titanic acid.) **Oxalic acid** produces a white precipitate (in this thoria differs from beryllia and alumina); the precipitate is not soluble either in oxalic acid or in dilute mineral acids, but it dissolves in a solution of acetate of ammonia containing free acetic acid (in this thoria differs from yttria and protoxide of cerium). The precipitate is soluble in a boiling solution of oxalate of ammonia, and is not reprecipitated on diluting the solution and allowing it to stand (difference from cerium, lanthanum, didymium, and yttrium, Bunsen). **Sulphate of potassa** in concentrated solution precipitates thoria slowly but completely (in this thoria differs from alumina and beryllia). The precipitate consists of the double sulphate of potassa and thoria; it is insoluble in concentrated solution of sulphate of potassa; it dissolves with difficulty in cold but readily in hot water. On heating the neutral solution of sulphate of thoria in cold water, it separates in the form of a heavy white curdy precipitate (difference between thoria and alumina and beryllia). This precipitate redissolves in cold water (in which it differs from titanic acid). On boiling a neutral or slightly acid solution with **hyposulphite of soda,** hyposulphite of thoria is precipitated mixed with sulphur; the precipitation, however, is not quite complete (difference between thoria and yttria and oxide of didymium).

3. Zirconia, ZrO_2 [ZrO_2].

Found in zircon and some other rare minerals. A white powder insoluble in hydrochloric acid, but after continued heating with a mixture of 2 parts of hydrated sulphuric acid and 1 part of water it is soluble in water. Soluble zirconia salts are also obtained on fusing it with the bisulphates of the alkalies or with hydrofluoride of potassium. The hydrate resembles hydrate of alumina, dissolving readily in hydrochloric acid when precipitated cold, and still moist, but with difficulty when precipitated hot, or after drying. The soluble zirconia salts redden litmus. The native silicates of zirconia may be decomposed by fusion with carbonate of soda; the finely elutriated silicate is fused at a high temperature, together with 4 parts of carbonate of soda. When the fused mass is treated with water, silicate of soda dissolves, and a sandy zirconate of soda is left behind; this is washed, and dissolved in hydrochloric acid. Zircon may easily be decomposed by fusion with acid fluoride of potassium at a red heat, silicofluoride of potassium and double fluoride of zirconium and potassium being produced. **Potassa, soda, ammonia,** and **sulphide of ammonium** throw down from solutions of zirconia salts a flocculent hydrate, which is insoluble in an excess of the precipitant, even of soda and potassa (difference between zirconia and alumina and beryllia), and is not dissolved even by a boiling solution of chloride of ammonium (difference between zirconia and beryllia). Tartaric acid prevents the precipitation by alkalies. **Carbonates of potassa, soda,** and **ammonia** gradually precipitate basic carbonate of zirconia as a flocculent precipitate, which redissolves in a large excess of carbonate of potassa, more readily in bicarbonate of potassa, and most readily in carbonate of ammonia (difference between zirconia and alumina); the gelatinous hydrate is precipitated from the solution on boiling. **Oxalic acid** produces a bulky precipitate of oxalate of zirconia (difference between zirconia and beryllia), soluble in excess of oxalic acid, especially on warming, soluble in hydrochloric acid, also in excess of oxalate of ammonia in the cold (difference between zirconia and thoria). A concentrated solution of **sulphate of potassa** speedily produces a white precipitate of sulphate of zirconia and potassa insoluble in excess of the precipitant (difference between zirconia and alumina and beryllia); this—if precipitated cold—dissolves readily in a large proportion of hydrochloric acid, but is almost absolutely insoluble in water and in hydrochloric acid if precipitated hot (difference between zirconia and thoria and protoxide of cerium). **Carbonate of baryta** does not precipitate zirconia salts completely, even on boiling. **Hydrofluoric acid** does not precipitate zirconia salts (difference between zirconia and thoria and yttria). **Hyposulphite of soda** precipitates zirconia salts (difference between zirconia and yttria, and oxide of didymium). The separation of the hyposulphite of zirconia takes place on boiling even in the presence of 100 parts of water to 1 part of the oxide (useful for separating zirconia from protoxide of cerium). **Turmeric paper** dipped into solutions of zirconia slightly acidified with hydrochloric or sulphuric acid acquires a brownish red colour after drying (difference between zirconia and thoria). In the presence of titanic acid, which also has the effect of turning turmeric paper brown, treat the acid solution with zinc first, to reduce the titanic acid to oxide of titanium, the solution of which does not affect turmeric paper (Pisani).

4. Yttria, Y_2O_3 [$\mathbf{Y_2O_3}$].

Yttria is a rare earth found in gadolinite, orthite, and yttro-tantalite. When pure, it is white; when ignited in the oxidizing flame, it emits a white light (difference between yttria and erbia) without fusing or volatilizing. It is sparingly soluble in nitric, hydrochloric, and dilute sulphuric acid in the cold, but on warming it dissolves completely after some time. The solutions are colourless, and likewise the salts; they have an acid reaction and a sweetish astringent taste. Yttria does not combine with water. Yttria under no circumstances yields a spectrum, nor do the solutions of its salts show any absorption bands (Bahr and Bunsen). Anhydrous chloride of yttrium is not volatile (difference between yttria and alumina, beryllia, and zirconia). **Potassa** precipitates a white hydrate, which is insoluble in an excess of the precipitant (difference between yttria and alumina and beryllia). **Ammonia** and **sulphide of ammonium** produce the same reaction. **Carbonates of the alkalies** produce a white precipitate, which dissolves with difficulty in carbonate of potassa, but more readily in bicarbonate of potassa and in carbonate of ammonia, although by no means so readily as the corresponding beryllia precipitate. On boiling the solution of the pure hydrate in carbonate of ammonia, the whole of the yttria is deposited; if chloride of ammonium is also present, this is decomposed on long-continued boiling, with separation of ammonia, and the precipitated yttria redissolves as chloride of yttrium. It should be borne in mind that saturated solutions of carbonate of yttria in carbonate of ammonia have a tendency to deposit carbonate of yttria and ammonia. **Oxalic acid** produces a white precipitate (difference between yttria and alumina and beryllia); this precipitate does not dissolve in oxalic acid, but it dissolves with difficulty in dilute hydrochloric acid, and is partially dissolved on boiling with oxalate of ammonia; on diluting and allowing it to cool the oxalate separates again almost completely (difference from thoria). **Sulphate of yttria and potassa** dissolves readily in water and in a solution of sulphate of potassa (difference between yttria and thoria, zirconia, and the bases of cerite). **Carbonate of baryta** produces no precipitate in the cold (difference between yttria and alumina, thoria, oxide of cerium, and the oxides of lanthanum and didymium); the precipitation is incomplete even on boiling. **Turmeric paper** is not altered by acidified solutions of salt of yttria (difference between yttria and zirconia). **Tartaric acid** does not interfere with the precipitation of yttria by alkalies (characteristic difference between yttria and alumina, beryllia, thoria, and zirconia); the precipitate is tartrate of yttria. The precipitation does not take place until after some time, but it is complete. **Hyposulphite of soda** does not precipitate yttria (difference between yttria and alumina, thoria, zirconia, and titanic acid). **Hydrofluoric acid** produces a precipitate (here yttria differs from alumina, beryllia, zirconia, and titanic acid); the precipitate is gelatinous, insoluble in water and hydrofluoric acid; before ignition it will dissolve in mineral acids, after ignition it is decomposed only by strong sulphuric acid. Yttria gives clear colourless beads with **borax and microcosmic salt** in both the outer and inner flame (difference between yttria and protoxide of cerium and oxide of didymium).

Besides yttrium, a number of similar metals—erbium, terbium, ytterbium, scandium, thulium, decipium, philippium, &c.—occur in gadolinite, &c. As the investigation of these substances, however, cannot be regarded as being by any means complete, their behaviour and reactions will not be noticed here.

5. Oxides of Cerium.

Cerium occurs rarely in Nature, chiefly as silicate of oxide of cerium in cerite and orthite, as phosphate in monacite, and combined with fluorine in fluocerite. It forms two oxides—oxide of cerium, Ce_2O_3 [Ce_2O_3], also called cerous oxide; and dioxide of cerium, CeO_2 [CeO_2], known also as cerium peroxide.

Oxide of cerium, obtained by igniting dioxide of cerium, or the carbonate or oxalate of oxide of cerium, in a current of hydrogen, forms a white or bluish-gray powder which rapidly absorbs oxygen from the air, and on heating is converted into the dioxide. The salts of oxide of cerium are white or colourless, and the aqueous solutions of the soluble salts are colourless, have a sweet astringent taste, and do not yield absorption spectra. Chloride of cerium is not volatile (difference between cerium and aluminium, beryllium, and zirconium). On boiling a solution of sulphate of oxide of cerium, part of the salt is precipitated, but is redissolved on cooling. Cerite (hydrated silicate of oxide of cerium) is decomposed by fusion with carbonate of soda, and also by concentrated sulphuric acid. **Potassa** throws down a white hydrate, which, on exposure to the air, absorbs oxygen and becomes yellow. It does not dissolve in an excess of the precipitant (difference from alumina and beryllia). **Ammonia** precipitates a basic salt, which is insoluble in an excess of the precipitant. Tartaric acid prevents the precipitation (difference from yttrium). **Carbonate of ammonia** produces a white amorphous precipitate of cerous carbonate, which gradually becomes crystalline, and is somewhat soluble in excess of the precipitant. **Oxalic acid** produces a white amorphous precipitate of the oxalate, which gradually becomes crystalline; the precipitation is complete even in moderately acid solutions (difference from alumina and beryllia). The precipitate is not dissolved by oxalic acid; but it dissolves in a large proportion of hydrochloric acid, and also in a boiling concentrated solution of oxalate of ammonia, but separates again almost entirely on diluting and cooling (difference from aluminium). A saturated solution of **sulphate of potassa** precipitates, even from somewhat acid solutions, white sulphate of potassa and oxide of cerium (difference from alumina and beryllia); this is sparingly soluble in cold water, more easily in hot water, and almost completely insoluble in a saturated solution of sulphate of potassa (difference from yttria). The precipitate may be dissolved by boiling it with a large quantity of water to which some hydrochloric acid has been added. **Carbonate of baryta** does not precipitate solutions of cerium in the cold, but completely on heating. **Hyposulphite of soda** does not precipitate cerium, even on boiling with very concentrated solutions. The precipitated sulphur only carries down traces of the salt with it. **Hypochlorites of the alkalies** throw down light yellow hydrated dioxide of cerium. If a salt of oxide of cerium be dissolved in nitric acid, with addition of an equal volume of water, a small quantity of **binoxide of lead** added, and the liquid boiled for some minutes, the solution will turn yellow, even if the quantity of cerium present be very small. On evaporating this solution to dryness, heating the residue until a portion of the acid escapes, and treating it with water acidified with nitric acid, no cerium will be dissolved, but any didymium and lanthanium present will be dissolved (Gibbs).

Cerium dioxide, obtained by the ignition of hydrated cerium oxide, or of oxalate, carbonate or nitrate of cerium, in the air, is an orange-yellow powder when hot, but on cooling becomes yellowish-white. Concentrated sulphuric acid dissolves it on warming, usually with disengagement of oxygen, forming a yellow solution of the sulphates of cerium oxide and cerium dioxide. Nitric and hydrochloric acids dissolve it but very sparingly even on heating; if, however, potassium iodide is added to the latter acid, it dissolves the oxide readily, iodine being set free and chloride of cerium, Ce_2Cl_3 [Ce_2Cl_6], being formed; if alcohol is added instead of potassium iodide, the same salt is obtained. Hydrated cerium dioxide is soluble in nitric and sulphuric acids; hydrochloric acid also dissolves it, the chloride being formed and chlorine disengaged. The salts of cerium dioxide are yellow or red, and their solutions are yellow, but the latter are decolorized by sulphurous acid, with formation of salts of the monoxide. Solutions of salts of cerium dioxide are slowly but completely precipitated in the cold by **carbonate of baryta. Hyposulphite of soda** precipitates a solution of the nitrate of cerium dioxide. **Borax** and **microcosmic salt** dissolve cerium oxides in the outer flame to yellowish-red beads (difference from the preceding earths); the coloration gets fainter on cooling, and often disappears altogether. In the inner flame, colourless beads are obtained.

6. Oxide of Lanthanum, La_2O_3 [La_2O_3].

This oxide is generally found associated with oxide of cerium. It is white and remains unaltered by ignition in the air (difference from oxide of cerium). In contact with cold water, it is slowly converted into a milk-white hydrate; with hot water, the change is rapid. The oxide and its hydrate change the colour of reddened litmus paper to blue; they dissolve in boiling chloride of ammonium solution and also in dilute acids; oxide of lanthanum resembles magnesia in this respect. The salts of oxide of lanthanum are colourless; the saturated solution of sulphate of oxide of lanthanum in cold water deposits a portion of the salt already at 30° (difference from oxide of cerium). **Sulphate of potassa, oxalic acid,** and **oxalate of ammonia** give the same reactions as with protoxide of cerium. **Potassa** throws down the hydrate, which is insoluble in an excess of the precipitant, and does not turn brown in the air. **Ammonia** precipitates basic salts, which pass milky through the filter on washing. The precipitate produced by carbonate of ammonia is insoluble in an excess of the precipitant (difference from protoxide of cerium). If a cold dilute solution of acetate of oxide of lanthanum is supersaturated with ammonia, the slimy precipitate repeatedly washed with cold water, and a little **iodine** in powder added, a blue coloration makes its appearance, which gradually pervades the entire mixture (characteristic difference between oxide of lanthanum and the other earths). **Carbonate of baryta** completely precipitates lanthanum oxide in the cold from solutions of its salts.

7. Oxide of Didymium, Di_2O_3 [Di_2O_3].

This oxide is found associated with oxide of cerium and oxide of lanthanum. After intense ignition, it appears white; moistened with nitric acid, and feebly ignited, it is dark-brown (peroxide), but on intense ignition again becomes white. In contact with water, it is slowly converted into the hydrate; it rapidly attracts carbonic acid; its reaction is not alkaline; it dissolves readily in acids, and also in boiling chloride of ammonium solution. The soluble salts and also their concentrated solutions have a reddish or pale-violet colour. When the nitrate is heated, it is first converted into a basic salt (difference from lanthanum), which is gray when hot and also when cold. The chloride is not volatile. The saturated solution of the sulphate deposits salt, not at 30°, but on boiling. **Potassa** precipitates the hydrate, which is insoluble in an excess of the precipitant, and does not alter on exposure to the air. **Ammonia** precipitates a basic salt, which is insoluble in ammonia, but slightly soluble in chloride of ammonium. **Carbonates of the alkalies** produce a copious precipitate, which is insoluble in an excess of the precipitant, even in an excess of carbonate of ammonia (difference from cerium), but dissolves slightly in concentrated solutions of chloride of ammonium. Tartaric acid prevents the precipitation by alkalies. **Oxalic acid** precipitates salts of didymium almost completely; the precipitate is only sparingly soluble in cold hydrochloric acid, but dissolves readily on warming; with **oxalate of ammonia**, it behaves like oxide of cerium. **Carbonate of baryta** precipitates oxide of didymium from its solutions slowly but completely. A concentrated solution of **sulphate of potassa** precipitates didymium solutions more slowly and less completely than protoxide of cerium solutions. The precipitate (sulphate of oxide of didymium) is insoluble in solution of sulphate of potassa, and in water (Delafontaine), but it dissolves in hot hydrochloric acid with difficulty. **Hyposulphite of soda** does not precipitate solutions of didymium.

Peroxide of didymium is brown; it dissolves in hydrochloric acid with evolution of chlorine, and in oxyacids with evolution of oxygen, forming soluble salts of didymium oxide. Oxide of didymium gives with **borax** in both flames a nearly colourless bead, which has a faint amethyst-red tinge if the quantity of didymium is large. **Microcosmic salt** dissolves the oxide in the oxidizing flame to an amethyst-red bead which becomes colourless in the reducing flame. With **carbonate of soda** in the outer flame, a grayish-white mass is obtained (difference from manganese). The **absorption spectrum** given by the solution of the salts is peculiarly characteristic for didymium. This was first described by Gladstone, and afterwards by O. L. Erdmann and Delafontaine. Bahr and Bunsen have laid down the exact position of the bands (Zeit. anal. Chem., **5**, 110).

For the separation of cerium from lanthanum and didymium, one of the following methods may be used:—*a*. The solution of the three metals is nearly neutralized, if acid, without allowing any permanent precipitate to form, a sufficient quantity of acetate of soda and an excess of hypochlorite of soda added, and the mixture boiled for some time; the cerium will be thrown down as peroxide (Popp), as basic acetate (Erk), which must be washed with acetate of soda solution; the lanthanum and didymium will remain in solution. (Popp, Annalen, **131**, 360.) *b.* The metals are precipitated with potassa, the precipitate washed, suspended in potassa solution, and chlorine passed into the mixture; the lanthanum and didymium will dissolve, whilst cerium dioxide remains behind. (Damour and St. Claire Deville, Compt. rend., **59**, 272.) *c.* The mixture may be dissolved in a large excess of nitric acid, boiled with peroxide of lead, the orange coloured solution evaporated to dryness, and the residue heated until a portion of the acid is driven off; the residue is treated with water acidified with nitric acid, and the insoluble basic nitrate of sesquioxide of cerium separated from the solution, which contains all the lanthanum and didymium. (Gibbs, Zeit. anal. Chem., **3**, 396.) When the last method is employed, the lead must be removed by sulphuretted hydrogen before proceeding with the residue or solution. *d.* The chromates are heated at 110°, and treated with hot water to extract the undecomposed compounds of lanthanum and didymium. The cerium remains behind as insoluble sesquioxide (Pattinson and Clark, Chem. News, **16**, 259). From the solution of lanthanum and didymium obtained by one or other of the above methods, the bases are precipitated with oxalate of ammonia (after removing lead), the oxalates ignited, and the oxides thus obtained are treated with dilute nitric acid; if the separation of cerium was incomplete, the remainder of the cerium will remain undissolved. The solution is evaporated to dryness in a dish with a flat bottom, and heated at 400° to 500°; the salts fuse and nitrous fumes escape. The residue is then treated with hot water, which dissolves the nitrate of lanthanum, leaving behind a gray residue consisting of basic nitrate of didymium. By several repetitions of the evaporation, &c., the two bases may be satisfactorily separated. (Damour and St. Claire Deville.) Mosander's method of separation, which is, however, less complete, consists in converting the didymium and lanthanum into sulphates, making a saturated solution of the dry salts in water at 5° or 6°, and heating the solution to 30°, when the sulphate of lanthanum is for the most part thrown down, whilst the sulphate of didymium for the most part remains in solution. For another method of separating lanthanum and didymium, which requires the presence of a considerable quantity of cerium, compare Cl. Winkler (Zeit. anal. Chem., **4**, 417), Zschiesche (*ibid.*, **9**, 541), Frerichs (*ibid.*, **13**, 217).

8. Titanic Acid.

Titanium forms two oxides—sesquioxide of titanium, Ti_2O_3 [Ti_2O_3], and titanic acid, TiO_2 [TiO_2]. The latter is more generally met with in analysis; it is found in the free state in rutile, brookite and anatase, and in combination with bases in titanite, titaniferous iron, &c. It occurs in small proportions in many iron ores, in clays, and generally in silicates, consequently also in blast furnace slags. The small copper-coloured cubes which are occasionally found in such slags consist of a combination of cyanide of titanium with nitride of titanium. Feebly ignited titanic acid is white; it transiently acquires a lemon-yellow tint when heated; very intense ignition gives a yellowish or brownish tint to it. It is infusible, insoluble in water, and its sp. gr. is 3·9 to 4·25. The chloride, $TiCl_2$ [$TiCl_4$], is a colourless volatile liquid, fuming strongly in the air.

a. **Behaviour with acids, and reactions of acid solutions of titanic acid.**—Ignited titanic acid is insoluble in acids, except in hydrofluoric acid and in concentrated sulphuric acid. If the solution in hydrofluoric acid is evaporated with sulphuric acid, no fluoride of titanium will volatilize (difference from silicic acid). If fused for a sufficient length of time with bisulphate of potassa, it yields a clear mass, which is completely soluble in a large proportion of cold water. Titanic acid is very easily obtained in the state of a clear solution, by fusing it with acid fluoride of potassium and dissolving the melt in dilute hydrochloric acid. The fluoride of potassium and titanium is sparingly soluble in water, 1 part requiring 96 parts at 14°. Hydrate of titanic acid whether moist or dried without the aid of heat dissolves in dilute acids, especially in hydrochloric and sulphuric acids; when a highly dilute solution of titanic acid in hydrochloric or sulphuric acid, but more particularly in the latter, also the one obtained by fusion with bisulphate is boiled for *a long time*, titanic acid is deposited as a white powder (hydrated metatitanic acid) insoluble in dilute acids; the presence of much free acid retards the separation and diminishes the quantity of the precipitate. The precipitate which separates from a hydrochloric acid solution may, indeed, be filtered, but on washing it will pass milky through the filter, unless chloride of ammonium or an acid be added to the washing water. **Solution of potassa** throws down titanic acid from its solutions in hydrochloric or sulphuric acid as a bulky white hydrate, which is insoluble in excess of the precipitant; **ammonia, sulphide of ammonium, and carbonate of baryta** act in the same way. The precipitate, if thrown down cold and washed with cold water, is soluble in hydrochloric acid and in dilute sulphuric acid; the presence of tartaric acid prevents its formation. **Ferrocyanide of potassium** produces a dark-brown precipitate in acid solutions of titanic acid; **infusion of galls** gives a brownish precipitate, which speedily turns orange-red. On boiling a solution of titanic acid with **hyposulphite of soda,** the whole of the titanic acid is thrown down. **Phosphate of soda** throws down the titanic acid almost completely as phosphate of titanic acid even from solutions containing much hydrochloric acid; the washed precipitate consists of $2TiO_2,PO_5$ [$Ti_2P_2O_9$] (Merz). Peroxide of hydrogen colours a solution of titanic acid orange-yellow, but the colour is not taken up by ether when the solution is shaken with it; stannous chloride and zinc dust discharge the colour. The yellow liquid obtained by the action of granulated zinc on aqueous sulphurous acid (hydrosulphurous acid according to Schützenberger, hyposulphurous [$H_2S_2O_4$] according to Bernthsen), produces a red coloration in solutions of titanic acid even when very dilute; on shaking this with ether, the coloured substance is taken up by the ether (R. Fresenius). **Zinc or Tin,** after a time, produces a pale violet or blue coloration; subsequently a blue precipitate is formed, which gradually becomes white; the coloration is caused by the reduction of the titanic acid to sesquioxide of titanium. If potassa or ammonia is added to the blue but still clear solution, blue hydrated sesquioxide of titanium separates, which is gradually converted into white hydrated titanic acid with decomposition of the water. The reduction of titanic acid in hydrochloric solution takes place also in the presence of fluoride of potassium (difference from niobic acid), the liquid becoming bright green. The solutions of chloride of titanium in water have different properties according to the way in which they are prepared. If, for example, chloride of titanium is dissolved in water, so that there is no development of heat, a slightly opalescent liquid is obtained, which becomes only slightly turbid on boiling it (titanium chloride solution), whilst the same solution, if kept for some weeks, gives an abundant precipitate when boiled (metatitanium chloride solution). The solutions are further distinguished by the fact that on adding sulphuric or oxalic acid to the former it remains clear, whilst the latter gives a precipitate. If the melt obtained by fusing titanic acid with acid sulphate of potassa is dissolved in cold water, precipitated with ammonia, and the precipitate washed with cold water and dissolved in the smallest possible quantity of hydrochloric acid, it yields a solution of metatitanium chloride; that is, the solution is precipitated by boiling or by adding to it sulphuric or oxalic acid.*

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* The accounts given by R. Weber (Pogg. Ann., **120**, 287) and C. Rammelsberg (Berlin Monatsb., 1874, 490, Zeit. anal. Chem., **13**, 447) of the mode of formation of the solutions of titanium and metatitanium chlorides differ. The matter requires further investigation.

b. **Reactions with alkalies.**—Recently precipitated hydrate of titanic acid is almost absolutely insoluble in solution of potassa; if titanic acid is fused with **hydrate of potassa** and the fused mass treated with water, the solution contains a little more titanic acid. By fusion with **carbonates of the alkalies**, neutral titanates of the alkalies are formed, with expulsion of carbonic acid; water extracts from the fused mass free alkali and alkaline carbonate, leaving behind acid titanate of the alkali; this is soluble in hydrochloric acid. Titanic acid mixed with charcoal and heated to redness in a **stream of chlorine**, gives chloride of titanium, a volatile liquid which emits copious fumes in the air. **Microcosmic salt**, dissolves titanic acid in the point of the outer blowpipe flame to a colourless bead, but with difficulty; in front of the point of the inner flame, titanic acid dissolves readily and in considerable quantity. If the clear and colourless bead is again held in the point of the outer flame, it becomes opaque if sufficiently saturated, and by the continued action of the flame titanic acid will separate in microscopic crystals of the form of anatase (G. Rose). According to A. Knop the crystals are phosphate of titanic acid, but according to G. Wunder they are rhombohedral, and consist of phosphate of titanic acid and soda. If the bead is held in a good reducing flame for some time, it will appear yellow while hot, red while cooling, and violet when cold. The reduction is promoted by the addition of a little tin. If some ferrous sulphate is added, the bead obtained in the reducing flame will appear blood-red.

9. Tantalic Acid.

Tantalum forms with oxygen tantalic acid, TaO_5 [$\mathbf{Ta_2O_5}$], and tantalic oxide, TaO_4 [$\mathbf{TaO_2}$]. Tantalic acid occurs in columbite and tantalite (almost always in conjunction with niobic acid). Tantalic acid is white, pale yellowish when hot (difference from titanic acid); when separated in the wet way, it contains water of hydration. The anhydrous acid has a sp. gr. of 7·0 to 8·25. Tantalic acid is not reduced by ignition in a current of hydrogen. It combines with acids as well as with bases.

a. **Acid solutions.**—When the acid is intimately mixed with charcoal, and ignited in a current of dry **chlorine**, chloride of tantalum, $TaCl_5$ [$\mathbf{TaCl_5}$], is formed; this is yellow, solid, fusible, and can be sublimed; it is completely decomposed by water, with formation of tantalic acid; it is entirely soluble in sulphuric acid, almost entirely soluble in hydrochloric acid, and partially in potassa solution. If titanic acid be present, on heating the mixture of acids with charcoal in a current of chlorine, chloride of titanium will be formed and will fume strongly in the air. Hydrated tantalic acid dissolves in **hydrofluoric acid**, and the solution when mixed with fluoride of potassium yields a very characteristic salt in fine needles, $2KF,TaF_5$ [$\mathbf{K_2TaF_7}$], which is distinguished by its sparing solubility in water acidified with hydrofluoric acid (1 of the acid to 150 or 200 of water). Hydrochloric and concentrated sulphuric acid do not dissolve the ignited acid. With bisulphate of potassa, it fuses to a colourless mass; if this is treated with water, the tantalic acid combined with the sulphuric acid remains undissolved (difference between tantalic acid and titanic acid; but this cannot be made the basis of a method of separation). When ignited in an atmosphere of carbonate of ammonia, the sulphate of tantalic acid is converted into pure tantalic acid. If a solution of alkaline tantalate is mixed with hydrochloric acid in excess, the first-formed precipitate redissolves to an opalescent liquid; on adding **ammonia** or **sulphide of ammonium** to this, the hydrate or an acid tantalate of ammonia is thrown down, but tartaric acid prevents the precipitation. **Sulphuric acid** precipitates sulphate of tantalic acid from the opalescent liquid. When acid solutions of tantalic acid are brought into contact with **zinc**, no blue coloration is observed (difference between tantalic acid and niobic acid).

b. **Behaviour with alkalies.**—By continued fusion with **hydrate of potassa**, tantalate of potassa is formed; the fused mass dissolves in water. If **hydrate of soda** is used, an opaque melt is obtained; a little water poured on this mass will dissolve out the excess of soda, leaving the whole of the tantalate of soda undissolved, as the latter is insoluble in solution of soda; but the tantalate of soda will dissolve in water after the removal of the excess of soda. On slowly adding solution of soda to this, the tantalate of soda is thrown down in the crystalline state. From solutions of tantalates of the alkalies, carbonic acid throws down acid salts, which are not dissolved by boiling with solution of carbonate of soda. **Sulphuric acid** throws down sulphate of tantalic acid even from dilute solutions of tantalates of the alkalies; **ferrocyanide of potassium** and **infusion of galls** produce precipitates only in acidified solutions; the precipitate produced by the former is yellow, by the latter light brown. **Microcosmic salt** dissolves tantalic acid to a colourless bead, which is colourless also when hot, remains colourless even in the inner flame, and does not acquire a blood-red tint on adding ferrous sulphate (difference between tantalic acid and titanic acid).

10. Niobic Acid.

Niobium combines with oxygen in several proportions. NbO_2 [NbO] and NbO_4 [NbO_2], are oxides, NbO_5 [Nb_2O_5] (niobic acid) is an acid. It is occasionally found in columbite, samarskite, &c., and is usually accompanied by tantalic acid. It is white, but turns transiently yellow when ignited (difference between niobic acid and tantalic acid). Its sp. gr. lies between 4·37 and 4·53 (difference between niobic acid and tantalic acid). By strong ignition in hydrogen, the niobic acid is converted into the black NbO_4 [NbO_2]. Niobic acid combines both with bases and with acids.

a. **Acid solutions of niobic acid.**—Concentrated **sulphuric acid** dissolves the acid on heating, unless it has been too strongly ignited; on the addition of much cold water, a clear solution is obtained. When fused with **bisulphate of potassa**, it dissolves readily to a colourless mass, and on treating the melt with boiling water, niobic acid containing sulphuric acid remains undissolved; this, however, is readily soluble in hydrofluoric acid (see below). By mixing niobic acid intimately with charcoal and heating it in a current of **chlorine**, a mixture is obtained of the white, infusible, difficultly volatile oxychloride, NbO_2Cl_3 [$NbOCl_3$], and the yellow more volatile chloride, $NbCl_5$ [$NbCl_5$]. On treatment with water both compounds give turbid solutions, in which a portion of the niobic acid is suspended, but the larger portion is dissolved. If the compounds are boiled with hydrochloric acid and water is subsequently added, clear solutions are obtained, which are not precipitated either by boiling or by sulphuric acid in the cold (difference from chloride of tantalum). By igniting niobic acid in the vapour of chloride of niobium the oxychloride is formed (difference from tantalic acid). From the acid solutions of niobic acid, **ammonia** and **sulphide of ammonium** throw down hydrate of niobic acid containing ammonia; this and generally the unignited forms of niobic acid dissolve in **hydrofluoric acid.** The solution when mixed with fluoride of potassium gives fluoride of potassium and niobium, KF,NbF_5 [$KNbF_6$], if hydrofluoric acid is in excess, otherwise it gives a combination of fluoride of potassium and oxyfluoride of niobium, KF,NbO_2F_3 [$KNbOF_4$]. The latter salt is also obtained when niobate of potassa is dissolved in hydrofluoric acid; it is readily soluble in cold water, 1 part dissolving in 12·5 parts (difference from fluoride of potassium and titanium, which requires 96 parts of water, and from fluoride of potassium and tantalum, which requires 200 parts of water). On digesting a hydrochloric or sulphuric acid solution of niobic acid with **zinc or tin,** it acquires a blue and generally also a brown colour, in consequence of the reduction of the niobic acid to lower oxides. In the presence of alkaline fluorides, the reduction does not take place (difference between niobic acid and titanic acid).

b. **Alkaline solutions.**—With **hydrate of potassa** niobic acid fuses to a clear mass, soluble in water. Towards **hydrate of soda,** niobic acid exhibits the same behaviour as tantalic acid; from the solution of niobate of potassa, solution of soda precipitates an almost insoluble niobate of soda. On boiling a solution of niobate of potassa with **bicarbonate of potassa**, an almost insoluble acid niobate of potassa is thrown down. On fusing niobic acid with **carbonate of soda** and boiling the melt with water, a crystalline acid niobate of soda remains undissolved. **Carbonic acid**, when passed into solutions of niobate of soda, precipitates all the niobic acid as an acid salt. **Microcosmic salt** dissolves niobic acid readily; the bead held in the outer flame appears colourless as long as it is hot; in the inner flame it has a violet, blue, or brown colour, according to the quantity of the acid present, and acquires a red colour on the addition of ferrous sulphate.

For the best methods of detecting the whole of the members of the third group in presence of each other, see Part II., Section III.

§ 105.

Fourth Group.

More common oxides:—Oxide of zinc, Protoxide of Manganese, Protoxide of Nickel, Protoxide of Cobalt, Protoxide of Iron, Sesquioxide of Iron.

Rarer oxides:—Sesquioxide of Uranium, Protoxide of Thallium, Oxide of Indium, Oxide of Gallium, Oxides of Vanadium.

Properties of the group.—The solutions of the oxides of the fourth group, if a strong free acid is present, are not precipitated by sulphuretted hydrogen; nor are neutral solutions, at least not completely. Alkaline solutions, however, are completely precipitated by sulphuretted hydrogen; and so are other solutions if a sulphide of an alkali metal is used as the precipitant, instead of sulphuretted hydrogen.* The precipitated metallic sulphides corresponding with the several oxides are insoluble in water; some of them are readily soluble in dilute acids; others (sulphide of nickel and sulphide of cobalt) dissolve only with very great difficulty in these menstrua. Some are insoluble in sulphides of the alkali metals, others (nickel) are sparingly soluble in them under certain circumstances, whilst others again (vanadium) are completely soluble. The oxides of the fourth group accordingly differ from those of the first and second groups in this, that their solutions are precipitated by sulphide of ammonium, and from those of the third group inasmuch as the precipitates produced by sulphide of ammonium are sulphides, and not hydrated oxides, as is the case with alumina, sesquioxide of chromium, &c.

Special Reactions of the more common Oxides of the fourth group.

§ 106.

a. Oxide of Zinc, ZnO [ZnO].

1. Metallic zinc is bluish-white and very bright; when exposed to the air, a thin coating of basic carbonate of zinc forms on its surface. It is of medium hardness, malleable at a temperature of

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* Vanadic acid behaves in a peculiar way with sulphide of ammonium: see § 113, *e*.

between 100° and 150°, but otherwise more or less brittle; it fuses readily on charcoal before the blowpipe, boils afterwards, and burns with a bluish-green flame, giving off white fumes, and coating the charcoal support with oxide. Zinc dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen; in dilute nitric acid, with evolution of nitrous oxide; in more concentrated nitric acid, with evolution of nitric oxide.

2. The oxide of zinc and its hydrate are white powders, which are insoluble in water, but dissolve readily in hydrochloric, nitric, and sulphuric acids. Oxide of zinc acquires a lemon-yellow tint when heated, but resumes its original white colour as it cools; when ignited before the blowpipe, it becomes brilliantly incandescent.

3. The salts of oxide of zinc are colourless; some of them are soluble in water, the others in acids. The neutral salts of zinc which are soluble in water redden litmus-paper, and are readily decomposed by heat, with the exception of sulphate of zinc, which is not decomposed at a dull red heat, but readily undergoes decomposition at a higher temperature. Chloride of zinc is volatile at a red heat.

4. **Sulphuretted hydrogen** throws down a part of the zinc from neutral solutions of zinc salts containing strong acids in the form of white hydrated sulphide of zinc, ZnS [ZnS]. On the other hand, from neutral solutions of zinc salts containing weak acids, acetate of zinc for example, or from solutions of neutral zinc salts which contain neutral salts of weak acids in sufficient quantity (for example, acetate of soda or sulphocyanate of ammonium), sulphuretted hydrogen throws down all the zinc. In acid solutions, no precipitate is produced if the free acid is one of the strong acids, and is present in sufficient quantity. Acid sulphates of the alkalies prevent the precipitation only when present in abundance; with small quantities, part of the zinc is precipitated. All the zinc is thrown down from a solution of zinc oxide in acetic acid.

5. **Sulphide of ammonium** throws down from neutral, and sulphuretted hydrogen from alkaline solutions the whole of the metal as hydrated sulphide of zinc, in the form of a white precipitate. Chloride of ammonium greatly promotes the separation of this precipitate. From very dilute solutions, the precipitate separates only after long standing. It is not redissolved by an excess of sulphide of ammonium, or by potassa or ammonia; but dissolves readily in hydrochloric acid, nitric acid, and dilute sulphuric acid. It is insoluble in acetic acid.

6. **Potassa and soda** throw down hydrated oxide of zinc, ZnO,HO [ZnH_2O_2], in the form of a white gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant. On boiling these alkaline solutions, they remain unaltered if concentrated; but if dilute, nearly the whole of the oxide of zinc separates as a white precipitate. Chloride of ammonium added to alkaline solutions, not containing a large excess of potassa or soda, produces a white precipitate of hydrated oxide of zinc, which, however, redissolves on addition of more chloride of ammonium; solutions which contain a large excess of potassa or soda give no precipitate with chloride of ammonium (difference between oxide of zinc and alumina).

7. **Ammonia** also produces a precipitate of hydrated oxide of zinc in solutions of zinc salts, if they do not contain a large excess of free acid; this precipitate dissolves readily in an excess of the precipitant; the concentrated solution becomes turbid when mixed with water,

and on boiling it part of the oxide of zinc separates immediately; on boiling the diluted solution, all the oxide of zinc precipitates. Ammonia salts interfere more or less with these precipitations.

8. **Carbonate of soda** produces a precipitate of basic carbonate of zinc, which is insoluble in an excess of the precipitant. The composition of the precipitate varies with the degree of concentration of the solution, the temperature, and the proportion of the precipitant employed. The presence of salts of ammonia in great excess prevents the formation of this precipitate.

9. **Carbonate of ammonia** also produces the same precipitate of basic carbonate of zinc as carbonate of soda does; but this precipitate redissolves on adding excess of the precipitant: on boiling the dilute solution, a white precipitate is formed; ammonia salts interfere more or less with this precipitation.

N.B.—Non-volatile organic acids interfere more or less with the precipitation of solutions of zinc by the caustic and carbonated alkalies. Sugar does not prevent the precipitations.

10. **Carbonate of baryta** does not precipitate solutions of salts of zinc in the cold, with the exception of the sulphate.

11. **Ferrocyanide of potassium** throws down ferrocyanide of zinc, Zn_2Cfy [$Zn_2Fe(CN)_6$], as a white slimy precipitate, somewhat soluble in excess of the precipitant, insoluble in hydrochloric acid.

12. **Ferricyanide of potassium** throws down ferricyanide of zinc, Zn_3Cfdy [$Zn_3Fe_2(CN)_{12}$], as a brownish orange-yellow precipitate, soluble in hydrochloric acid and in ammonia.

13. If a mixture of oxide of zinc or one of its salts with **carbonate of soda** is exposed to the **reducing flame** of the blowpipe, the charcoal support becomes covered with a slight coating of oxide of zinc, which is yellow while hot, but turns white on cooling; this coating is produced by the reduced metallic zinc volatilizing at the moment of its reduction, and being reoxidized in passing through the outer flame. The metallic incrustation obtained according to p. 25 is black with a brown edge, the incrustation of oxide is white, and therefore invisible upon porcelain. It may be dissolved in nitric acid and examined according to 14.

14. If oxide of zinc or a zinc salt is moistened with solution of **nitrate of cobalt**, and then heated before the blowpipe, an unfused mass is obtained of a beautiful green colour; this mass is a compound of oxide of zinc with protoxide of cobalt. If, therefore, in the first experiment described in 13 the charcoal is moistened around the little cavity with solution of cobalt and ignited, the coating appears **green when cold.** This test may be applied with great delicacy by mixing the solution to be tested with a very little of the cobalt solution (not enough to give a bright red colour), adding carbonate of soda in slight excess, boiling, collecting the precipitate, washing it, and igniting on platinum foil. On triturating the residue, the green colour may be distinctly and readily observed (Bloxam).

§ 107.

b. Manganous Oxide, or Protoxide of Manganese,

MnO [MnO].

1. Metallic manganese is whitish-gray, dull, very hard, brittle, and fuses with very great difficulty. It oxidizes rapidly in moist air, and in water with evolution of hydrogen, and crumbles to a dark gray powder. It dissolves readily in acids, the solutions containing the corresponding salt of the protoxide.

2. Protoxide of manganese is light green; the hydrated protoxide is white. The former smoulders to brown protosesquioxide when heated in the air, the latter even at the ordinary temperature rapidly absorbs oxygen from the air and passes into brown hydrated protosesquioxide; they are both readily soluble in hydrochloric, nitric, and sulphuric acids. All the higher oxides of manganese without exception dissolve to protochloride, with evolution of chlorine, when heated with hydrochloric acid; and to sulphate of protoxide, with evolution of oxygen, when heated with concentrated sulphuric acid.

3. The salts of protoxide of manganese are colourless or pale red: some are soluble in water, the others in acids. The salts soluble in water are readily decomposed by a red heat, with the exception of the sulphate. The solutions do not alter vegetable colours.

4. **Sulphuretted hydrogen** does not precipitate acid solutions; neutral solutions also it fails to precipitate, or precipitates them but very imperfectly.

5. **Sulphide of ammonium** throws down from neutral, and sulphuretted hydrogen from alkaline solutions the whole of the metal as hydrated sulphide of manganese, MnS,HO [MnS,H_2O], in the form of a light flesh-coloured* precipitate, which becomes dark-brown on exposure to air; this precipitate is insoluble in sulphide of ammonium and in alkalies, but readily soluble in hydrochloric, nitric, and acetic acids. The separation of the precipitate is materially promoted by the addition of chloride of ammonium. From very dilute solutions, the precipitate separates only after standing for some time in a warm place. Oxalate of ammonia, tartrate of ammonia, and especially citrate of ammonia retard the precipitation, the latter salt also keeps some of the manganese in solution. In the presence of ammonia and sulphide of ammonium in large excess, the flesh-coloured hydrated precipitate occasionally passes into the green crystalline sulphide, $3MnS,2HO$ [$3MnS,2H_2O$], even in the cold, the change being greatly facilitated by boiling, and being hindered more or less by the presence of chloride of ammonium; solutions containing much free ammonia should first be nearly neutralized with hydrochloric acid before adding the sulphide of ammonium.

6. **Potassa, soda**, and **ammonia** produce whitish precipitates of hydrate of protoxide of manganese, MnO,HO [MnH_2O_2], which on exposure to the air speedily become brownish and finally of a deep blackish-brown, owing to the conversion of the hydrated protoxide of manganese into the hydrated protosesquioxide by the absorption of

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* If the quantity of the precipitate is only trifling, the colour appears yellowish white.

oxygen from the air. **Ammonia** precipitates half only of the manganese as hydrate (comp. § 98, 4, p. 99). Ammonia and carbonate of ammonia do not redissolve this precipitate; but the presence of chloride of ammonium prevents the precipitation by ammonia altogether, and that by potassa partly; solution of chloride of ammonium redissolves only those portions of already formed precipitates which have not yet undergone peroxidation. The dissolution of the hydrate in chloride of ammonium is owing to the disposition of the salts of protoxide of manganese to form double salts with salts of ammonia. The ammoniacal solutions of these double salts turn brown on exposure to air, and deposit dark-brown hydrate of protosesquioxide of manganese.

7. If potassa or soda or acetate of soda is added to a solution of a manganese salt and then **"chloride of soda"** or a **solution of bromine,** and the mixture heated, the whole of the manganese separates as the brownish-black hydrated peroxide.

N.B. Non-volatile organic acids impede or prevent the precipitation of the hydrates of manganous and manganic oxides. Sugar impedes the precipitation of manganous oxide but not of the peroxide.

8. **Carbonate of ammonia** throws down white carbonate of protoxide of manganese, MnO,CO_2+HO [$MnCO_3,H_2O$]. The precipitation is complete after some time, even in presence of chloride of ammonium. **Carbonates of the fixed alkalies** give a white precipitate which is either hydrated carbonate of manganese, hydrated protoxide of manganese, or a mixture of these, according to circumstances. When freshly precipitated, it dissolves in chloride of ammonium solution, but it is insoluble in excess of the precipitant.

N.B. Non-volatile acids interfere with or prevent the precipitation by fixed alkaline carbonates, whilst the precipitation with carbonate of ammonia is retarded, but not prevented.

9. **Ferrocyanide of potassium** throws down ferrocyanide of manganese, Mn_2Cfy [$Mn_2Fe(CN)_6$], as a reddish-white precipitate, soluble in hydrochloric acid.

10. **Ferricyanide of potassium** precipitates brown ferricyanide of manganese, Mn_3Cfdy [$Mn_3Fe_2(CN)_{12}$], insoluble in hydrochloric acid or ammonia.

11. If a few drops of a solution containing protoxide of manganese, and free from chlorine, are sprinkled on **binoxide of lead,** nitric acid free from chlorine added, and the mixture boiled and allowed to settle, the solution acquires a red colour, from the formation of permanganic acid (Hoppe-Seyler).

12. **Carbonate of baryta** does not precipitate protoxide of manganese from aqueous solutions of its salts by digestion in the cold, except in the case of sulphate of protoxide of manganese.

13. If any compound of manganese, in a state of minute division, is fused with 2 to 3 parts of **carbonate of soda** on a platinum wire, or on a small strip of platinum foil (heated by directing the flame on to the lower surface), in the **outer flame** of the Bunsen or blowpipe, manganate of soda, NaO,MnO_3 [Na_2MnO_4], is formed, which makes the melt appear green while hot, and of a bluish-green tint after cooling, the bead at the same time losing its transparency. This reaction enables us to detect the smallest traces of manganese.

14. **Borax** and **microcosmic salt** dissolve manganese compounds in the outer gas or blowpipe flame to clear violet-red beads, which on cooling acquire an amethyst-red tint: they lose their colour in the inner flame, owing to a reduction of the sesquioxide to protoxide. The borax bead appears black when containing a considerable portion of sesquioxide of manganese, but that formed by microcosmic salt never loses its transparency; the latter loses its colour in the inner flame of the blowpipe far more readily than the former.

§ 108.

c. Nickelous Oxide or Protoxide of Nickel, NiO [NiO].

1. Metallic nickel in the fused state is silvery white, inclining to gray; it is bright, hard, malleable, difficultly fusible; it does not oxidize in the air at the common temperature, but it oxidizes slowly on ignition; it is attracted by the magnet and may itself become magnetic. It dissolves slowly in hydrochloric acid or dilute sulphuric acid on applying heat, with evolution of hydrogen. It dissolves readily in nitric acid. The solution contains a salt of protoxide of nickel.

2. Hydrate of protoxide of nickel is light green, and remains unaltered in the air, but is converted into green protoxide of nickel at a white heat. Both the protoxide and its hydrate are readily soluble in hydrochloric, nitric, and sulphuric acids; the protoxide crystallized in octahedrons is, however, insoluble in acids, but dissolves in fusing bisulphate of potassa. Sesquioxide of nickel, Ni_2O_3 [Ni_2O_3], is black; it dissolves in hydrochloric acid to protochloride with evolution of chlorine. By gentle ignition of the hydrate, carbonate, or nitrate, a residue of grayish-green colour is obtained consisting of the protoxide containing sesquioxide.

3. Most of the salts of protoxide of nickel are yellow in the anhydrous, green in the hydrated state; their solutions are light green. The soluble neutral salts slightly redden litmus-paper. The salts of nickel containing volatile acids are as a rule easily decomposed by ignition; the sulphate, however, will stand a low red heat.

4. **Sulphuretted hydrogen** does not precipitate solutions of nickel salts of strong acids in presence of free acids; in the absence of a free acid, a small portion of the nickel gradually separates as black sulphide of nickel, NiS [NiS].—Acetate of protoxide of nickel is not precipitated, or but very slightly in presence of free acetic acid; but in the absence of free acid, however, the greater part of the nickel is thrown down by long-continued action of sulphuretted hydrogen; moreover, if the solution contain sufficient of the acetate of an alkali, sulphuretted hydrogen will precipitate the whole of the nickel from the hot solution, even when excess of acetic acid is present.

5. **Sulphide of ammonium** in neutral, and sulphuretted hydrogen in alkaline solutions, produces a black precipitate of hydrated sulphide of nickel, NiS [NiS], which is not altogether insoluble in sulphide of ammonium, especially if the latter contains free ammonia; the solution from which the precipitate has been thrown down is usually therefore of a brownish colour, and yields a slight precipitate of sulphide of nickel, on being neutralized with acetic acid and warmed. The presence of chloride of ammonium, and still more of acetate of

ammonia, considerably promotes the precipitation. Sulphide of nickel dissolves scarcely at all in acetic acid, with great difficulty in hydrochloric acid. Sulphide of nickel precipitated boiling is almost insoluble in dilute hydrochloric acid, but dissolves readily when warmed with nitric acid or nitro-hydrochloric acid.

6. **Potassa** and **soda** give a light green precipitate of hydrate of protoxide of nickel, NiO,HO [NiH_2O_2], which is insoluble in excess of the precipitants, and not altered by exposure to the air, or by boiling (even on adding iodine or alcohol). Carbonate of ammonia dissolves this precipitate, when collected and washed, to a greenish-blue liquid, from which potassa or soda reprecipitates the nickel as an apple-green hydrate of the protoxide.

7. **Ammonia** added in small quantity produces a trifling greenish turbidity; a larger quantity of the reagent redissolves this precipitate readily to a blue solution containing a compound of protoxide of nickel and ammonia. Potassa and soda added to this solution precipitate hydrate of protoxide of nickel. Solutions containing salts of ammonia or free acid are not rendered turbid by ammonia.

8. If potassa or soda is added to a solution of a nickel salt and then **bromine water** or a solution of **"chloride of soda"** (not iodine, distinction from cobalt) in sufficient quantity, and the mixture is heated, the whole of the nickel is thrown down as black hydrated peroxide of nickel, which on adding cyanide of potassium dissolves with formation of potassium nickel cyanide. It is also reduced by a solution of ammonia and chloride of ammonium, and dissolves as ammonio-nickel oxide. The black precipitate must be filtered off from the solution, before heating it with these reagents. Dissolution takes place somewhat slowly in the cold, rapidly on heating.

N.B. The presence of non-volatile organic acids, and of sugar, prevents or impedes the precipitation of the nickel as protoxide or peroxide.

9. **Ferrocyanide of potassium** precipitates greenish-white ferrocyanide of nickel, Ni_2Cfy [$Ni_2Fe(CN)_6$], which is insoluble in hydrochloric acid.

10. **Ferricyanide of potassium** precipitates yellowish-brown ferricyanide of nickel, Ni_3Cfdy [$Ni_3Fe_2(CN)_{12}$], which is insoluble in hydrochloric acid. In presence of chloride of ammonium and ammonia, precipitation does not take place until the solution is boiled.

11. **Cyanide of potassium** produces a yellowish-green precipitate of cyanide of nickel, NiCy [$Ni(CN)_2$], which redissolves readily in excess of the precipitant as the double cyanide of nickel and potassium, NiCy,KCy [$Ni(CN)_2,2KCN$]; the solution is brownish-yellow, and does not darken on exposure to the air. If sulphuric acid or hydrochloric acid is added to this solution, the cyanide of potassium is decomposed, and the cyanide of nickel reprecipitated; from very dilute solutions, the cyanide of nickel separates only after some time. It is very sparingly soluble in an excess of the precipitating acids in the cold, but more readily on boiling. If the solution of the double cyanide is rendered alkaline by solution of soda, being also kept so by a further addition of soda if necessary, and chlorine gas is passed into it without warming, or if bromine is added, the whole of the nickel gradually separates as black hydrate of sesquioxide.

12. On adding to solutions which are not too dilute, and which have

been rendered alkaline by ammonia, a solution of sulphocarbonate of potassium,* a deep brownish-red liquid is obtained, which is barely translucent, and appears almost black by reflected light. If the solution of nickel is extremely dilute, the addition of the reagent will produce a delicate pink colour (C. D. Braun). The production of this colour in highly dilute solutions is characteristic of nickel.

13. **Carbonate of baryta**, on digestion in the cold, does no precipitate nickel from solutions of its salts, unless sulphuric acid is present.

14. **Nitrite of potassa** with acetic acid does not throw down the nickel, even from concentrated solutions. In the presence of lime, baryta, or strontia, however, a yellow crystalline nitrite of protoxide of nickel and the alkaline earth is precipitated if the solution is not too dilute. The precipitate is sparingly soluble in cold water or dilute acetic acid, more readily in hot water to a green solution (Künzel, O. L. Erdmann).

15. **Borax** and **microcosmic salt** dissolve compounds of protoxide of nickel in the outer flame to clear beads. The borax bead is violet while hot, reddish-brown when cold; the microcosmic bead is reddish or brownish-red while hot, yellow or reddish-yellow when cold. In the inner flame, the microcosmic bead remains unaltered, but the borax bead becomes gray and cloudy from reduced metal. On continued heating, the particles of nickel collect together without fusing, and the bead loses its colour.

16. By the reduction in the **stick of charcoal**, according to p. 24, the compounds of nickel yield after trituration white, shining, ductile spangles, which will be deposited on the point of a magnetic knife in the form of a brush. With nitric acid, they give a green solution, which can be further examined.

§ 109.

d. Cobaltous Oxide or Protoxide of Cobalt, CoO [CoO].

1. Metallic cobalt in the fused state is steel-gray, pretty hard, malleable, difficultly fusible, and magnetic; susceptible of polish; it does not oxidize in the air at the common temperature, but it oxidizes at a red heat; with acids it behaves like nickel. The solutions contain protoxide of cobalt.

2. Protoxide of cobalt is light brown, its hydrate a pale red powder. Both dissolve readily in hydrochloric, nitric, and sulphuric acids. Sesquioxide of cobalt, Co_2O_3 [Co_2O_3], is black; it dissolves in hydrochloric acid to protochloride, with evolution of chlorine.

3. The salts of protoxide of cobalt containing water of crystallization are red, the anhydrous salts mostly blue. The moderately concentrated solutions appear of a light red colour, which they retain even though considerably diluted. The soluble neutral salts redden litmus slightly, and are decomposed at a red heat; sulphate of protoxide of cobalt alone can bear a moderate red heat without suffering decomposition. When a solution of chloride of cobalt is evaporated, the pale red

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* Prepared by taking a solution of hydrate of potassa containing about 5 per cent., saturating one-half with sulphuretted hydrogen, adding the other half and then $\frac{1}{25}$ of its volume of bisulphide of carbon, digesting at a gentle heat, and finally separating the dark orange-red solution from the undissolved bisulphide of carbon. The solution must be kept in a well-closed bottle.

colour changes towards the end of the operation to blue; on adding water the red colour is restored.

4. **Sulphuretted hydrogen** does not precipitate solutions of cobalt salts of strong acids, if they contain free acid; from neutral solutions, it gradually precipitates part of the cobalt as black sulphide of cobalt, CoS [**CoS**]. Acetate of protoxide of cobalt is not precipitated, or only to a very slight extent, in presence of free acetic acid, but in the absence of free acid it is precipitated completely, or almost completely. If the solution contain enough of an acetate of an alkali, sulphuretted hydrogen will precipitate the whole of the cobalt from the hot solution, even when excess of acetic acid is present.

5. **Sulphide of ammonium** precipitates from neutral, and sulphuretted hydrogen from alkaline solutions, the whole of the metal as black hydrated sulphide of cobalt, CoS [**CoS**]. Chloride of ammonium promotes the precipitation most materially. Sulphide of cobalt is insoluble in alkalies and sulphide of ammonium, almost insoluble in acetic acid, very sparingly soluble in hydrochloric acid, and if precipitated from hot solutions almost insoluble in the latter. Nitric acid or nitro-hydrochloric acid, however, readily dissolves it on application of heat.

6. **Potassa** and **soda** produce blue precipitates of basic salts of cobalt, which, if the solutions are sufficiently dilute, are insoluble in excess of the precipitants; the precipitate on exposure to the air absorbs oxygen and turns dirty green; this subsequently passes to a grayish-yellow, and on boiling is converted into the pale red hydrate of protoxide of cobalt, which contains alkali, and generally appears rather discoloured from sesquioxide formed in the process. If alcohol is added before boiling, the precipitate is rapidly converted into the dark-brown hydrate of the sesquioxide. If sufficient chloride of ammonium is present, caustic alkalies do not produce a precipitate. Neutral carbonate of ammonia dissolves the washed precipitates of basic salt or hydrated protoxide completely to an intensely violet-red solution, in which a somewhat larger proportion of potassa or soda produces a blue precipitate, the liquid still retaining its violet colour.

If a very concentrated solution of potassa in excess is added to a solution of a salt of cobalt, or if hydrated oxide of cobalt is heated with a very little water and some solid potash, the whole of the cobalt dissolves to a blue liquid containing cobaltate of potassa.

7. **Ammonia** produces the same precipitate as potassa, but it redissolves in excess of ammonia to a reddish solution, which turns brownish-red on exposure to the air; the addition of potassa or soda to this throws down a portion of the cobalt as blue basic salt. Ammonia produces no precipitate in solutions containing ammonia salts or a free acid.

8. If potassa or soda is added to a solution of a cobalt salt and then **bromine water,** a solution of **"chloride of soda"** or **iodine,** and the mixture is boiled, the whole of the cobalt is precipitated as the brownish-black hydrated peroxide of cobalt, provided the solution is sufficiently dilute. This precipitate is insoluble in a mixture of ammonia with chloride of ammonium solution, and in cyanide of potassium. If, however, a large quantity of hydrated peroxide of nickel is present, the cobalt oxide dissolves in cyanide of potassium along with the nickel oxide.

N.B. The presence of non-volatile organic acids or sugar interferes with or prevents the precipitation of cobalt as oxide or peroxide.

9. **Ferrocyanide of potassium** throws down green ferrocyanide of cobalt, Co_2Cfy [$Co_2Fe(CN)_6$], insoluble in hydrochloric acid.

10. **Ferricyanide of potassium** throws down brownish-red ferricyanide of cobalt, Co_3Cfdy [$Co_3Fe_2(CN)_{12}$], insoluble in hydrochloric acid.

If bitartrate of potassa or chloride of ammonium is added to a solution of a cobalt salt, then excess of ammonia, and lastly ferricyanide of potassium to the clear strongly ammoniacal solution thus formed, a deep yellowish-red liquid is obtained if it is concentrated, but rose-red when very dilute (Skey, Gintl). This is a very delicate reaction, adapted for the detection of cobalt in the presence of nickel.

11. The addition of **cyanide of potassium** to a cobalt solution gives a brownish-white precipitate of protocyanide of cobalt, $CoCy$ [$Co(CN)_2$], which dissolves readily in excess of the precipitant as the double cyanide of cobalt and potassium. Acids precipitate cyanide of cobalt from this solution; but if it is previously boiled with cyanide of potassium in excess, in presence of free hydrocyanic acid (liberated by adding one or two drops of hydrochloric acid), or if the solution is mixed with potassa or soda and chlorine is passed through it without warming, or bromine water added, the double cyanide is converted into cobalticyanide of potassium, $K_3Co_2Cy_6 = K_3Ccdy$ [$K_6Co_2(CN)_{12}$], and acids will no longer produce a precipitate (essential difference between cobalt and nickel). Nitrite of potassa and acetic acid added to the unaltered solution of the double cyanide produces a blood-red colour in consequence of the formation of nitrocyanide of cobalt and potassium; when the solution is very dilute, the colour is orange-red. Solution of soda added to the double cyanide produces a brown colour when the liquid is shaken up, oxygen being absorbed (C. D. Braun): if yellow sulphide of ammonium is added, it turns blood-red (Tattersall and Papasogli. These reactions distinguish cobalt from nickel).

12. **Sulphocarbonate of potassa,** added to solutions which have been rendered alkaline by ammonia, produces a dark-brown colour, almost black; very dilute solutions become pale straw colour.

13. **Carbonate of baryta** behaves in the same way as with solutions of nickel.

14. If **nitrite of potassa** is added, in not too small proportion, to a solution containing protoxide of cobalt, then acetic acid to strongly acid reaction, and the mixture allowed to remain in a moderately warm place, all the cobalt separates in the form of a beautiful yellow crystalline precipitate, from concentrated solutions very soon, from dilute solutions only after some time (Fischer, Stromeyer). Stromeyer considers this precipitate to be a nitrite of sesquioxide of cobalt and potassa, $Co_2O_3,3KO,6NO_3,3HO$ [$K_6Co_2(NO_2)_{12},3H_2O$]. The precipitate is very perceptibly soluble in water, almost insoluble in concentrated solutions of potassa salts and in alcohol, insoluble in presence of nitrite of potassa. When boiled with water, it dissolves, although not copiously, forming a red solution, which remains clear on cooling, and from which alkalies throw down hydrate of protoxide of cobalt. This excellent reaction serves well to distinguish and separate cobalt from nickel.

15. **Borax** dissolves compounds of cobalt in the inner and outer flame to clear beads of a magnificent blue colour, which appear violet by candle light, and are almost black in the presence of a large quantity

of cobalt. This test is as delicate as it is characteristic. **Microcosmic salt** gives the same reaction, but it is less delicate.

16. In the reduction with the **stick of charcoal**, as described p. 24, compounds of cobalt behave in the same way as compounds of nickel. The solution with nitric acid is red.

§ 110.

e. Ferrous Oxide or Protoxide of Iron, FeO [FeO].

1. Metallic iron in the pure state is of a light whitish-gray colour (iron containing carbon is more or less gray); the metal is hard, lustrous, malleable, ductile, exceedingly difficult to fuse, and is attracted by the magnet. In contact with air and moisture, a coating of rust (hydrated ferric oxide) forms on its surface: and when ignited in the air a coating of black protosesquioxide. Hydrochloric acid and dilute sulphuric acid dissolve iron with evolution of hydrogen; if the iron contains carbide, the hydrogen is mixed with carbide of hydrogen. The solutions contain protoxide. Dilute nitric acid dissolves iron in the cold to nitrate of protoxide, without evolution of gas (nitrate of ammonia being formed), or with evolution of nitrous oxide; at a higher temperature nitrate of the sesquioxide is formed, with evolution of nitric oxide; if the iron contains carbide, some carbonic acid is also evolved, and a brown substance is left undissolved which resembles humus, and is soluble in alkalies; when graphite is present, it also is left undissolved.

2. Protoxide of iron is black; its hydrate is white, and in the moist state absorbs oxygen and speedily acquires a grayish-green, and ultimately a brownish-red colour. Both the protoxide and its hydrate are readily dissolved by hydrochloric, sulphuric, and nitric acids.

3. The salts of protoxide of iron or ferrous salts in the anhydrous state have a white, in the hydrated state a greenish colour; their solutions only look greenish when concentrated. The latter absorb oxygen when exposed to the air, and are converted into salts of the protosesquioxide, with precipitation of basic ferric salts. At the boiling temperature chlorine or nitric acid converts them into ferric salts. With respect to the transitory brownish-black coloration produced during the oxidation by nitric acid, see § 159, 6. The soluble neutral salts if quite pure and free from sesquioxide do not redden litmus-paper. The salts which ferrous oxide forms with volatile acids are decomposed at a red heat.

4. Solutions of ferrous salts made acid by strong acids are not precipitated by **sulphuretted hydrogen**; moreover, neutral solutions or solutions acidified with weak acids are not precipitated by this reagent, or at the most but very incompletely with black coloration. Their hot solutions mixed with acetate of soda and some free acetic acid are also but imperfectly precipitated.

5. **Sulphide of ammonium** precipitates from neutral, and sulphuretted hydrogen from alkaline solutions, the whole of the metal as black hydrated ferrous sulphide, FeS [FeS], which is insoluble in alkalies and sulphides of the alkali metals, but dissolves readily in hydrochloric or nitric acid: this black precipitate oxidizes and turns reddish-brown on exposure to the air. Sulphide of ammonium imparts a green colour to highly dilute solutions, and it is only after some time

that the protosulphide of iron separates as a black precipitate. Chloride of ammonium promotes the precipitation most materially.

6. **Potassa, soda** and **ammonia** produce a precipitate of hydrate of ferrous oxide, FeO,HO $[FeH_2O_2]$, which in the first moment looks almost white, but after a very short time acquires a dirty green, and ultimately a reddish-brown colour, owing to absorption of oxygen from the air. The presence of salts of ammonia prevents the precipitation by potassa partly, and that by ammonia altogether. If alkaline solutions of ferrous oxide obtained in this way by the agency of salts of ammonia are exposed to the air, hydrate of protosesquioxide of iron and hydrate of ferric oxide are precipitated. Non-volatile organic acids, sugar, &c., check the precipitation by alkalies.

7. **Ferrocyanide of potassium** produces a bluish-white precipitate of ferrocyanide of potassium and iron, KFe_3Cfy_2 $[K_2Fe_3(FeC_6N_6)_2]$, which, on exposure to the air, absorbs oxygen and speedily acquires a blue colour. Nitric acid or chlorine converts it immediately into Prussian blue,

$$3KFe_3Cfy_2 + 4Cl = 3KCl + FeCl + 2Fe_4Cfy_3$$

$$[3K_2Fe_3(FeC_6N_6)_2 + 4Cl_2 = 6KCl + FeCl_2 + 2Fe_4(FeC_6N_6)_3].$$

8. **Ferricyanide of potassium** produces a splendid blue precipitate of ferricyanide of iron, Fe_3Cfdy $[Fe_3(Fe_2C_{12}N_{12})]$. This precipitate does not differ in colour from Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by potassa. In highly dilute solutions, the reagent produces merely a deep blue-green coloration.

9. **Sulphocyanate of potassium** does not alter solutions of ferrous oxide free from ferric oxide.

10. **Carbonate of baryta** does not precipitate solutions of ferrous oxide in the cold, with the exception of the sulphate.

11. **Borax** dissolves protoxide of iron compounds in the oxidizing flame, giving beads varying in colour from yellow to dark red; when cold, the beads vary from colourless to dark yellow. In the inner flame, the beads change to bottle-green, owing to the reduction of the newly-formed sesquioxide to protosesquioxide. **Microcosmic salt** shows a similar reaction; the beads produced with this reagent lose their colour on cooling still more completely than those obtained with borax; the signs of reduction in the reducing flame are also less marked.

12. When reduced on the **stick of charcoal** (p. 24), compounds of protoxide of iron give a dull black powder, which is attracted by a magnetised knife. The reduced metal, when dissolved in a few drops of aqua regia, gives a yellow solution which can be further tested according to § 111.

§ 111.

f. Ferric Oxide or Sesquioxide of Iron, Fe_2O_3 $[Fe_2O_3]$.

1. The native crystallized ferric oxide is steel-gray; the native as well as the artificially prepared ferric oxide when triturated gives a brownish-red powder; the colour of hydrate of ferric oxide is more inclined to reddish-brown. Both ferric oxide and its hydrate dissolve in hydrochloric, nitric, and sulphuric acids; the hydrate dissolves readily in these acids, but the anhydrous sesquioxide dissolves with greater difficulty, and completely only after long heating with the acid. Ferrosoferric oxide or protosesquioxide of iron,

FeO,Fe_2O_3 [Fe_3O_4], is black; it dissolves in hydrochloric acid to ferrous and ferric chlorides, in aqua regia to ferric chloride.

2. The neutral anhydrous salts of ferric oxide are nearly white; the basic salts are yellow or reddish-brown. The colour of the solutions is brownish-yellow, and becomes reddish-yellow on heating. The soluble neutral salts redden litmus-paper, and the salts containing volatile acids are decomposed by heat.

3. **Sulphuretted hydrogen** in solutions made acid by the stronger acids produces a milky white turbidity, due to separated sulphur; the ferric salt being at the same time converted into a ferrous salt:

$$Fe_2O_3,3SO_3 + HS = 2(FeOSO_3) + HO,SO_3 + S$$

$$[Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S].$$

If solution of sulphuretted hydrogen is rapidly added to neutral solutions, a transient blackening of the liquid also occurs. Sulphuretted hydrogen throws down the greater part of the iron from solutions of neutral acetate of ferric oxide; but in the presence of a sufficient quantity of free acetic acid, sulphur alone separates. When sulphuretted hydrogen is passed into a solution of a ferric salt mixed with acetate of soda and acetic acid, scarcely anything but sulphur is thrown down in the cold, but on warming a part of the iron is precipitated.

4. **Sulphide of ammonium** precipitates from neutral, and sulphuretted hydrogen from alkaline solutions, the whole of the metal as black hydrated ferrous sulphide or protosulphide of iron, FeS [FeS], mixed with sulphur, $Fe_2Cl_3 + 3NH_4S = 2FeS + 3NH_4Cl + S$ [$Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + 6NH_4Cl + S$]. In very dilute solutions, the reagent produces only a blackish-green coloration. The minutely divided ferrous sulphide subsides in such cases only after long standing. Chloride of ammonium most materially promotes the precipitation. Ferrous sulphide, as already stated (§ 110, 5), is insoluble in alkalies and alkaline sulphides, but dissolves readily in hydrochloric and nitric acids.

5. **Potassa, soda** and **ammonia** produce bulky reddish-brown precipitates of hydrated ferric oxide, $Fe_2O_3,2HO$ [$Fe_2(OH)_6$], which are insoluble in an excess of the precipitant as well as in salts of ammonia. Non-volatile organic acids and sugar, when present in sufficient quantity, entirely prevent the precipitation.

6. **Ferrocyanide of potassium**, even in highly dilute solutions, produces a deep blue precipitate of ferric ferrocyanide, or Prussian blue, Fe_4Cfy_3 [$Fe_4(FeC_6N_6)_3$]:

$$2Fe_2Cl_3 + 3K_2Cfy = Fe_4Cfy_3 + 6KCl$$

$$[2Fe_2Cl_6 + 3K_4FeC_6N_6 = Fe_4(FeC_6N_6)_3 + 12KCl].$$

This precipitate is insoluble in hydrochloric acid, but is decomposed by potassa with separation of hydrated ferric oxide.

7. **Ferricyanide of potassium** deepens the colour of solutions of ferric salts to reddish-brown; but it does not produce a precipitate.

8. **Sulphocyanate of potassium** imparts a most intense blood-red colour to acid ferric solutions; this is due to the formation of a soluble sulphocyanate of iron. The colour does not disappear on the addition of a little alcohol and warming (difference from the analogous reaction of hyponitric acid, § 158). Solutions of ferric salts, containing acetate of soda (which consequently are more or less red from ferric acetate), do not show the blood-red colour of the sulpho-

cyanate until after the addition of much hydrochloric acid. The same is the case when the solution contains oxalic acid, tartaric acid, citric acid, malic acid, iodic acid, phosphoric acid, arsenic acid, or hydrofluoric acid. This test will indicate the presence of iron even in solutions which are so dilute that every other reagent fails to produce in them the slightest visible alteration. The red coloration may in such cases be detected most distinctly by resting the test-tube upon a sheet of white paper, and looking through it from the top. The delicacy of the reaction may also be increased by shaking gently with ether after the addition of hydrochloric acid and excess of sulphocyanate of potassium solution freshly prepared from the crystals. The sulphocyanate of iron dissolves in the ether, and the layer of the latter acquires a more or less red colour.

9. **Carbonate of baryta** even in the cold precipitates all the iron as hydrate of sesquioxide mixed with a basic salt.

10. The reactions before the **blowpipe** are the same as with the protoxide.

§ 112.

Recapitulation and Remarks.

On observing the reactions of the several oxides of the fourth group with solution of potassa or soda, it would appear that the separation of oxide of zinc, which is soluble in an excess of this reagent, might be readily effected by its means; but in actual experiment we find that rather notable quantities of oxide of zinc are thrown down with the ferric oxide, oxide of cobalt, &c. To such an extent indeed does this take place that it is often impossible to detect the presence of oxide of zinc in the alkaline filtrate. This method would be entirely inadmissible in the presence of sesquioxide of chromium, as solutions of the latter and of oxide of zinc in potassa mutually precipitate each other.

Again, the reactions of the different oxides with chloride of ammonium and an excess of ammonia would lead to the conclusion that the separation of sesquioxide of iron from the protoxides of cobalt, nickel, and manganese, and from oxide of zinc, might be readily effected by these agents. But this method also, if applied to the mixed oxides, is inaccurate, since larger or smaller portions of the other oxides will always be precipitated along with the ferric oxide; and it may therefore happen that small quantities of cobalt, manganese, &c., altogether escape detection in this process.

It is far safer, therefore, to separate the other oxides of the fourth group from ferric oxide by carbonate of baryta, as in that case the iron is precipitated free from oxide of zinc and protoxide of manganese, and, if chloride of ammonium is added previously to the addition of the carbonate of baryta, almost entirely free also from protoxide of nickel and protoxide of cobalt. Instead of using carbonate of baryta for the separation of ferric oxide, we may proceed as follows: nearly neutralize any excess of acid with carbonate of soda, add acetate of soda, and boil; or mix the sufficiently diluted solution with a rather large quantity of chloride of ammonium, cautiously add carbonate of ammonia until the fluid commences to become cloudy—the reaction still remaining acid—and then boil. In each of the last two methods, the basic ferric salt must be filtered off hot.

Protoxide of manganese may conveniently be separated from the protoxides of cobalt and nickel, as well as from oxide of zinc, by treating the washed precipitated sulphides with moderately dilute acetic acid, which dissolves the sulphide of manganese, leaving the other sulphides undissolved. If the acetic acid solution is now evaporated and mixed with solution of potassa, the least trace of a precipitate will be sufficient to recognize the manganese before the blowpipe with carbonate of soda. If the sulphides left undissolved by the acetic acid are washed and treated with very dilute hydrochloric acid, the sulphide of zinc dissolves, leaving almost the whole of the sulphides of cobalt and nickel behind. If the solution is then boiled, strongly concentrated to expel all the sulphuretted hydrogen, and afterwards treated with solution of potassa or soda in excess without warming, the zinc is sure to be detected in the filtrate by sulphuretted hydrogen.

On drying the filter containing the sulphides of nickel and cobalt, incinerating it in a small porcelain dish, and testing a portion of the residue with borax in the inner blowpipe flame, the cobalt may generally be detected with certainty even in the presence of nickel. The detection of nickel in presence of cobalt is not quite so simple a matter. It is best done by warming the rest of the residue with a little aqua regia, diluting, filtering, evaporating the solution to a small bulk, mixing with a sufficiency of nitrite of *potassa*, adding acetic acid to strongly acid reaction, and setting aside in a moderately warm place for at least twelve hours. The cobalt then separates as nitrite of sesquioxide of cobalt and potassa; the nickel may be precipitated from the filtrate by solution of soda, and, to prevent mistakes, tested before the blowpipe, or according to § 108, 11, after considerable dilution. For the detection of small quantities of nickel in presence of large quantities of cobalt, it is still better to use the solution of the cyanides in cyanide of potassium mixed with solution of soda. In this solution, the presence of cobalt will be shown by a dark colour on exposure to the air, the presence of nickel by the separation of black sesquioxide on treatment with chlorine (§ 108, 11, and § 109, 11). Nickel may also be detected in the presence of cobalt by the brown coloration of the solution obtained on adding chloride of ammonium, ammonia, and sulphide of ammonium, and filtering. The difference in the behaviour of the hydrated peroxides with cyanide of potassium solution and with chloride of ammonium and ammonia (§ 108, 8, and § 109, 8) is adapted rather for distinguishing between nickel and cobalt than for separating them. A careful use of these solvents, however, will serve to obtain from the mixed precipitates a solution containing a portion of the nickel free from cobalt; this can then be tested more readily for the former.

In practical analysis, we generally separate the whole of the oxides of the fourth group as sulphides by precipitation with sulphide of ammonium. It is therefore in most cases still more convenient to separate nickel and cobalt, or at least by far the larger portion of these two metals, at the outset. For this purpose, the moist precipitate of the sulphides is treated with water and some hydrochloric acid, with active stirring, but without application of heat. Nearly the whole of the sulphide of nickel and sulphide of cobalt is left behind undissolved, whilst all the other sulphides are dissolved. The undissolved residue of sulphide of cobalt and sulphide of nickel is filtered and washed, and treated as directed above. (If it still contains some sulphide of iron, it must be treated as in § 194, **147**.) By boiling the filtrate with nitric acid, the iron is converted from the ferrous state, as it existed in the solution of the sulphide, to the ferric state. After the free acid has been nearly neutralized by carbonate of soda, the iron may be thrown down as basic salt either by carbonate of baryta in the cold, or by acetate of soda and boiling. Manganese and zinc alone remain in the filtrate; these may be separated by one of the following methods:—

a. Both the metals are precipitated by adding to the solution chloride of ammonium, ammonia, and sulphide of ammonium; the precipitate is collected, washed, and the separation of the sulphides effected by means of acetic acid as described above.

b. A more accurate but somewhat more troublesome method is to add to the solution ammonia in excess (if baryta has been used to throw down the iron, the baryta in the solution must be removed by sulphuric acid before adding the ammonia), then acetic acid to acid reaction, and lastly acetate of soda. On passing sulphuretted hydrogen into the warmed solution, all the zinc is thrown down as sulphide of zinc, which is collected, and the manganese precipitated from the filtrate by adding ammonia until alkaline, and then sulphide of ammonium.

c. The least accurate method consists in removing any baryta which may be present by sulphuric acid, concentrating, and adding potassa or soda in excess.

The traces of cobalt and nickel, dissolved on the first treatment of the precipitated sulphides with dilute hydrochloric acid, remain with the sulphide of zinc in the separation of the latter by *a* or *b*, or with the protoxide of manganese if the separation is effected by *c*. The sulphide of zinc may be extracted from the blackish precipitate by dilute hydrochloric acid, and the detection of the manganese in presence of the cobalt and nickel may be readily effected by means of carbonate of soda in the outer flame.

In the presence of non-volatile organic substances, the second method must be employed—namely, that depending on the preliminary precipitation of the whole of the metals as sulphides, since such organic substances would check the precipitation of the ferric oxide by carbonate of baryta.

Ferrous and ferric oxide may be detected in presence of each other by testing for the former with ferricyanide of potassium, for the latter with ferrocyanide or sulphocyanate of potassium.

Special Reactions of the rarer Oxides of the fourth group.

§ 113.

a. **Oxides of Uranium.**

This metal is found in a few minerals, as pitchblende, uranium-ochre, &c. The sesquioxide of the metal is used to stain glass yellowish-green. Uranium[*] forms two oxides, the protoxide named uranous oxide, UO [UO_2], and the oxide or uranic oxide, UO_3 [UO_3]. The protoxide is brown or black; it dissolves in nitric acid to nitrate of the oxide. The hydrate of the oxide is yellow; at about 300°, it loses its water and turns red; it is converted by ignition into

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[*] Equiv. 118·8, atomic weight, 237·6.

the dark blackish-green uranoso-uranic oxide. The solutions of oxide of uranium in acids are yellow. **Sulphuretted hydrogen** does not alter them; the addition of **sulphide of ammonium**, after the free acid has been neutralized, throws down a slowly subsiding precipitate, which is readily soluble in acids, even acetic acid; the precipitation is promoted by chloride of ammonium. The precipitate, when formed in the cold, is chocolate-brown, and contains oxysulphide of uranium, sulphide of ammonium, and water. It is insoluble in yellow sulphide of ammonium; but, when free from other sulphides, it dissolves in colourless or yellow sulphide of ammonium containing carbonate of ammonia, yielding a black solution. By washing, the precipitate is gradually converted into yellow hydrated uranic oxide. On warming or boiling the mixture of uranium solution and sulphide of ammonium, the oxysulphide at first thrown down splits up into sulphur and black protoxide, which last is insoluble in the excess of sulphide of ammonium (Remelé). The oxysulphide of uranium (but not the precipitate which has been converted into protoxide and sulphur) dissolves readily in carbonate of ammonia. (This reaction may be used as a means of separating uranium from zinc, manganese, iron, &c.) If the oxysulphide remains long in contact with excess of sulphide of ammonium with access of air, it gradually turns blood-red, hyposulphite of ammonia being formed; if air is excluded, however, the product is black. **Ammonia, potassa,** and **soda** produce yellow precipitates containing uranic oxide and alkali; these are insoluble in excess of the precipitants. **Carbonate of ammonia** and **bicarbonate of potassa or soda** produce yellow precipitates of carbonate of oxide of uranium and alkali, which **readily redissolve in an excess of the precipitants**; potassa and soda throw down from such solutions the whole of the oxide of uranium. **Carbonate of baryta** completely precipitates solutions of oxide of uranium, even in the cold (essential difference from nickel, cobalt, manganese, and zinc, and means of separating uranium from these metals). **Ferrocyanide of potassium** produces a reddish-brown precipitate or coloration (a most delicate test). **Borax** and **microcosmic salt** give green beads, with uranium compounds in the inner flame of the blowpipe, in the outer flame yellow beads are obtained, which acquire a yellowish-green tint on cooling.

b. Oxides of Thallium.

Thallium occurs, but invariably in extremely minute quantities, in many kinds of copper and iron pyrites, in many kinds of crude sulphur, and accumulated in the flue-dust of the lead vitriol-chambers, where the furnaces are fed with thalliferous pyrites. It is occasionally found in commercial sulphuric and hydrochloric acids, and it has been discovered in lepidolite, preparations of cadmium and bismuth, in ores of zinc, mercury, and antimony, in the ashes of plants, and in some saline waters. Thallium is a metal resembling lead, of 11·8–11·9 sp. gr.; it is soft; melts at 285–290°, is volatile at a white heat, and in a current of hydrogen at a red heat, crackling like tin when bent; it does not decompose water, until an acid is added. Dilute sulphuric and nitric acids readily dissolve it, hydrochloric acid dissolves it with difficulty. Thallium forms two oxides, thallious oxide, TlO [Tl_2O], and thallic oxide, TlO_3 [Tl_2O_3]. Thallious oxide is brown and fusible; when in the melted state it attacks glass or porcelain. It dissolves in water; the solution is colourless, alkaline, caustic, and absorbs carbonic acid; it is also soluble in alcohol. The thallic oxide is insoluble in water and dark violet, its hydrate is brown. Trioxide of thallium is hardly acted on by concentrated sulphuric acid in the cold, but on heating they combine; on continued heating, oxygen escapes and sulphate of the protoxide is formed. Treated with hydrochloric acid, the trioxide yields the corresponding chloride as a white crystalline mass, which yields chlorine and compounds of thallious and thallic chlorides when heated. Thallic salts are decomposed by water with separation of hydrated oxide, alkalies throw down hydrate of the trioxide from acid solution, sulphuretted hydrogen produces salts of the protoxide with separation of sulphur, iodide of potassium yields thallious iodide and iodine, hydrochloric acid produces no change. The salts of thallious oxide are colourless, some are readily soluble in water (sulphate, nitrate, phosphate, tartrate, acetate), some are sparingly soluble (carbonate, chloride, basic phosphate), some are almost insoluble (iodide, &c.). On boiling solutions of thallious salts with nitric acid, the protoxide is not converted into trioxide, but it is completely by boiling and evaporating with aqua regia. **Potassa, soda, and ammonia** do not precipitate aqueous solutions of thallious salts, **carbonated alkalies** throw down carbonate of the protoxide, but only from very concentrated solutions (for 100 parts of water dissolve 5·23 parts at 18°). If the solutions are not extremely dilute, **hydrochloric acid** throws down the protochloride in the form of a white readily subsiding precipitate, unalterable on exposure to light, and even less soluble in dilute hydrochloric acid than in water. **Iodide of potassium** precipitates even from the most dilute solutions, the light yellow proto-iodide, which is almost insoluble in water, and even less soluble in excess of solution of iodide of potassium. **Chloride of platinum** precipitates from solutions which are not extremely dilute the pale orange platinochloride, $TlCl,PtCl_2$ [Tl_2PtCl_6], which is very sparingly soluble. **Sulphuretted hydrogen** does not precipitate solutions rendered strongly acid by mineral acids, unless arsenious acid or antimony is present, when a brownish-red precipitate of the mixed sulphides is formed, which contains the arsenic or antimony along with the thallium. Neutral or very slightly acid solutions are incompletely precipitated by this reagent; from acetic acid solutions, the whole of the thallium is thrown down as black protosulphide. **Sulphide of ammonium** precipitates the whole of the thallium as black sulphide, which readily collects into lumps, especially on warming; sulphuretted hydrogen added to alkaline solutions has the same effect. The sulphide thrown down is insoluble in ammonia, alkaline sulphides, or cyanide of potassium; it oxidizes rapidly in the air to thallious sulphate, dissolves readily in dilute hydrochloric, sulphuric, or nitric acid, but is acted on only with difficulty by acetic acid. On heating, the sulphide first fuses and then volatilizes. **Zinc** throws down the metal in the form of black crystalline laminæ. **Colourless flames** are tinged intensely green by combinations of thallium. The **spectrum** of thallium exhibits only one line (compare the plate of spectra), of an emerald green colour, extremely characteristic. If the quantity of metal is small, the line soon disappears. The spectroscope generally affords the best means of detecting thallium; thalliferous pyrites often gives the green line at once. If you want to look for thallium in crude sulphur, it is best to remove the greater part of the sulphur by treatment with bisulphide of carbon, and then to test the residue. In the presence of much sodium, with very small quantities of thallium, the green line will not be seen, unless the substance is moistened and the spectrum examined at the first moment. If traces of thallium platinochloride are present along with much potassium, cæsium, and rubidium platinochloride in the precipitate produced by platinum chloride, this should be boiled repeatedly with water and the small quantity of residual substance tested spectroscopically for thallium. For the detection of thallium in the wet way, iodide of potassium is the most delicate reagent; if iron is present, it must previously be reduced by sulphite of soda.

c. Oxide of Indium.

Indium was first discovered in the Freiberg blende, in the zinc prepared from it, subsequently in other zinc blendes, and also in wolfram. It is a white highly lustrous metal, and resembles platinum in colour; it is very soft, ductile, makes a mark on paper, is capable of receiving a polish, and is only slowly oxidized by contact with air or water, less readily than zinc. Indium melts at 176°. It melts on charcoal before the blowpipe with a shining metallic surface, colours the flame blue, and yields an incrustation which is dark yellow whilst hot, light yellow when cold, and cannot be easily dispersed by the blowpipe flame. Indium dissolves in dilute hydrochloric or sulphuric acid with evolution of hydrogen, slowly in the cold, more rapidly on heating; with cold concentrated sulphuric acid, it also evolves hydrogen and becomes converted into anhydrous sulphate of indium; in nitric acid, even when cold and dilute, it dissolves with ease. The oxide, In_2O_3 [In_2O_3], is reddish-brown when hot, straw-coloured when cold; it does not colour vitreous fluxes; when ignited in hydrogen or with charcoal, it is readily reduced, and if a flux is used metallic globules are obtained. The ignited oxide dissolves slowly in acids in the cold, but readily and completely if heated. The salts are colourless; the sulphate, nitrate, and chloride are readily soluble in water. The chloride is volatile and hygroscopic. **Alkalies** throw down the hydrate in the form of a white bulky precipitate, like hydrate of alumina; tartaric acid prevents the precipitation. The precipitate is insoluble in ammonia but dissolves in potassa or soda forming a liquid which soon becomes turbid. On boiling the solution, or on adding chloride of ammonium, hydrated oxide of indium separates. **Alkaline carbonates** precipitate a white gelatinous carbonate; when recently thrown down, the precipitate dissolves in carbonate of ammonia, but not in carbonate of potassa or carbonate of soda; if the solution in carbonate of ammonia is boiled, the carbonate of indium separates again. **Phosphate of soda** throws down a white bulky precipitate. **Alkaline oxalates** produce a crystalline precipitate. If **acetate of soda** is added to the nearly neutral solution of the sulphate, and it is then boiled, a basic sulphate is precipitated. By digestion with **carbonate of baryta** in the cold, the whole of the indium is thrown down in the form of basic salt. (This affords a means of separating indium from zinc, manganese, cobalt, nickel, and ferrous oxide.) **Sulphuretted hydrogen** throws down the whole of the indium as yellow sulphide of indium from a neutral or acetic acid solution even when the latter is strongly acidified with acetic acid. If the solution is strongly acidified with a mineral acid and moderately concentrated, it is not precipitated, but yellow sulphide of indium is thrown down if the solution is very dilute. Sulphuretted hydrogen with alkaline solutions, and **sulphide of ammonium** with neutral solutions, yield a white precipitate (probably hydrosulphide of indium). If yellow sulphide of indium is boiled with yellow sulphide of ammonium, it also becomes white and partially dissolves. On cooling, sulphide of indium (?) separates as a white voluminous precipitate. **Ferrocyanide of potassium** produces a white precipitate. **Ferricyanide and sulphocyanate of potassium** and **dichromate of potassa** produce no precipitate, but **chromate of potassa** gives a yellow precipitate. **Zinc** precipitates the metal in the form of white shining laminæ. Indium compounds produce a peculiar bluish violet tinge in a **colourless flame.** The **spectrum** has two characteristic blue lines (see the spectrum table). With the chloride, the lines, especially *a*, appear brightest, but they are very transient. For obtaining more persistent lines, the sulphide is the most suitable compound.

d. Oxide of Gallium.

Hitherto gallium has been found only in some zinc blendes, and only in very minute quantity. It is a white metal, which, when fused, is silver-white; on solidifying it becomes crystalline, duller, and of a bluish white; it melts at 30·16°. Its sp. gr. is 5·956, it is hard, not very ductile, and remains unaltered on exposure to the air at the ordinary temperature; it is only oxidized slightly when heated to redness, and does not volatilize at that temperature. Water, even when boiling, is not decomposed by gallium. Nitric acid has hardly any action on gallium in the cold, but on warming, it dissolves with evolution of red fumes. Hydrochloric acid, potassa, and ammonia readily dissolve gallium, hydrogen being given off. Gallium oxide, Ga_2O_3 [Ga_2O_3], and its hydrate are white. On heating the oxide to redness in a stream of hydrogen, it sublimes, and is partially reduced to what is probably a lower oxide. The salts of gallium oxide are colourless or white, the sulphate and nitrate are readily soluble in water, and are decomposed on ignition; the sulphate combines with ammonium sulphate, forming an alum. On boiling solutions of the sulphate or of the alum prepared from it, a basic salt is precipitated. Gallium combines with chlorine, forming a readily oxidizable subchloride, GaCl [$GaCl_2$], and a chloride corresponding with the oxide, Ga_2Cl_3 [Ga_2Cl_6]; the latter is a colourless volatile mass, which melts at 75° and boils at 215°–220°. On adding an alkali to an aqueous solution of a gallium salt, a white flocculent precipitate is formed, readily soluble in excess of the reagent. If, however, a solution of a gallium salt to which excess of ammonia has been added is boiled for some time, the whole of the gallium is precipitated as the hydrated oxide; tartaric acid prevents the precipitation by ammonia. The **alkaline carbonates** yield white precipitates; that formed by carbonate of ammonia is soluble in excess of the reagent. **Barium carbonate** completely precipitates gallium even in the cold. **Sulphuretted hydrogen** gives no precipitate in solutions acidified with hydrochloric acid, but in solutions containing acetate of ammonia and free acetic acid a white precipitate of gallium sulphide is formed. **Sulphide of ammonium** throws down a white precipitate of gallium sulphide insoluble in excess of the precipitant; the presence of tartaric acid prevents this precipitation. **Acetate of ammonia** precipitates almost all the gallium from a boiling solution acidified with acetic acid, but not if too much of the acetate is added. **Ferrocyanide of potassium** throws down a bluish precipitate, the colour of which is probably due to the presence of iron; it is less soluble in hydrochloric acid than in water. This is a delicate reaction. Gallium compounds exhibit a **spectrum** having two violet lines between G and H, which can, however, only be clearly seen when the electric spark is employed. On heating a gallium compound in the Bunsen flame, only one of these lines is visible, and that but indistinctly.

e. Oxides of Vanadium.

Vanadium occurs in the form of vanadates, and occasionally in small quantities in iron and copper ores, and in the slags obtained from them. There are four oxides of vanadium, the protoxide, VO_2 [VO], the sesquioxide, VO_3 [V_2O_3], the dioxide, VO_4 [VO_2], and vanadic acid, VO_5 [V_2O_5]. The protoxide is gray, possesses metallic lustre, is insoluble in water, but soluble in dilute acids, with evolution of hydrogen, forming blue solutions which bleach organic colouring matters by reducing them. The sesquioxide is black, insoluble, not reduced by ignition in hydrogen; when exposed to the air, it is gradually converted into the dioxide: acid solutions containing the sesquioxide are green. The dioxide is dark blue, acid solutions in which it is present are pure blue. All the lower oxides pass into vanadic acid when heated with nitric acid or aqua regia, or by fusion with nitrate of potassa, or on igniting them in oxygen or air. Vanadic acid is non-volatile and fusible, solidifying to a crystalline mass, dark red to orange-red in colour. When heated to redness in a current of hydrogen, it is converted into the sesquioxide. Vanadic acid is sparingly soluble in water, but reddens litmus-paper strongly. It combines with acids and with bases.

a. **Acid solutions.**—The stronger acids dissolve vanadic acid to red or yellow solutions, which gradually become green on exposure to the air (by the reducing action of dust). The sulphuric acid solution when much diluted, treated with zinc and warmed gently, first passes through green to blue (reduction to dioxide), then through greenish blue to green (reduction to sesquioxide), and finally from violet to lavender (reduction to protoxide); on adding ammonia to this solution, a brown precipitate of the hydrate of the protoxide forms, which readily absorbs oxygen. **Sulphurous acid, sulphuretted hydrogen** (with separation of sulphur), **boiling hydrochloric acid, oxalic acid,** &c., also reduce the solutions, but only to the dioxide; hence the colour produced is only blue. **Alkalies** produce a brown precipitate soluble in excess of the precipitant to a yellowish-brown solution. **Sulphide of ammonium** produces a brown precipitate of the sulphide, which dissolves with difficulty in excess of sulphide of ammonium with a brownish-red colour; acids throw down the brown pentasulphide. **Ferrocyanide of potassium** throws down a green flocculent precipitate insoluble in acids. In solutions free from excess of acid, **tannic acid** produces a blueish-black precipitate after some time.

β. **Vanadates.**—Vanadic acid forms ortho-, pyro- and meta-vanadates. The vanadic minerals contain mostly orthovanadates. The soluble ortho-salts, when their solutions are kept, are converted into pyro- and meta-vanadates, and the same change takes place on treating the insoluble salts with acids; the pyrovanadates of the alkalies easily change into meta-vanadates even on passing carbonic acid into their solutions. Metavanadates of the alkalies are obtained by dissolving vanadic acid in potassa or soda solution, also when vanadic acid is fused with the carbonates or nitrates of the alkalies. The solutions are colourless; if solid chloride of ammonium is added to them, the whole of the vanadic acid is precipitated as colourless crystalline metavanadate of ammonia, which is insoluble in chloride of ammonium solution; when heated to redness in an atmosphere of oxygen, it leaves pure vanadic acid. This is a very characteristic reaction. On adding strong acids to solutions of metavanadates of the alkalies, they acquire a red tint, but become colourless again after a time. **Chloride of barium, nitrate of silver,** and **acetate of lead** produce yellow precipitates in solutions of the metavanadates of the alkalies; these become colourless on standing, more quickly on warming. With **hydrochloride of aniline,** metavanadates of the alkalies yield aniline-black and the chloride corresponding with vanadium dioxide. Both **sulphide of ammonium** and a solution of **tannic acid** containing acetic acid act on the metavanadates in the same way as they do on the solutions of vanadic acid mentioned in *a*.

If an acidified solution of a metavanadate of an alkali is shaken with **peroxide of hydrogen,** the liquid acquires a red tint; if ether is then added, and the mixture shaken, the solution retains its colour, the ether remaining colourless (most delicate reaction) (Werther). **Borax** dissolves vanadic acid in the inner and outer flame to a clear bead; the bead produced in the outer flame is colourless, with large quantities of vanadic acid, yellow; the bead produced in the inner flame is of a beautiful green; with larger quantities of vanadic acid, it looks brownish whilst hot, and only turns green on cooling.

§ 114.

Fifth Group.

More common oxides:—Oxide of Silver, Mercurous Oxide, Mercuric Oxide, Oxide of Lead, Oxide of Bismuth, Oxide of Copper, Oxide of Cadmium.

Rarer oxides:—Oxides of Palladium, Rhodium, Osmium, Ruthenium.

Properties of the group.—The sulphides corresponding with the oxides of this group are insoluble both in dilute acids and in alkaline sulphides.* The solutions of these oxides are therefore completely precipitated by sulphuretted hydrogen, no matter whether they are neutral, or contain free acid or free alkali. The fact that the solutions of the oxides of the fifth group are precipitated by sulphuretted hydrogen in presence of a free strong acid distinguishes them from the oxides of the fourth group and generally from the oxides of all the preceding groups.

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* Consult, however, the paragraphs on oxide of copper and mercurous and mercuric oxides, as the latter remark applies only partially to them.

For the sake of greater clearness and simplicity, we divide the more common oxides of this group into two classes, and distinguish,

1. Oxides precipitable by hydrochloric acid, viz., oxide of silver, mercurous oxide, oxide of lead.

2. Oxides not precipitable by hydrochloric acid, viz., mercuric oxide, oxide of copper, oxide of bismuth, oxide of cadmium.

Lead must be considered in both classes, since the sparing solubility of its chloride might lead to its oxide being mistaken for mercurous oxide or oxide of silver, without affording us on the other hand any means of effecting its perfect separation from the oxides of the second division.

Special Reactions of the more common Oxides of the fifth group.

First Division: Oxides which are precipitated by Hydrochloric Acid.

§ 115.

a. Oxide of Silver, AgO [Ag_2O].

1. Metallic silver is white, very lustrous, moderately hard, very malleable, rather difficultly fusible. It is not oxidized by fusion in the air. Nitric acid dissolves silver readily; the metal is insoluble in dilute sulphuric acid and in hydrochloric acid.

2. Oxide of silver is a grayish-brown powder; it is not altogether insoluble in water, and dissolves readily in dilute nitric acid. It forms no hydrate. Both the oxide and the peroxide of silver, AgO_2 [Ag_2O_2], are decomposed by heat into metallic silver and oxygen.

3. The salts of oxide of silver are non-volatile and colourless; but many of them become black on exposure to light. The soluble neutra salts do not alter vegetable colours, and are decomposed at a red heat.

4. **Sulphuretted hydrogen** and **sulphide of ammonium** yield a precipitate of black sulphide of silver, AgS [Ag_2S], which is insoluble in dilute acids, alkalies, alkaline sulphides, but soluble in cyanide of potassium. Boiling nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

5. **Potassa** and **soda** precipitate oxide of silver in the form of a grayish-brown powder, which is insoluble in an excess of the precipitants, but dissolves readily in ammonia.

6. **Ammonia**, if added in very small quantity to neutral solutions, throws down the oxide as a brown precipitate, which readily redissolves in an excess of ammonia. Acid solutions are not precipitated.

7. **Hydrochloric acid** and soluble metallic **chlorides** produce a white curdy precipitate of chloride of silver, AgCl [AgCl]. If the solutions are very dilute, however, there is merely a bluish-white opalescence at first; but on long standing in a warm place the chloride of silver collects at the bottom of the vessel. By the action of light, the white chloride of silver loses chlorine, first acquiring a violet tint, and ultimately turning black; it is insoluble in nitric acid, but dissolves readily in ammonia as ammonio-chloride of silver, from which double compound

the chloride of silver is again separated by acids. Concentrated hydrochloric acid and concentrated solutions of chlorides of the alkali metals dissolve chloride of silver to a very perceptible extent, more particularly on application of heat; but the dissolved chloride separates again on dilution. When strongly heated, chloride of silver fuses without decomposition, and on cooling forms a translucent horny mass.

8. If compounds of silver are mixed with **carbonate of soda** and exposed on a charcoal support to the **inner flame of the blowpipe**, white brilliant malleable metallic globules are obtained, with or without a slight dark red incrustation of the charcoal. The metal is also readily reduced in the **stick of charcoal** (p. 24).

§ 116.

b. Mercurous Oxide or Suboxide of Mercury,

Hg_2O [Hg_2O].

1. Metallic mercury is a grayish-white, lustrous liquid at ordinary temperatures; it solidifies at – 39°, and boils at 360°. It is insoluble in hydrochloric acid; but dissolves in cold dilute nitric acid to nitrate of mercurous oxide, in concentrated hot nitric acid to nitrate of mercuric oxide.

2. Mercurous oxide is a black powder, readily soluble in nitric acid. It is decomposed by the action of heat, the mercury volatilizing in the metallic state. It forms no hydrate.

3. The salts of mercurous oxide, when ignited, volatilize usually with decomposition; mercurous chloride and bromide, however, volatilize unaltered. Most of the salts of mercurous oxide are colourless. The soluble salts in the neutral state redden litmus-paper. On addition of much water, nitrate of mercurous oxide is decomposed into a light yellow insoluble basic salt and a soluble acid salt.

4. **Sulphuretted hydrogen** and **sulphide of ammonium** produce black precipitates, which are insoluble in dilute acids, sulphide of ammonium, and cyanide of potassium. The precipitates consist, not of mercurous sulphide, but of mercuric sulphide mixed with mercury. Monosulphide of sodium, in presence of some caustic soda, dissolves this precipitate with separation of metallic mercury; bisulphide of sodium dissolves it without separation of metallic mercury; the solutions contain sulphide of mercury HgS [HgS]. The precipitate gives up mercury to boiling concentrated nitric acid with formation of a white double compound, namely, $2HgS + HgO,NO_5$ [$2HgS,Hg(NO_3)_2$]. The precipitate is readily dissolved by aqua regia.

5. **Potassa, soda,** and **ammonia** produce black precipitates, which are insoluble in an excess of the precipitants. The precipitates produced by the fixed alkalies consist of mercurous oxide, whilst those produced by ammonia consist of basic salts containing ammonia or amidogen.

6. **Hydrochloric acid** and soluble metallic **chlorides** precipitate mercurous chloride, Hg_2Cl [Hg_2Cl], as a fine powder of dazzling whiteness. Cold hydrochloric acid and cold nitric acid do not dissolve this precipitate; it dissolves, however, although with great difficulty and very slowly, on long-continued boiling with these acids, being resolved

by hydrochloric acid into mercuric chloride, and metallic mercury which separates; whilst nitric acid converts it into mercuric chloride and nitrate of mercuric oxide. Nitrohydrochloric acid and chlorine water dissolve the mercurous chloride readily, converting it into mercuric chloride. Ammonia and potassa decompose mercurous chloride, separating from it, the former a compound of subamide of mercury with mercurous chloride, Hg_2NH_2,Hg_2Cl [Hg_2NH_2Cl] the latter mercurous oxide.

7. If a drop of a neutral or slightly acid solution is put on a **clean and smooth surface of copper,** washed off after some time, and the spot then gently rubbed with cloth, paper, &c., it will appear white and lustrous like silver. The application of a gentle heat to the copper causes the metallic mercury precipitated on its surface to volatilize, and thus removes the silvering.

8. **Stannous chloride** produces first of all a white precipitate of mercurous chloride, which, however, soon changes to a gray precipitate of metallic mercury. This can be united into globules by pouring off the solution and boiling the residue of mercury with hydrochloric acid, to which a little stannous chloride may also be added.

9. If an intimate mixture of an anhydrous compound of mercury with dry **carbonate of soda** is introduced into a glass tube sealed at one end, covered with a layer of carbonate of soda, and strongly heated, the mercurial compound is decomposed, and metallic mercury separates, and forms a gray sublimate above the heated part of the tube. By means of a lens or microscope, the sublimate will be seen to consist of minute globules of metal, which may be united so as to form larger globules by rubbing the sublimate with a glass rod.

§ 117.

c. Oxide of Lead, PbO [PbO].

1. Metallic lead is bluish-gray; its surface recently cut exhibits a metallic lustre; it is soft, malleable, readily fusible, and volatile at a white heat. Fused upon charcoal before the blowpipe, it forms a coating of yellow oxide on the support. Hydrochloric acid and moderately concentrated sulphuric acid act on it but little, even with the aid of heat; dilute nitric acid, however, dissolves it readily, more particularly on heating.

2. Oxide of lead is a yellow or reddish-yellow powder, which appears brownish-red whilst hot; it is fusible at a red heat. Hydrated oxide of lead is white. Both the oxide and its hydrate dissolve readily in nitric and acetic acids. The peroxide of lead, PbO_2 [PbO_2], is brown, and on ignition is converted into the oxide. It is not dissolved by heating with nitric acid alone, but dissolves readily if some sugar or spirit of wine is added. The solution contains nitrate of oxide of lead. Minium, $2PbO,PbO_2$ [Pb_3O_4], which is red, may be regarded as a compound of lead oxide with peroxide of lead. When treated with nitric acid, oxide of lead is dissolved and lead peroxide is left.

3. The salts of oxide of lead are not volatile, and mostly colourless; the neutral soluble salts redden litmus-paper, and are decomposed at a red heat. Only a few of the insoluble lead salts—carbonate of oxide of lead, for example—are decomposed by ignition. If chloride

of lead is ignited in the air, part of it volatilizes, and leaves behind oxychloride of lead.

4. **Sulphuretted hydrogen** and **sulphide of ammonium** produce black precipitates of sulphide of lead, PbS [PbS], which are insoluble in *cold* dilute acids, in alkalies, alkaline sulphides, and cyanide of potassium. Sulphide of lead is decomposed by hot nitric acid. If the acid is dilute, the whole of the lead is obtained in solution as nitrate of oxide of lead, and sulphur separates—if fuming acid is used, the sulphur is also completely oxidized, and insoluble sulphate of lead alone is obtained;—if the acid was of medium concentration, both reactions take place, a portion of the lead being obtained in solution as nitrate of lead, whilst the remainder separates as sulphate of lead, together with the unoxidized sulphur. In solutions of salts of lead containing a large excess of a concentrated mineral acid, sulphuretted hydrogen produces a precipitate only after the addition of water or after partial neutralization of the free acid by an alkali. If a solution of lead is precipitated by sulphuretted hydrogen in presence of a large quantity of free hydrochloric acid, a red precipitate is occasionally formed, consisting of chloride and sulphide of lead, which is, however, converted by an excess of sulphuretted hydrogen into black sulphide of lead.

5. **Potassa**, **soda**, and **ammonia** throw down basic salts in the form of white precipitates, which are insoluble in ammonia but soluble in potassa and soda. In solutions of acetate of lead, ammonia (free from carbonic acid) does not immediately produce a precipitate, owing to the formation of a soluble di- or triacetate of lead.

6. **Carbonate of soda** in the cold throws down neutral carbonate, and in a hot solution a more or less basic carbonate of lead as a white precipitate, which is not quite insoluble in a large excess of the precipitant, especially on heating, but is insoluble in cyanide of potassium.

7. **Hydrochloric acid** and soluble **chlorides** produce in concentrated solutions a heavy white precipitate of chloride of lead, $PbCl$ [$PbCl_2$], which is soluble in a large amount of water, especially on heating: ammonia converts this into basic chloride of lead, $PbCl,3PbO + 4HO$, [$PbCl_2,3PbO,4H_2O$], which is also a white powder, but almost absolutely insoluble in water. Chloride of lead is more sparingly soluble in dilute nitric or hydrochloric acid than in water.

8. **Sulphuric acid** and **sulphates** produce a white precipitate of sulphate of lead, PbO,SO_3 [$PbSO_4$], which is nearly insoluble in water and dilute acids. From dilute solutions, especially from such as contain much free acid, the sulphate of lead precipitates only after some time, frequently only after a long time. It is advisable to add a considerable excess of dilute sulphuric acid, as this tends to increase the delicacy of the reaction, sulphate of lead being more insoluble in dilute sulphuric acid than in water. The separation of small quantities of sulphate of lead is best effected by evaporating, after the addition of the sulphuric acid, as far as practicable on the water-bath, and then treating the residue with water; or, if allowable, with spirit. Sulphate of lead is slightly soluble in concentrated nitric acid; it dissolves with difficulty in boiling concentrated hydrochloric acid, but more readily in solution of potassa. It dissolves also pretty readily in the solutions of some of the salts of ammonia, particularly in solution of acetate of ammonia; dilute sulphuric acid precipitates it again from these solutions.

9. **Chromate of potassa** produces a yellow precipitate of chro-

mate of lead, PbO,CrO_3 [$PbCrO_4$], which is readily soluble in potassa, but only sparingly in dilute nitric acid.

10. If a mixture of a lead compound with **carbonate of soda** is exposed on a charcoal support to the **reducing flame of the blowpipe,** soft malleable metallic globules of lead are readily obtained, the charcoal becoming covered at the same time with a yellow incrustation of oxide of lead. The reduction may be also readily effected by means of the **stick of charcoal.**

11. The metallic **incrustation** obtained according to p. 25 is black with a brown edge, the incrustation of oxide is light yellow-ochre, the incrustation of iodide varies from the yellow of the lemon to that of the yolk of an egg, the incrustation of sulphide varies from brownish-red to black, and is not dissolved by sulphide of ammonium (Bunsen).

§ 118.

Recapitulation and Remarks.

The metallic oxides of the first division of the fifth group are most distinctly characterized in their corresponding chlorides; since the different reactions of these chlorides with water and ammonia afford us a simple means both of detecting them and of effecting their separation from one another. For if the precipitate containing the three metallic chlorides is boiled with a somewhat large quantity of water, or if boiling water is repeatedly poured over it on the filter, the chloride of lead dissolves, whilst the chloride of silver and the mercurous chloride remain undissolved. If these two chlorides are then treated with ammonia, the mercurous chloride is converted into the black basic salt, insoluble in an excess of ammonia, described in § 116, 5, whilst the chloride of silver dissolves readily in the ammonia, and is precipitated again from this solution on adding nitric acid. (When operating on small quantities, it is advisable first to expel the greater part of the ammonia by heat.) Lead is readily detected in an aqueous solution of chloride of lead, by means of sulphuric acid.*

SECOND DIVISION: OXIDES WHICH ARE NOT PRECIPITATED BY HYDROCHLORIC ACID.

§ 119.

a. Mercuric Oxide or Oxide of Mercury, HgO [HgO].

1. Mercuric oxide is usually crystalline, and of a bright red colour, which changes to a dull yellowish red when it is reduced to powder: the oxide precipitated from solutions of the nitrate or chloride is a yellow powder. It is not quite insoluble in water, it turns gray when exposed to light, and it transiently acquires a deeper tint on heating; at a dull red heat, it is resolved into metallic mercury and oxygen. Both the crystalline and non-crystalline oxide dissolve readily in hydrochloric acid and in nitric acid.

2. When ignited, the salts of mercuric oxide volatilize with decomposition; mercuric chloride, bromide, and iodide volatilize unaltered. On boiling a solution of the chloride, some of the salt escapes with the

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* For the detection of small quantities of mercury see note to § 123, and of very small quantities of silver in presence of much lead, see Krutwig, Zeit. anal. Chem. **22**, 428.

steam. The salts are very poisonous and most of them are colourless. The soluble neutral salts redden litmus-paper. The nitrate and sulphate are decomposed by a large quantity of water into soluble acid and insoluble basic salts.

3. The addition of a very small quantity of **sulphuretted hydrogen** or **sulphide of ammonium** produces, after shaking, a perfectly white precipitate; a somewhat larger quantity of the reagent causes the precipitate to acquire a yellow, orange, or brownish-red colour; whilst an excess produces a black precipitate of mercuric sulphide, HgS [HgS]. This progressive variation of colour from white to black, which depends on the proportion of the sulphuretted hydrogen or sulphide of ammonium added, distinguishes mercuric oxide from all other bases. The white precipitate which forms at first consists of a double compound of mercuric sulphide with the still undecomposed portion of the salt of mercuric oxide, in a solution of mercuric chloride, for instance, $2HgS + HgCl$ [$2HgS, HgCl_2$]; the gradually increasing admixture of black sulphide causes the precipitate to pass through the several gradations of colour above mentioned. Sulphide of ammonium dissolves the merest trace of mercuric sulphide; least of all when the precipitate is digested with hot yellow sulphide of ammonium. Potassa and cyanide of potassium do not dissolve mercuric sulphide, and it is entirely insoluble in nitric acid, even on boiling. By the very protracted action of hot concentrated nitric acid the precipitate is converted into a white compound, consisting of $2HgS + HgO,NO_5$ [$2HgS, Hg(NO_3)_2$]. Hot concentrated hydrochloric acid dissolves it comparatively easily, but it is less soluble in the cold acid; if dilute, the acid dissolves it to some extent when boiling but scarcely at all in the cold. Sulphide of potassium and sulphide of sodium in the presence of potash or soda dissolve the precipitate completely, but it is insoluble in hydrosulphide of potassium, and in hydrosulphide of sodium. Aqua regia decomposes the precipitate and dissolves it with ease. In solutions of mercuric oxide containing a large excess of concentrated mineral acid, sulphuretted hydrogen produces a precipitate only after the solution has been diluted with water.

4. **Potassa** or **soda** added in small quantity to neutral or slightly acid solutions produces a reddish-brown precipitate, which becomes yellow when the reagent is in excess; the reddish-brown precipitate is a basic salt; the yellow precipitate consists of mercuric oxide. It is not soluble in an excess of the precipitant. In very acid solutions, this reaction does not take place at all, or at least the precipitation is very incomplete. In presence of salts of ammonia, potassa produces white precipitates. The precipitate thrown down by potassa from a solution of mercuric chloride containing an excess of chloride of ammonium is analogous in composition to the precipitate produced by ammonia (see 5).

5. **Ammonia** produces white precipitates quite analogous to those produced by potassa in presence of chloride of ammonium; thus, for instance, ammonia precipitates from solutions of mercuric chloride, NH_2Hg_2Cl [NH_2HgCl], the so-called "infusible white precipitate," which may be regarded as a chloride of dimercur-ammonium, or as mercurammonic chloride, or as mercury amidochloride. If the solution contains much free acid, ammonia produces no precipitate. The white precipitate is insoluble in ammonia, but easily soluble in hydrochloric acid.

6. **Stannous chloride** added in small quantity to solution of mercuric chloride, or to solutions of salts of mercuric oxide in presence of hydrochloric acid, throws down mercurous chloride,

$2HgCl + SnCl = Hg_2Cl + SnCl_2$ **[$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$].**

On adding a larger quantity of the reagent, the precipitated chloride is reduced to metal,

$Hg_2Cl + SnCl = 2Hg + SnCl_2$ **[$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$],**

and the precipitate, which was white at first, now acquires a gray tint, and may, after it has subsided, be readily united into globules of metallic mercury by boiling with hydrochloric acid and a little stannous chloride.

7. If a little **galvanic element**, made out of a slip of platinum foil and a slip of tinfoil, joined at one end with a wooden clamp and elsewhere apart from each other, be introduced into a solution of mercuric oxide acidified with hydrochloric acid, all the mercury will gradually be precipitated, by preference upon the platinum. On drying the platinum foil, rolling it up and heating it strongly in a glass tube, globules of mercury will be obtained, which may be more distinctly seen under the microscope. On heating this mercury with a fragment of iodine, it will be converted into red iodide of mercury (Van den Broek*).

8. Several other methods may be employed for the separation of traces of mercury from its acid solution by precipitation on metals (gold, platinum, copper, zinc). One of the most convenient of these Fürbringers',† is to render the solution distinctly acid with hydrochloric, sulphuric, or acetic acid, and warm it to 60° to 80°; from 0·25 to 0·5 gram of unravelled brass wool or Dutch metal (Teubner‡) is first rolled up into a ball and then teased out and put into the solution, with which it is left in contact with constant shaking for from five to ten minutes. The metal, which is now amalgamated, is washed with water (and if organic matters are present it is also washed with alcohol and ether) and dried between filter-paper; it is then rolled into a cylindrical shape and placed in a piece of hard glass tube, one end of which is drawn out into a capillary tube, the other end of the tube is then also drawn out into a capillary tube close to the metallic plug, and the amalgamated metal is heated by slowly and regularly turning the tube round over a steady gas flame, until it approaches a low red heat. The mercury collects in both the capillary tubes in the form of rings. Zinc also often forms similar rings, but in this case they are always situated nearer to the heated metal than the mercury ring. If, after cooling the tube, a small crystal of iodine be placed near the mercury ring and gently warmed, the mercury is converted into a red incrustation of mercuric iodide, or if there is deficiency of iodine vapour, a crust of yellow mercurous iodide is formed.

9. The salts of mercuric oxide show the same reaction as the salts of mercurous oxide with metallic **copper**, or when heated with **carbonate of soda** in a glass tube.

§ 120.

b. Oxide of Copper or Cupric Oxide, CuO **[CuO].**

1. Metallic copper has a peculiar red colour, and a brilliant lustre; it is moderately hard, malleable, rather difficultly fusible; in

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* Zeit. anal. Chem., 1, 512.

† *Ibid.*, 17, 526.

‡ *Ibid.*, 19, 199.

contact with water and air, it becomes covered with a green crust of basic carbonate of oxide of copper; and when ignited in the air it becomes coated over with suboxide and oxide. In hydrochloric acid and dilute sulphuric acid, it is insoluble or nearly so, even on boiling. Nitric acid dissolves the metal readily. Concentrated sulphuric acid converts it into sulphate of oxide of copper, with evolution of sulphurous acid.

2. Cuprous oxide or suboxide of copper, Cu_2O [Cu_2O], is red, its hydrate is yellow; both change to oxide when ignited in the air. On treating the suboxide with dilute sulphuric acid, metallic copper separates, whilst sulphate of oxide of copper dissolves; on treating suboxide of copper with hydrochloric acid, white cuprous chloride is formed, which dissolves in an excess of the acid, but is reprecipitated on adding water.

3. Oxide of copper is a black powder, which is not decomposed at a red heat; at a very high temperature, however, it loses oxygen and is converted into suboxide; its hydrate, CuO,HO [CuH_2O_2], is light blue. Both oxide of copper and its hydrate dissolve readily in hydrochloric, sulphuric, and nitric acids.

4. Most of the neutral salts of oxide of copper are soluble in water; the soluble salts redden litmus, and those containing volatile acids suffer decomposition when heated to low redness, with the exception of the sulphate, which can bear a somewhat higher temperature. They are usually white in the anhydrous state; but the hydrated salts are generally blue or green, and their solutions exhibit the same colour even when considerably diluted.

5. **Sulphuretted hydrogen** and **sulphide of ammonium** produce in alkaline, neutral, and acid solutions brownish-black precipitates of sulphide of copper, CuS [CuS].* This sulphide is insoluble in dilute acids and in caustic alkalies. Hot solutions of sulphide of potassium and sulphide of sodium remove sulphur but do not dissolve it, or only to a very trifling extent; it is a little more soluble in sulphide of ammonium, however, especially when yellow and hot, so that this reagent is not well adapted to effect the perfect separation of sulphide of copper from other metallic sulphides. Sulphide of copper is readily decomposed and dissolved by boiling nitric acid, but it remains altogether unaffected by boiling dilute sulphuric acid. It dissolves completely in solution of cyanide of potassium, if freshly precipitated. If the solutions of salts of copper contain a very large excess of a concentrated mineral acid, sulphuretted hydrogen produces a precipitate only after the addition of water.

6. **Potassa** or **soda** produces a light-blue bulky precipitate of hydrate of oxide of copper, CuO,HO [CuH_2O_2]. If the solution is highly concentrated, and the precipitant is added in excess, the precipitate turns brownish-black after the lapse of some time, and loses its bulkiness, even in the cold; but the change takes place immediately if the precipitate is boiled with the liquid in which it is suspended, and which must, if necessary, be diluted for the purpose. This change is brought about by the conversion of the blue hydrate of oxide of copper, into another hydrate containing less water. The light-blue hydrate dissolves in a large excess of very concentrated potassa or soda, forming a blue solution.

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* According to J. Thomsen this precipitate is Cu_4S_3+S [Cu_4S_3+S].

7. **Carbonate of soda** produces a greenish-blue precipitate of hydrated basic carbonate of copper,

$$\mathrm{CuO,CO_2 + CuO,HO}\ [\mathrm{CuCO_3,CuH_2O_2}],$$

which on boiling loses most of its carbonic acid, and changes to brownish-black. It dissolves in ammonia to an azure-blue, and in cyanide of potassium to a colourless liquid.

8. **Ammonia** added in small quantity to solutions of neutral salts produces a greenish-blue precipitate, consisting of a basic salt of copper. This precipitate redissolves readily on adding more ammonia to a transparent magnificent azure-blue solution, which owes its colour to the formation of a basic salt of ammonia and oxide of copper. Thus, for instance, in a solution of sulphate of oxide of copper, ammonia produces a precipitate of $\mathrm{NH_3,CuO + NH_4O,SO_3}$ $[\mathrm{(NH_3)_2CuO,(NH_4)_2SO_4}]$. In solutions containing a certain amount of free acid, ammonia produces no precipitate, but this azure-blue coloration makes its appearance as soon as ever the ammonia is in excess. The blue colour ceases to be perceptible only in very dilute solutions. When hydrate of potassa or soda is added to such blue solutions, after the lapse of some time, in the cold, a precipitate of blue hydrate of oxide of copper is produced; but on boiling the solution the whole of the copper is precipitated as black hydrated oxide. Carbonate of ammonia exhibits the same reactions as ammonia.

N.B. In the presence of non-volatile organic acids, the salts of copper are not precipitated by caustic or carbonated alkalies, the resulting solutions having a deep blue colour. In presence of sugar or similar organic substances, caustic alkalies produce precipitates which are soluble in excess of the precipitants; carbonate of soda, however, produces a permanent precipitate.

9. **Ferrocyanide of potassium** produces in moderately dilute solutions a reddish-brown precipitate of ferrocyanide of copper, $\mathrm{Cu_2Cfy}$ $[\mathrm{Cu_2Fe(CN)_6}]$, insoluble in dilute acids, but decomposed by potassa or soda. In very dilute solutions, the reagent merely produces a reddish coloration.

10. If the solution of a salt of oxide of copper is mixed with sulphurous acid or with hydrochloric acid and sulphite of soda, and **sulphocyanate of potassium** is then added, the cuprous sulphocyanate, $\mathrm{Cu_2CyS_2}$ $[\mathrm{Cu_2(CNS)_2}]$, is thrown down; the precipitate is white, and is practically insoluble in water or dilute acids. If there is no sulphurous acid present, black cupric sulphocyanate will be precipitated.

11. When **metallic iron** is brought into contact with concentrated solutions of salts of copper it is almost immediately covered with a red coating of metallic copper; in very dilute solutions, this coating is formed only after some time. The presence of a little free acid accelerates the reaction. Instead of iron, a small voltaic element may be used consisting of a strip of platinum foil, and a strip of clean sheet zinc or tinfoil, tied together at one end; a strip of cork is inserted between the two metals, and is fastened by tying it with thread. The plates, which should be nearly parallel, are dipped into the slightly acidified copper solution, leaving the ends where they are bound together out of the liquid. In very dilute solutions the copper is precipitated after the lapse of twelve hours, chiefly on the platinum, which is coloured copper-red to black. The advantage of depositing the copper on the platinum consists in being able to readily dissolve it off with nitric

acid. The solution thus obtained can then be tested further; for this purpose it is evaporated almost to dryness, a few drops of water are added, and then a drop of solution of ferrocyanide of potassium.

12. If a mixture of a compound of copper with **carbonate of soda** is exposed on a charcoal support to the **inner flame of the blowpipe**, metallic copper is obtained, without incrustation of the charcoal. The reduction may be also very conveniently effected in the **stick of charcoal** (p. 24). The best method of freeing the copper from the particles of charcoal is to triturate the fused mass in a small mortar with water, and to wash off the charcoal powder, when the copper-red metallic particles will be left behind.

13. If copper, or some alloy containing copper, or a trace of a salt of copper, or even simply the loop of a platinum wire dipped in a highly dilute copper solution, is introduced into the fusing zone of the **gas flame**, or exposed to the inner **blowpipe flame**, the upper or outer portion of the flame shows a magnificent emerald-green tint. Addition of hydrochloric acid to the sample considerably heightens the beauty and delicacy of this reaction. The flame is then of an azure-blue colour.

14. **Borax** readily dissolves oxide of copper in the outer gas- or blowpipe-flame. The beads are green while hot, blue when cold. In the inner flame, the bead is colourless unless a very large quantity of copper is present; when cold it is red and opaque. In the lower reducing zone of the Bunsen gas flame, the bead does not become reddish-brown until the addition of binoxide of tin, when this change rapidly takes place, owing to the production of cuprous oxide. If the bead is introduced alternately into the lower oxidizing zone and the lower reducing zone, it becomes ruby red and transparent.

§ 121.

c. Oxide of Bismuth, BiO_3 [Bi_2O_3].

1. Bismuth is of a reddish-white colour and moderate metallic lustre; it is of medium hardness, brittle, and melts at 264°; it does not change in air at the ordinary temperature, but if fused upon charcoal it forms an incrustation of yellow oxide. It dissolves readily in nitric acid, but is nearly insoluble in hydrochloric acid and altogether so in dilute sulphuric acid. Concentrated sulphuric acid converts it into sulphate of oxide of bismuth, with evolution of sulphurous acid.

2. Oxide of bismuth is a yellow powder, which transiently acquires a deeper tint when heated. It fuses at a red heat. Hydrate of oxide of bismuth is white. Both the oxide and its hydrate dissolve readily in hydrochloric, sulphuric, and nitric acids: fused with cyanide of potassium, they yield metallic bismuth. The grayish-black suboxide of bismuth, BiO_2 [BiO], and the red bismuthic acid, BiO_5 [Bi_2O_5], are converted into teroxide by ignition in the air. By heating with nitric acid, they are converted into nitrate of oxide of bismuth.

3. The salts of oxide of bismuth are not volatile; most of them are decomposed at a red heat. Chloride of bismuth is volatile. The salts of oxide of bismuth are colourless or white; some are soluble in water, others insoluble. The normal soluble salts redden litmus-paper; they are decomposed by a large quantity of water into insoluble

basic salts, which separate, while the greater portion of the acid remains in solution together with some teroxide of bismuth.

4. **Sulphuretted hydrogen** and **sulphide of ammonium** produce in neutral and acid solutions a black precipitate of sulphide of bismuth, which is insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium, but is readily decomposed and dissolved by boiling nitric acid. In solutions of salts of bismuth which contain a very considerable excess of hydrochloric or nitric acid, sulphuretted hydrogen produces a precipitate only after they have been diluted with water.

5. **Potassa, soda,** and **ammonia** throw down hydrate of oxide of bismuth as a white precipitate, which is insoluble in an excess of the precipitant.

6. **Carbonate of soda** and **carbonate of ammonia** throw down basic carbonate of oxide of bismuth, BiO_3,CO_2 [$(BiO)_2CO_3$], as a white bulky precipitate, which is insoluble in excess of the precipitant and in cyanide of potassium. Warming assists the precipitation.

7. **Dichromate of potassa** precipitates chromate of oxide of bismuth, $BiO_3,2CrO_3$ [$(BiO)_2,Cr_2O_7$], as a yellow powder. This substance differs from chromate of lead in being readily soluble in dilute nitric acid and insoluble in potassa.

8. **Dilute sulphuric acid** gives no precipitate in moderately dilute solutions of nitrate of oxide of bismuth. On evaporating to dryness, on the water-bath, with an excess of sulphuric acid, a white saline mass is left which always dissolves readily to a clear liquid in water acidified with sulphuric acid (characteristic difference between oxide of bismuth and oxide of lead). After long standing (several days occasionally), basic sulphate of oxide of bismuth, $BiO_3,2SO_3+3aq$ [$(BiO)_2S_2O_7,3H_2O$], separates from this solution in white microscopic needle-shaped crystals, soluble in nitric acid.

9. The reaction which characterizes oxide of bismuth more particularly is the decomposition of its neutral salts by **water**, which is attended with separation of insoluble basic salts. The addition of a large amount of water to solutions of salts of bismuth causes the immediate formation of a dazzling white precipitate, provided there be not too much free acid present. This reaction is the most sensitive with chloride of bismuth, as the basic chloride of bismuth, $BiCl_3,2BiO_3$ [$BiOCl$], is almost absolutely insoluble in water. Where water fails to precipitate nitric acid solutions of bismuth, owing to the presence of too much free acid, a precipitate will almost invariably make its appearance on adding solution of chloride of sodium or chloride of ammonium. The presence of tartaric acid does not interfere with this precipitation of bismuth solutions by water.

10. On mixing a solution of bismuth with an excess of solution of stannous chloride in potassa or soda, a black precipitate of suboxide of bismuth, BiO_2 [BiO], is formed. This is a very characteristic and delicate reaction.

11. If a mixture of a bismuth compound with **carbonate of soda** is exposed on a charcoal support to the **reducing flame**, brittle globules of bismuth are obtained, which fly to pieces under the stroke of a hammer. The charcoal becomes covered at the same time with a slight incrustation of oxide of bismuth, which is orange-coloured while hot, yellow when cold. The reduction may be also

conveniently affected in the **stick of charcoal** (p. 24). On triturating the end of the charcoal stick containing the reduced metal, yellowish spangles will be obtained.

12. The metallic **incrustation**, obtained according to p. 25, is black with a brown edge. The incrustation of oxide is yellowish-white; it is turned black by stannous chloride and soda, see 10 (difference from the incrustation of oxide of lead). The incrustation of iodide is bluish-brown with red edge. The incrustation of sulphide is umber-coloured with coffee-coloured edge, not dissolved by sulphide of ammonium (Bunsen).

13. If a bismuth compound is heated before the blowpipe on charcoal with a mixture of equal parts of iodide of potassium and sulphur (if the substance already contains enough sulphur to decompose the iodide of potassium, the addition of sulphur is unnecessary) a very volatile scarlet incrustation of iodide of bismuth is formed. Lead compounds treated in the same way give a deep yellow incrustation, their presence does not interfere with the bismuth reaction (v. Kobell). The reaction also takes place when the mixture is heated in a glass tube sealed at one end (Cornwall).

§ 122.

d. Oxide of Cadmium, CdO [CdO].

1. Metallic cadmium has a tin-white colour; it is lustrous, not very hard, malleable; it melts at 315–316° and boils at about 770°, so that it may easily be sublimed in a glass tube. When heated on charcoal before the blowpipe, it takes fire and burns, emitting brown fumes of oxide of cadmium, which form a coating on the charcoal. Hydrochloric acid and dilute sulphuric acid dissolve it with evolution of hydrogen; but nitric acid dissolves it most readily.

2. Oxide of cadmium is a brown, non-volatile powder; its hydrate is white. Both the oxide and hydrate dissolve readily in hydrochloric, nitric, and sulphuric acids.

3. The salts of oxide of cadmium are colourless or white; some of them are soluble in water. The normal soluble salts redden litmus-paper, and those containing volatile acids are decomposed at a red heat.

4. **Sulphuretted hydrogen** or **sulphide of ammonium** produces a bright yellow precipitate of sulphide of cadmium, CdS [CdS], in alkaline, neutral, and acid solutions; this is insoluble in dilute acids, alkalies, alkaline sulphides, and cyanide of potassium (difference from copper). It is readily decomposed and dissolved by boiling nitric acid, as well as by boiling hydrochloric acid and by boiling dilute sulphuric acid (difference from copper). In solutions of salts of cadmium containing a large excess of acid, sulphuretted hydrogen produces a precipitate only after dilution with water.

5. **Potassa** or **soda** produces a white precipitate of hydrate of oxide of cadmium, CdO,HO [CdH_2O_2], which is insoluble in an excess of the precipitant.

6. **Ammonia** likewise precipitates white hydrate of oxide of cadmium, which, however, redissolves readily and completely in excess of the precipitant to a colourless solution. The ammoniacal solution

becomes turbid on boiling, or when largely diluted with water, or if ammonium salts are absent. Potassa or soda also produces a precipitate of hydrate of oxide of cadmium in the ammoniacal solution.

7. **Carbonate of soda** or **carbonate of ammonia** produces a white precipitate of carbonate of cadmium, CdO,CO_2 [$CdCO_3$], which is insoluble in excess of the soda salt, and but slightly soluble in carbonate of ammonia. Salts of ammonia impede precipitation in the cold, but not on boiling; free ammonia prevents it. The precipitate is readily soluble in cyanide of potassium. It takes some time to separate from dilute solutions, but warming assists the separation greatly.

8. **Sulphocyanate of potassium** does not precipitate solutions of cadmium, even on adding sulphurous acid (difference from copper).

9. If a mixture of a compound of cadmium with **carbonate of soda** is exposed on a charcoal support to the **reducing flame**, the charcoal becomes covered with a yellowish-brown coating of oxide of cadmium owing to the volatilization of the reduced metal and its subsequent re-oxidation in passing through the oxidizing flame. The coating is seen most distinctly after cooling.

10. The metallic **incrustation** obtained according to p. 25 is black with a brown edge; the incrustation of oxide is brownish black, the edge passing from brown to white. The incrustation of iodide is white. The incrustation of sulphide is lemon yellow, not dissolved by sulphide of ammonium (Bunsen).

§ 123.

Recapitulation and Remarks.

The perfect separation of the metallic oxides of the second division of the fifth group from mercurous oxide and oxide of silver may, as already stated, be effected by means of hydrochloric acid; but this agent fails to separate them completely from oxide of lead. Traces of the salt of mercuric oxide, which are at first retained by the precipitated chloride of silver by surface attraction, are dissolved out completely by washing (G. J. Mulder). The mercuric oxide is distinguished from the other oxides of this division by the insolubility of its sulphide in boiling nitric acid; this affords a convenient means for its separation. Great care, however, must always be taken to free the sulphides *completely* by washing from all traces of hydrochloric acid or any chloride which may happen to be present, before proceeding to boil them with nitric acid. Moreover, the reactions with stannous chloride or with metallic copper, as well as those in the dry way, will, after the previous removal of the suboxide, always readily indicate the presence of oxide of mercury. When the moist way is chosen, the sulphide of mercury is dissolved most conveniently by heating it with hydrochloric acid and a small crystal of chlorate of potassa.

Oxide of lead is separated from the other oxides by means of sulphuric acid. The separation is the most complete if after addition of dilute sulphuric acid in excess, the mixture is evaporated on the water-bath, the residue diluted with water, slightly acidified with sulphuric acid, and the undissolved sulphate of lead filtered off immediately. The sulphate of lead may be further examined in the dry way by the reaction described in § 117, 10, or also as follows:—A small quantity of a solution of chromate of potassa is poured over a small portion of the sulphate of lead, and the mixture heated; this will convert the white precipitate into yellow chromate of lead. After this has been washed, a little solution of potassa or soda is added, and heat is applied; the precipitate will dissolve, forming a clear solution, and on acidifying this with acetic acid, a yellow precipitate of chromate of lead will again be produced. After the removal of the oxides of mercury and lead, the oxide of bismuth may be separated from oxide of copper and oxide of cadmium by adding ammonia in excess, as the two oxides last mentioned are soluble in an excess of this reagent. If the precipitate, after being collected on a filter, is dissolved in one or two drops of hydrochloric acid on a watchglass, and water added, the appearance of a milky turbidity is a confirmation of the presence of bismuth. The method for detecting bismuth given in § 121, 10, may also be employed.

The presence of a notable quantity of oxide of copper is revealed by the blue colour of the ammoniacal solution; smaller quantities are detected by evaporating the ammoniacal solution nearly to dryness, adding a little acetic acid, and then ferrocyanide of potassium. The separation of oxide of copper from oxide of cadmium may be effected by evaporating the ammoniacal solution to a small bulk, acidifying with hydrochloric acid, adding a little sulphurous acid and sulphocyanate of potassium, warming, filtering off the cuprous sulphocyanide, and precipitating the cadmium in the filtrate by sulphuretted hydrogen (an unnecessarily large excess of sulphurous acid must of course be avoided). The separation of oxide of copper from oxide of cadmium may also be effected by acting on the sulphides with cyanide of potassium or with boiling dilute sulphuric acid (5 parts of water to 1 part of concentrated acid). In the last two methods, the solution containing the copper and cadmium is precipitated by sulphuretted hydrogen, and the precipitate separated by decantation or filtration and washed. If the precipitate is now treated with some water and a small lump of cyanide of potassium, the sulphide of copper will dissolve, leaving the yellow sulphide of cadmium undissolved. By boiling the precipitate of the mixed sulphides, on the other hand, with dilute sulphuric acid, the sulphide of copper remains undissolved, whilst the sulphide of cadmium is obtained in solution; sulphuretted hydrogen will now throw down from the filtrate yellow sulphide of cadmium (A. W. Hofmann).*

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* For the detection of very minute traces of mercury, see Mayençon and Bergeret (Pharm. Centralhalle, 1873, 317), Merget (Zeit. anal. Chem., **14**, 191), Teubner (*ibid.*, **19**, 198), and Biewend (*ibid.*, **22**, 89). For the detection of traces of copper, see Wildenstein (*ibid.*, **2**, 9), Bellamy (*ibid.*, **9**, 382), Schaer (*ibid.*, **9**, 100), Schönn (*ibid.*, **9**, 210), Purgotti (*ibid.*, **18**, 476), Endemann and Prochazka (*ibid.*, **21**, 265), and for its detection in presence of organic matters, see V. (Detection of inorganic poisons in food, &c.) in the Second Section.

Special Reactions of the rarer Oxides of the fifth group.

§ 124.

a. Palladious Oxide or Protoxide of Palladium, PdO [PdO].

Palladium is found in the metallic state, occasionally alloyed with gold and silver, but more particularly in platinum ores. It greatly resembles platinum, but is somewhat darker in colour. It fuses with great difficulty. Heated to dull redness in the air, it becomes covered with a blue film, but it recovers its light colour and metallic lustre when more strongly heated. It is sparingly soluble in pure nitric acid, but dissolves somewhat more readily in nitric acid containing nitrous acid; it dissolves very sparingly in boiling concentrated sulphuric acid, but is soluble in fusing bisulphate of potassa, and readily soluble in nitrohydrochloric acid. There are three oxides, the suboxide, Pd_2O [Pd_2O], palladious oxide, PdO [PdO], and palladic oxide, PdO_2 [PdO_2]. Palladious oxide or protoxide of palladium is black, its hydrate dark-brown; both are resolved into oxygen and metallic palladium by intense ignition. Oxide of palladium is black; when heated with dilute hydrochloric acid, it is dissolved as protochloride, with evolution of chlorine. The salts of palladious oxide are mostly soluble in water; they are brown or reddish-brown; their concentrated solutions are reddish-brown; their dilute solutions yellow. From a solution of nitrate of protoxide of palladium containing a slight excess of acid, water precipitates a brown basic salt. The oxygen salts, as well as the protochloride, are decomposed by ignition, leaving metallic palladium behind. **Sulphuretted hydrogen** and **sulphide of ammonium** throw down from acid or neutral solutions black palladious sulphide, which does not dissolve in sulphide of ammonium, but is soluble in boiling hydrochloric acid, and readily soluble in nitrohydrochloric acid. From the solution of the protochloride, **potassa** precipitates a brown basic salt, soluble in an excess of the precipitant; **ammonia**, the flesh-coloured palladiochloride of ammonium, soluble in excess of ammonia (quickly on heating, slowly in the cold) to a colourless liquid, from which hydrochloric acid throws down yellow, crystalline palladiochloride of ammonium, $NPdH_3,Cl$ [$(NH_3)_2PdCl_2$]. **Cyanide of mercury** throws down yellowish-white protocyanide of palladium as a gelatinous precipitate, slightly soluble in hydrochloric acid, readily soluble in ammonia (especially characteristic). **Stannous chloride**, in absence of free hydrochloric acid, produces a brownish-black precipitate; if free hydrochloric acid is present, a red solution is obtained, which speedily turns brown and ultimately green, and on addition of water brownish-red. **Formate of soda** precipitates all the palladium in the metallic state from its solutions, if heated at 50°. **Iodide of potassium** precipitates black protiodide of palladium (very characteristic). **Chloride of potassium** precipitates from highly concentrated solutions potassium palladiochloride, $KCl,PdCl$ [K_2PdCl_4], in the form of golden-yellow needles, which dissolve readily in water to a dark red liquid, but are insoluble in absolute alcohol. In solutions which are not too dilute, **nitrite of potassa** produces a yellowish, crystalline precipitate which becomes reddish on long standing and is soluble in much water. **Sulphocyanate of potassium** does not precipitate palladium, even after the addition of sulphurous acid (difference from copper, and the best means of separating the two). On treatment with **carbonate of soda** in the upper oxidizing flame (p. 23), all the compounds of palladium yield a gray metallic sponge. On rubbing this in an agate mortar, silvery-white ductile metallic spangles are obtained.

b. Sesquioxide of Rhodium, Rh_2O_3 [Rh_2O_3].

Rhodium is found in small quantity in platinum ores. It is almost as white as silver, malleable, and very difficultly fusible. When prepared in the wet way, it is a gray powder. Rhodium is insoluble in all acids; it dissolves in aqua regia only when alloyed with platinum, copper, &c., and not when alloyed with gold or silver. Fusing metaphosphoric acid and fusing bisulphate of potassa dissolve it, forming a salt of the sesquioxide. When heated in chlorine, it forms a chloride. There are three oxides: the protoxide, RhO [RhO], sesquioxide, Rh_2O_3 [Rh_2O_3], and the peroxide, RhO_2 [RhO_2]. The sesquioxide is gray or black, it forms a yellow and a brownish-black hydrate; it is insoluble in acids, but dissolves in fusing metaphosphoric acid or bisulphate of potassa. The solutions are rose-coloured. **Sulphuretted hydrogen** and **sulphide of ammonium**, after some time, and especially when assisted by heat, precipitate a brown sulphide, which is insoluble in sulphide of ammonium, but dissolves in sulphide of potassium and in boiling nitric acid. **Potassa** if added in not too large excess, throws down at once a yellow precipitate of the hydrated oxide, $Rh_2O_3,5HO$ [$Rh_2O_3,5H_2O$], which is soluble in excess of the precipitant at the ordinary temperature; on boiling the yellow solution, blackish-brown $Rh_2O_3,3HO$ [$Rh_2O_3,3H_2O$] is precipitated. In a solution of the sesquichloride, potassa at first produces no precipitate, but, on adding alcohol, the black hydrated oxide soon separates (Claus). **Ammonia**, after some time, produces a yellow precipitate, soluble in hydrochloric acid. **Zinc** precipitates black metallic rhodium. On heating with **nitrite of potassa**, the sesquichloride of rhodium becomes yellow, and an orange-yellow precipitate is formed, which is slightly soluble in water, but readily in hydrochloric acid; at the same time another portion of the rhodium is converted into a yellow salt, which remains in solution and is precipitated by alcohol (Gibbs). All solid compounds of rhodium, when ignited in **hydrogen**, or on a platinum wire with **carbonate of soda** in the upper oxidizing flame, yield the metal, which is well characterized by its insolubility in aqua regia, its solubility in fusing bisulphate of potassa, and the behaviour of its solution towards potassa.

c. Oxides of Osmium.

Osmium is occasionally found in platinum ores as a native alloy of osmium and iridium. It is a black powder, or gray and with metallic lustre; it is infusible. The metal, the protoxide, OsO [OsO], the sesquioxide, Os_2O_3 [Os_2O_3], and the peroxide, OsO_2 [OsO_2], oxidize readily when heated to redness in the air, yielding osmic acid, OsO_4 [OsO_4], which volatilizes and makes its presence speedily known by its peculiar, exceedingly irritating, offensive smell, resembling that of chlorine and iodine (highly characteristic). If a little osmium is placed on a strip of platinum foil and held in the outer mantle of a **gas** or **alcohol flame**, at half height, the flame becomes most strikingly luminous. Even minute traces of osmium may by this reaction be detected in alloys of iridium and osmium; but the reaction is in that case only momentary; it may, however, be reproduced by holding the sample first in the reducing flame, then again in the outer mantle. **Nitric acid**, more particularly red fuming nitric acid, and aqua regia dissolve osmium as osmic acid; the application of heat promotes the solution, which is, however, attended in that case with volatilization of osmic acid. Very intensely ignited osmium is insoluble in acids. If it is fused with nitrate of potassa, and the fused mass distilled with nitric acid, the osmic acid volatilizes and is found in the distillate (a characteristic reaction for all osmium compounds). By heating osmium in dry **chlorine** free from air, bluish-black protochloride, $OsCl$ [$OsCl_2$], is first formed, but always in small quantity, then the more volatile bright red bichloride, $OsCl_2$ [$OsCl_4$]; if moist chlorine is used, a green mixture of the two chlorides is obtained. The protochloride dissolves with a blue colour, the bichloride with a yellow colour, and both together with a green colour, which turns to red. The solutions are soon decomposed, osmic acid, hydrochloric acid, and a mixture of protoxide and binoxide being formed, the mixed oxides separating as a black powder. On heating a mixture of osmium, in powder, or of sulphide of osmium, with chloride of potassium, in chlorine, potassium osmiochloride is produced in the form of octahedra, which are slightly soluble in cold water, but more readily in hot water. On adding spirit to the yellow solution, the salt is precipitated as a red crystalline powder; on heating the solution with hydrate of potassa, the black hydrated oxide is precipitated. When potassium osmiochloride is fused with carbonate of soda, it yields grayish-black oxide of osmium insoluble in water and in hydrochloric acid. Potassium osmiosesquichloride is easily soluble in water; the deep cherry-red solution readily decomposes, especially on warming, with separation of black oxychloride; on adding potassa to the solution, the reddish-brown hydrated sesquioxide is precipitated. Anhydrous osmic acid is white, crystalline, melts at a gentle heat, and boils at 100°; the odour of its vapour is insupportable, attacking eyes and nose in the highest degree. When heated with water, it melts and slowly dissolves; the solution is colourless, has no acid reaction, but a strong, unpleasant, irritating odour. Concentrated potash solution colours the solution yellow; on distilling, the greater part of the osmic acid passes over (very characteristic), the remainder splits up into oxygen and osmite of potassa, KO,OsO_3 [K_2OsO_4], or, by long-continued boiling, into osmic acid, hydrated oxide of osmium, and potassa. Osmic acid decolorizes **indigo solution**, separates iodine from **iodide of potassium**, and converts **alcohol** into aldehyde and acetic acid. **Nitrite of potassa** readily reduces it to osmite of potassa, which separates in garnet coloured crystals. **Sulphuretted hydrogen** colours an aqueous solution of osmic acid brownish-black, when a strong acid is present, the brownish-black sulphide is precipitated; this is insoluble in caustic or carbonated alkalies and also in sulphide of ammonium or potassium. When sulphurous acid is gradually added, it causes the solution to become yellow, passing into a reddish-brown, then green, and finally indigo-blue. **Ferrous sulphate** produces a black precipitate of oxide. **Stannous chloride** produces a brown precipitate, soluble in hydrochloric acid to a brown liquid. **Zinc** and many metals in the presence of a strong acid precipitate metallic osmium. All the compounds of osmium yield the metal when ignited in a current of **hydrogen**; in the oxidixing flame, on the contrary, they volatilize with the characteristic odour of osmic acid.

d. Oxides of Ruthenium.

Ruthenium is found in small quantity in platinum ores. It is a grayish-white, brittle, and exceedingly infusible metal. It forms a grayish-black powder which is barely acted on by aqua regia; fusing bisulphate of potassa fails altogether to affect it. It combines with oxygen forming ruthenious oxide, RuO [RuO], the sesquioxide, Ru_2O_3 [Ru_2O_3], ruthenic oxide, RuO_2 [RuO_2], ruthenic acid, RuO_3 [RuO_3], and perruthenic acid, RuO_4 [RuO_4].

When the powdered metal is ignited in the air, it is converted into the black sesquioxide insoluble in acids; by ignition with chloride of potassium in a current of chlorine gas, it forms ruthenio-sesquichloride of potassium, which dissolves in water with an orange-yellow colour. This solution, after standing for some time, or immediately on heating, yields a voluminous black precipitate, which remains suspended for a long time, and has very powerful tinctorial powers (characteristic reaction). **Potassa, soda, or ammonia** throws down the brownish-black hydrate of sesquioxide of ruthenium, which is insoluble in excess of the fixed alkalies, but dissolves in excess of ammonia with a greenish-brown colour, and in hydrochloric acid forming an orange-yellow solution. **Sulphuretted hydrogen**, after a time, throws down a black precipitate which is a mixture of black sulphide of ruthenium with sulphur; the precipitate gradually becomes darker, whilst the solution acquires a deep blue colour. **Sulphide of ammonium** produces a brownish-black precipitate scarcely soluble in an excess of the precipitant. **Zinc** at first colours the solution blue, but after a time metallic ruthenium is precipitated. In the absence of other metals of the platinum ores, sulphocyanate of potassium produces, after some time, a red coloration, which gradually changes to purple-red, and upon heating to a fine violet tint, very characteristic. If the solution is made slightly alkaline with carbonate of soda, **nitrite of potassa** added, and the solution heated to boiling, the solution acquires a crimson tint when mixed with a little colourless sulphide of ammonium, which afterwards changes to brown (this reaction is not affected by the presence of other platinum metals) turns crimson; on the addition of more sulphide of ammonium, a brown precipitate is formed. If a few drops of a solution of ruthenium sesquichloride are added to an ammoniacal solution of **hyposulphite of soda**, the liquid becomes of an intense purple-red.

Ruthenium oxide is a bluish-black powder, insoluble in acids, but soluble in fused potassa with a brown colour; its hydrate is dark ochre-coloured and dissolves in acids, forming a light yellow solution. On fusing metallic ruthenium with hydrate of potassa, and nitrate of potassa or chlorate of potassa, it yields ruthenate of potassa; this dissolves in water, yielding an orange-coloured solution which dyes organic substances black, from separation of black oxide. Acids or alcohol throw down the hydrated sesquioxide.

Perruthenic acid is a yellow crystalline substance volatile at the ordinary temperature. It melts easily, and boils at a little over 100°. The golden-yellow vapour has an odour resembling that of nitrous acid. Perruthenic acid dissolves in water slowly and with difficulty; when heated with **hydrochloric acid**, it yields sesquichloride of ruthenium with evolution of chlorine; **sulphurous acid** colours it first purplish-red, then bluish-violet; **sulphuretted hydrogen** imparts a transient red tint to the liquid, and then precipitates the black oxysulphide.

§ 125.

Sixth Group.

More common oxides:—Oxide of Gold, Oxide of Platinum, Protoxide of Tin, Binoxide of Tin, Teroxide of Antimony, Arsenious Acid and Arsenic Acid.

Rarer oxides:—Oxides of Iridium, Molybdenum, Tungsten, Tellurium, Selenium.

The higher oxides of the elements belonging to the sixth group are all of them more or less strongly pronounced acids. But we class them here with the bases, as they cannot well be separated from the lower degrees of oxidation of the same elements, to which they are very closely allied in their reactions with sulphuretted hydrogen.

Properties of the group.—The sulphides corresponding with the oxides of the sixth group are insoluble in dilute acids. These combine with alkaline sulphides (either directly, or by taking up sulphur) to form soluble sulphur salts, in which they play the part of the acid. Sulphuretted hydrogen, therefore, completely precipitates these oxides, like those of the fifth group, from acidified solutions. The precipitated sulphides differ, however, from those of the fifth group in that they are soluble in sulphide of ammonium, sulphide of potassium, &c., and are reprecipitated from these solutions on adding an acid.

We divide the more common oxides of this group into two classes, and distinguish,

1. Oxides of the noble metals: gold and platinum oxides. These oxides are decomposed at a red heat into the metal and oxygen, and the corresponding chlorides into the metal and chlorine. The pre-

cipitates thrown down from hot solutions by sulphuretted hydrogen are not soluble in boiling hydrochloric acid, and are insoluble, or nearly so, in nitric acid. The metallic sulphides, when heated in a stream of chlorine or with a mixture of 5 parts of chloride of ammonium and 1 part of nitrate of ammonia, leave the metal.

2. Oxides or acids of the base metals. The oxygen compounds of antimony, tin, and arsenic, already mentioned, are not decomposed into the metals and oxygen by heating, and the chlorides of these metals volatilize when heated. The sulphides dissolve in boiling hydrochloric acid (with the exception of the sulphides of arsenic), and are dissolved or decomposed by boiling nitric acid. The sulphides of the metals are completely volatilized when heated in a stream of chlorine or with a mixture of 5 parts of chloride of ammonium and 1 part of nitrate of ammonia.

FIRST DIVISION.

Special Reactions.

§ 126.

a. **Auric Oxide or Oxide of Gold**, AuO_3 [Au_2O_3].

1. Metallic gold has a yellow colour and a high metallic lustre: it is rather soft, exceedingly malleable, difficultly fusible: it does not oxidize when ignited in the air, and is insoluble in hydrochloric, nitric, or sulphuric acid, but dissolves somewhat in hot concentrated nitric acid containing sulphuric acid, and easily in liquids which contain or evolve chlorine, such as nitrohydrochloric acid. The solution contains terchloride of gold. Liquids containing free bromine or iodine also dissolve gold. Fusing bisulphate of potassa has no action on it, but the hydrated alkalies and nitrate of potassa attack it at a high temperature.

2. Oxide of gold is a brownish-black powder, its hydrate is chestnut-brown, or brownish-black. Both are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric and sulphuric acids dissolve a little hydrated oxide of gold; water reprecipitates it from these solutions. Aurous oxide or protoxide of gold, AuO [Au_2O], is violet-black; it is decomposed by heat into gold and oxygen.

3. Oxygen salts of gold are practically unknown. Auric chloride or chloride of gold, $AuCl_3$ [$AuCl_3$], is red to brown-red, and when heated at 150°–200° it gives off chlorine, leaving the yellowish-white aurous chloride, $AuCl$ [$AuCl$]; when more strongly heated, this decomposes into gold and chlorine, and on treatment with water is resolved into gold and chloride of gold. The solution of chloride of gold is brownish-red when concentrated, reddish-yellow when more dilute, and is distinctly yellow even when very dilute; the solution reddens litmus. Hydrogen aurochloride, $AuCl_3,HCl + 6aq$ [$HAuCl_4,3H_2O$], forms bright yellow crystals which dissolve in water with a deep yellow colour, yielding solution of chloride of gold, so called.

4. **Sulphuretted hydrogen** precipitates the whole of the metal from neutral or acid solutions; the brownish-black precipitate always consists of a mixture of sulphide of gold with metallic gold or with sulphur, and that whether the solutions are hot or cold, dilute or concentrated (v. Schrötter and Priwoznik). The precipitates are insoluble in hydrochloric and in nitric acid, even when hot, but are soluble in nitro-

hydrochloric acid. They are soluble both in colourless and in yellow sulphide of ammonium, especially on heating, and still more easily in sulphide of sodium or sulphide of potassium; sometimes a black residue of pulverulent gold is left. If heated to redness in a current of chlorine, or with a mixture of 5 parts of chloride of ammonium and 1 of nitrate of ammonia, they leave metallic gold.

5. **Sulphide of ammonium** precipitates brownish-black sulphide of gold, AuS_2 [Au_2S_3], which redissolves in an excess of the precipitant, especially on heating.

6. **Ammonia** produces, although only in concentrated solutions of gold, a reddish-yellow precipitate of fulminating gold. The more acid the solution and the greater the excess of ammonia added, the more gold remains in solution.

7. **Stannic chloride** containing **stannous chloride** (which may be easily prepared by mixing solution of stannous chloride with a little chlorine water) produces, even in extremely dilute solutions of gold, a purple-red precipitate (or coloration at least), which sometimes inclines rather to violet or to brownish-red. This precipitate, which has received the name of purple of cassius, is insoluble in hydrochloric acid. Its composition has not been as yet definitely established.

8. **Ferrous salts** reduce chloride of gold, and precipitate metallic gold from the solution in the form of a most minutely divided brown powder. The liquid in which the precipitate is suspended appears of a blueish-black colour by transmitted light. The dried precipitate shows metallic lustre when pressed with the blade of a knife.

9. **Nitrite of potassa** produces a precipitate of metallic gold even in dilute solutions. In very dilute solutions, the liquid at first only appears coloured blue, but in time the whole of the gold separates.

10. Potassa or soda added in excess to terchloride of gold leaves the liquid clear, but on adding **tannic acid** metallic gold separates. Warming assists the precipitation.

11. All compounds of gold are reduced in the **stick of charcoal** (p. 24). By triturating the charcoal afterwards, spangles of metal will be obtained, which are insoluble in nitric acid, but readily soluble in aqua regia.

§ 127.

b. Platinic Oxide, PtO_2 [PtO_2].

1. Metallic platinum is of a light steel-gray colour; it is very lustrous, moderately hard, very malleable and very difficultly fusible; it does not oxidize when ignited in the air. Platinum sponge is dull gray, and platinum black is a fine black powder. Platinum is insoluble in hydrochloric, nitric, or sulphuric acid, but it dissolves in nitrohydrochloric acid, especially on heating; if excess of hydrochloric acid is used, the solution contains hydrogen platinochloride. Fusing bisulphate of potassa does not attack platinum, but it is oxidized at a red heat by the nitrates of the alkalies and also by their hydrates with access of air.

2. Oxide of platinum is a brownish-black powder, its hydrate, $PtO_2,2HO$ [$Pt(OH_4)$], is reddish-brown. Both are reduced by heat; the hydrate is readily soluble in dilute acids and in soda solution. Platinous oxide, PtO [PtO], is dark violet, its hydrate is black; both are reduced to the metallic state by ignition.

3. The salts of platinic oxide are decomposed at a red heat. They are yellow or brown. Platinic chloride, $PtCl_2 + 5aq$ [$PtCl_4,5H_4O$], forms red crystals; hydrogen platinochloride, $PtCl_2,HCl + 6aq$ [$H_2PtCl_6,6H_2O$], forms brownish-red crystals. What is ordinarily called a solution of chloride of platinum is really a solution of hydrogen platinochloride; it has an acid reaction. Both platinic chloride and hydrogen platinochloride yield platinous chloride, $PtCl$ [$PtCl_2$], when heated to low redness (better at 240°); at a higher temperature, platinum is left. Solution of chloride of platinum containing platinous chloride has a deep brown colour.

4. **Sulphuretted hydrogen** gradually colours acid and neutral solutions brown, but, after the lapse of some time, a brownish-black precipitate of sulphide of platinum, PtS_2 [PtS_2], is produced. If the solution is heated after the addition of the sulphuretted hydrogen, the precipitate forms immediately. It dissolves in a great excess of hot alkaline sulphides, more particularly of the higher degrees of sulphuration, but it is always difficult to obtain complete solution. Hot nitric acid easily dissolves platinic sulphide if it has been precipitated from a cold solution, but that thrown down from a hot solution is almost insoluble; hot hydrochloric acid does not dissolve platinic sulphide, but it is readily soluble in nitrohydrochloric acid. When heated to redness in a current of chlorine, or ignited with a mixture of 5 parts of chloride of ammonium and 1 of nitrate of ammonia, it leaves metallic platinum.

5. **Sulphide of ammonium** produces the same precipitate; this redissolves completely, though slowly and with difficulty, in a large excess of the precipitant if the latter contains an excess of sulphur. It is somewhat more easily soluble in hot sulphide, but it is always difficult to dissolve it completely. Acids reprecipitate the platinic sulphide unaltered from the reddish-brown solution.

6. **Chloride of potassium** and **chloride of ammonium** (and accordingly, of course, also potassa and ammonia in presence of hydrochloric acid) produce in solutions of chloride of platinum, if not too dilute, yellow crystalline precipitates of platinochloride of potassium or ammonium. From dilute solutions, these precipitates are obtained by evaporating the solution mixed with the precipitants on the water-bath, and treating the residue with a little water or with dilute spirit of wine. The precipitates are somewhat more soluble in acids than in water; soluble in concentrated potassa or soda on heating. On igniting platinochloride of ammonium, spongy platinum is left; the potassium salt leaves platinum and chloride of potassium. The decomposition of the latter compound is incomplete unless the ignition is effected in a current of hydrogen gas or with addition of some oxalic acid.

7. **Stannous chloride** added to solutions containing much free hydrochloric acid imparts to them an intensely dark-red or brownish-red colour, owing to a reduction of the platinic chloride to platinous chloride, but no precipitate is produced.

8. **Ferrous sulphate** does not precipitate solution of platinic chloride except on very long continued boiling, in which case the chloride ultimately is reduced and platinum separates. If, however, caustic soda be added to the solution, after the sulphate of iron, and then hydrochloric acid, platinum black will be formed.

9. If **iodide of potassium** in excess is added to a solution of hydrogen platinochloride, a characteristic deep-red coloration is produced; in very dilute solutions it is rose-red.

10. On igniting a compound of platinum mixed with **carbonate of soda** on a loop of platinum wire in the upper **oxidizing flame**, a gray spongy mass is obtained, which on trituration in an agate mortar yields silvery spangles, insoluble in hydrochloric and nitric acid, but soluble in aqua regia.

§ 128.

Recapitulation and Remarks.

The reactions of gold and platinum enable us, at least partially, to detect those two metals in the presence of many other oxides, and more particularly where platinum and gold are present in the same solution. In the latter case, the solution is most conveniently evaporated to dryness at a gentle heat with chloride of ammonium, and the residue treated with dilute spirit of wine, in order to obtain the gold in solution and the platinum in the residue. The precipitate will thus give platinum by ignition, and the gold may be thrown down from the solution by ferrous sulphate, after removing the spirit of wine by evaporation, or the gold may be precipitated from the hydrochloric acid solution by ferrous sulphate, and the platinum from the heated filtrate by sulphuretted hydrogen.

SECOND DIVISION.

Special Reactions.

§ 129.

a. **Stannous Oxide or Protoxide of Tin,** SnO [SnO].

1. Metallic tin is of a light grayish-white colour and has a high metallic lustre; it is soft and malleable; when bent it produces a crackling sound. It melts at 228·5°, and boils at a white heat; when heated in the air, it absorbs oxygen, and is slowly converted into the white binoxide; heated on charcoal before the blowpipe, it forms a white incrustation. Concentrated hydrochloric acid dissolves tin to stannous chloride, with evolution of hydrogen; nitrohydrochloric acid dissolves it, according to circumstances, forming stannic chloride or a mixture of stannous and stannic chlorides. Tin dissolves with difficulty in dilute sulphuric acid; concentrated sulphuric acid converts it, with the aid of heat, into sulphate of binoxide; moderately concentrated nitric acid oxidizes it readily, particularly if hot; the white hydrate of metastannic acid, $SnO_2,2HO$ [$Sn(OH)_4$], does not redissolve in excess of the acid.

2. Stannous oxide is a black or grayish-black powder; its hydrate is white; it is reduced by fusion with cyanide of potassium. It is readily soluble in hydrochloric acid. Nitric acid converts it into hydrate of metastannic acid, insoluble in excess of the acid.

3. The salts of stannous oxide are colourless; they are decomposed at a red heat, leaving stannic oxide if air has free access. The soluble salts, in the neutral state, redden litmus-paper; those which are soluble in water dissolve in hydrochloric acid if they have not been previously ignited. Stannous salts rapidly absorb oxygen from the air, and are partially or entirely converted into salts of stannic oxide. Stannous chloride, whether in crystals or in solution, also absorbs oxygen from the air, forming insoluble stannous oxychloride and stannic chloride;

so that a solution of stannous chloride becomes speedily turbid if the bottle is often opened and there is but little free acid present: hence it is only quite recently prepared stannous chloride which will completely dissolve in water free from air, whilst crystals of stannous chloride that have been kept for any time will dissolve to a clear solution only in water containing hydrochloric acid.

4. **Sulphuretted hydrogen** throws down from neutral and acid solutions a dark-brown precipitate of hydrated stannous sulphide, SnS [SnS]. This reagent does not precipitate alkaline solutions, or at least not completely; moreover, the precipitation may be prevented by the presence of a very large quantity of free hydrochloric acid. The precipitate is insoluble, or nearly so, in protosulphide of ammonium, but dissolves readily in the higher yellow sulphide if warmed. From this solution, acids precipitate yellow stannic sulphide, mixed with sulphur. Stannous sulphide dissolves also in solution of soda and potassa; acids precipitate the brown sulphide from these solutions. Boiling hydrochloric acid dissolves it, with evolution of sulphuretted hydrogen; boiling nitric acid converts it into insoluble hydrate of metastannic acid. When sulphide of tin is heated to redness in a current of chlorine, or with a mixture of 5 parts of chloride of ammonium and 1 of nitrate of ammonia, it is decomposed and volatilizes completely. If the operation is performed in a glass tube the tin sublimes as chloride.

5. **Sulphide of ammonium** produces the same precipitate of hydrated stannous sulphide.

6. **Potassa, soda, ammonia,** and **carbonates of the alkalies** produce a white bulky precipitate of hydrate of stannous oxide, SnO,HO [SnH_2O_2], which redissolves readily in excess of potassa or soda, but is insoluble in an excess of the other precipitants. If the solution of hydrate of stannous oxide in potassa is briskly evaporated, a compound of stannic oxide and potassa is formed, which remains in solution, whilst metallic tin is precipitated; but on evaporating slowly, crystalline anhydrous stannous oxide separates.

7. **Chloride of gold** produces in solutions of stannous chloride and in solutions of salts of stannous oxide mixed with hydrochloric acid a precipitate which varies in colour between brown, reddish-brown, and purple-red, according to the presence of more or less stannic chloride and the state of concentration (compare § 126, 7). In very dilute solutions, a more or less brown or red coloration merely is produced.

8. Solution of **mercuric chloride**, added in excess to solutions of stannous chloride or oxide mixed with hydrochloric acid, produces a white precipitate of mercurous chloride, owing to the protosalt of tin withdrawing from the mercuric chloride half of its chlorine.

9. If a solution containing stannous oxide or chloride and hydrochloric acid is added to a mixture of **ferricyanide of potassium** and **ferric chloride** a precipitate of Prussian blue separates immediately, owing to the reduction of the ferricyanide of iron, Fe_2Cfdy [$Fe_2(Fe_2C_{12}N_{12})$], to ferrocyanide, Fe_4Cfy_3 [$Fe_4(FeC_6N_6)_3$].

$$Fe_4Cfy_4{}^* + 2HCl + 2SnCl = Fe_4Cfy_3 + H_2Cfy + 2SnCl_2$$

$$[2Fe_2(Fe_2C_{12}N_{12}) + 4HCl + 2SnCl_2 = Fe_4(FeC_6N_6)_3 + H_4FeC_6N_6 + 2SnCl_4].$$

This reaction is extremely delicate, but it can be held to be decisive only in cases where no other reducing agent is present.

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[*] $2\ Fe_2Cfdy = Fe_4Cfy_4$; for $Cfdy = C_{12}N_6Fe_2 = 2Cfy$.

10. **Zinc** precipitates from solutions mixed with hydrochloric acid metallic tin in the form of gray laminæ or of a spongy mass. If the experiment is made in a platinum capsule, the latter is not coloured black.

11. If compounds of stannous oxide, mixed with **carbonate of soda** and some **borax**, or, better still, with a mixture of equal parts of **carbonate of soda** and **cyanide of potassium**, are exposed on a charcoal support to the **inner blowpipe flame**, malleable grains of metallic tin are obtained. The best way of making quite sure of the real nature of these grains is to triturate them and the surrounding parts of charcoal with water in a small mortar, pressing heavily upon the pestle; then to wash the charcoal off from the metallic particles. Upon strongly heating the grains of metallic tin on a charcoal support, the latter becomes covered with an incrustation of white binoxide. The **stick of charcoal** (p. 24) is also admirably adapted for the reduction of tin.

12. If to a borax bead coloured slightly blue by copper a trace of a compound of tin is added and the bead is heated in the **lower reducing zone** of the gas-lamp (p. 23), it will become reddish-brown to ruby-red in consequence of the reduction of the oxide of copper to suboxide (compare § 120, 14). A compound of tin is essential to this reaction. The blowpipe flame cannot be substituted for the gas-lamp flame, as in the former the copper is reduced to suboxide even when tin is absent.

§ 130.

b. Stannic Oxide or Binoxide of Tin, SnO_2 [SnO_2].

1. Tin oxide is a white or straw-coloured powder, which becomes transiently brown on heating. When heated with concentrated sulphuric acid, or on fusion with acid sulphate of potassa, it forms compounds from which water separates all the stannic oxide. Other acids do not act on stannic oxide, but when heated with chloride of ammonium the tin is volatilized as chloride. Stannic oxide forms with acids, bases, and water, two distinct series of compounds: namely, stannic oxide or stannic acid compounds, and those of metastannic acid; the compounds with acids correspond with the two chlorides, stannic chloride and metastannic chloride. The hydrate thrown down by alkalies from a solution of stannic chloride is readily soluble in hydrochloric acid, whilst the hydrated metastannic acid obtained by the action of nitric acid on tin is insoluble; if, however, the latter compound is boiled with it for a short time, metastannic chloride (which is but little soluble in hydrochloric acid) is formed, and if the excess of hydrochloric acid is poured off and water added, a solution of metastannic chloride is obtained, which is generally somewhat opalescent.

2. The salts of stannic oxide are colourless. The solutions of the neutral salts redden litmus-paper. The salts containing volatile acids are easily decomposed. Anhydrous stannic chloride is a mobile liquid fuming strongly on exposure to the air. It is soluble in cold water, forming a solution of stannic chloride. This solution is not precipitated by hydrochloric or by sulphuric acid unless **very** dilute, and is not coloured yellow on adding stannous chloride, whilst the aqueous solution of metastannic chloride is precipitated both by concentrated hydrochloric acid and by sulphuric acid, and is coloured yellow by stannous chloride. The dilute solutions of both chlorides, and more especially that of metastannic chloride, are precipitated on boiling.

3. On fusing stannic oxide, hydrated stannic oxide, or hydrated metastannic acid with hydrates of the alkali, alkaline stannates are formed; these are soluble in water, and on adding an acid, even carbonic acid, hydrated stannic oxide is precipitated. By fusion with carbonates of the alkalies, a portion only of the stannic oxide is converted into stannate of the alkali.

4. **Sulphuretted hydrogen** in excess, in a concentrated solution of stannic chloride containing free hydrochloric acid, forms a bright yellow stable precipitate of hydrated stannic sulphide, SnS_2 [$\mathbf{SnS_2}$], containing hydrated stannic oxide; with a weak acid or in feebly acid solutions, the precipitation does not always take place immediately, and gradually becomes deep yellow. In very dilute solutions not containing any free acid, the precipitate which is slowly formed is at first white, but afterwards becomes yellow; warming assists the precipitation. Alkaline solutions are not precipitated by sulphuretted hydrogen, and the presence of a very large quantity of free hydrochloric acid may also prevent precipitation. The precipitate dissolves with some difficulty in ammonia, and scarcely at all in carbonate of ammonia; it is insoluble in acid sulphite of potassa, readily soluble in potassa or soda, in alkaline sulphides, or in concentrated boiling hydrochloric acid or aqua regia. The precipitate thrown down from a solution of metastannic chloride by sulphuretted hydrogen, and consisting of hydrate of metastannic acid containing hydrated stannic sulphide, becomes more or less brown, on remaining for a long time in contact with the liquid and on treating it with excess of soda solution stannic sulphide is dissolved, leaving a residue of metastannate of soda (Barfoed). Concentrated nitric acid converts the sulphuretted hydrogen precipitates into hydrate of metastannic acid. When heated with a mixture of 5 parts of chloride of ammonium and 1 part of nitrate of ammonia, these precipitates behave like stannous sulphide (§ 129, 4). On deflagrating them with nitrate and carbonate of soda, they yield sulphate of soda, stannic oxide, and some stannate of soda. If a solution of the precipitate in potassa or soda is boiled with oxide of bismuth or oxide of copper, a sulphide of the metal is formed, and stannate of the alkali remains in solution.

5. **Sulphide of ammonium** precipitates yellow hydrated stannic sulphide, readily soluble in excess of the precipitant; from this solution, acids reprecipitate the sulphide unaltered.

6. **Potassa** and **soda** produce a white precipitate of hydrated stannic oxide in a solution of stannic chloride; this is insoluble in excess of the precipitant. In metastannic chloride solution, potassa produces a precipitate of hydrated metastannic acid, soluble in a moderate excess of the precipitant; with a large excess, metastannate of potassa separates, sparingly soluble in potassa, but soluble in water. From metastannic chloride, soda precipitates metastannate of soda, which is insoluble in excess of soda.

7. **Carbonate of potassa** gives a white precipitate with stannic chloride solution. The precipitate, consisting of hydrate of stannic oxide containing potassa, dissolves in excess of the precipitant, but separates again on standing. The precipitate thrown down by **carbonate of soda** is not soluble in excess of the precipitant. The white precipitate produced by carbonates of the alkalies in a solution of metastannic chloride are insoluble, or almost insoluble, in excess of the precipitant.

8. **Sulphate of soda** or **nitrate of ammonia** (in fact, most neutral salts of the alkalies), when added in excess, throws down the whole of the tin from solutions of the two modifications of stannic oxide, provided they are not too acid, either as hydrated stannic oxide or as hydrated metastannic acid. Heating promotes the precipitation:

$$SnCl_2 + 4(NaO,SO_3) + 4HO = SnO_2,2HO + 2NaCl + 2(NaO,HO,2SO_3)$$

$$[SnCl_4 + 4Na_2SO_4 + 4H_2O = Sn(OH)_4 + 4NaCl + 4NaHSO_4].$$

9. **Metallic zinc** in the presence of free acid precipitates from solutions of stannic chloride metallic tin in the shape of small gray scales, or as a spongy mass. If the operation is conducted in a platinum dish, no blackening of the latter is observed (difference between tin and antimony).

10. If solution of stannic chloride is boiled for a long time with metallic copper, the stannic chloride is reduced to stannous chloride, and the solution then precipitates mercurous chloride from a solution of mercuric chloride (Pattison Muir).

11. The compounds of stannic oxide show the same reactions before the **blowpipe** or in the **gas flame** as those of stannous oxide. Stannic oxide is also readily reduced when fused with cyanide of potassium in a glass tube or in a crucible.

§ 131.

c. Oxide of Antimony, SbO_3 $[SbO_3]$.

1. Metallic antimony has a bluish-white colour and is lustrous; it is hard, brittle, melts at 430°, and is volatile at a very high temperature. When heated on charcoal before the blowpipe, it emits thick white fumes of oxide of antimony, which form an incrustation on the charcoal; this combustion continues for some time even after the removal of the metal from the flame; it is most distinctly visible if a current of air is directed with the blowpipe on to the sample on the charcoal. If the sample on the support is kept steady, that the fumes may ascend vertically, the metallic bead becomes surrounded with a net of brilliant acicular crystals of teroxide of antimony. Nitric acid oxidizes antimony readily: the dilute acid converts it almost entirely into teroxide; the more concentrated the acid, the more antimonic acid is formed, whilst the boiling concentrated acid converts it almost completely into antimonic acid. Neither of the two oxides is altogether insoluble in nitric acid; traces of antimony are therefore always found in the acid liquid filtered from the precipitate. Hydrochloric acid, even boiling, does not attack antimony, but in nitrohydrochloric acid, the metal dissolves readily; the solution contains terchloride, $SbCl_3$ $[SbCl_3]$, or pentachloride, $SbCl_5$ $[SbCl_5]$, according to the degree of concentration of the acid and the duration of the action.

2. According to the different modes of its preparation, oxide of antimony occurs either in the form of white and brilliant crystalline needles, or as a white powder. It fuses at a moderate red heat in a closed vessel, and when exposed to a higher temperature it volatilizes without decomposition. It is almost insoluble in nitric acid, but dissolves readily in hydrochloric acid and in tartaric acid. No separation of iodine takes place on boiling it with hydrochloric acid free from chlorine and iodide of potassium (free from iodic acid) (Bunsen). Ter-

oxide of antimony is easily reduced to the metallic state by fusion with cyanide of potassium.

3. Antimonic acid, SbO_5 [Sb_2O_5], is pale yellow; its hydrates are white. Both the acid and its hydrates redden moist litmus-paper; they are only very sparingly soluble in water, and almost insoluble in nitric acid, but dissolve pretty readily in hot concentrated hydrochloric acid: the solution contains pentachloride of antimony, $SbCl_5$ [$SbCl_5$], and becomes turbid on addition of water. On boiling antimonic acid with hydrochloric acid and iodide of potassium, iodine separates, and dissolving in the hydriodic acid present colours it brown (Bunsen). On ignition, antimonic acid loses oxygen, and is converted into infusible antimonate of oxide of antimony, SbO_3,SbO_5 [Sb_2O_4]. Of the antimonates and metantimonates, the potassa salts are almost the only ones soluble in water: acids precipitate hydrate of the corresponding antimonic acid from the solutions, chloride of sodium throws down metantimonate of soda (§ 90, 2) from the solution of metantimonate of potassa.

4. The salts of oxide of antimony which contain volatile acids are decomposed by ignition; the haloid salts volatilize readily and unaltered. The soluble neutral salts of antimony redden litmus-paper. With a large quantity of water, they give insoluble basic salts and acid solutions containing oxide of antimony. Thus, for instance, **water** throws down from solutions of terchloride of antimony in hydrochloric acid a white bulky precipitate of basic chloride of antimony (powder of Algaroth), $SbCl_3,5SbO_3$ [$Sb_4O_5Cl_2$], which after some time becomes heavy and crystalline. Tartaric acid dissolves this precipitate readily, and therefore prevents its formation if mixed with the solution previously to the addition of the water. It is by this property that the basic terchloride of antimony is distinguished from the basic salts of bismuth formed under similar circumstances.

5. **Sulphuretted hydrogen** precipitates from acid solutions of the oxide (if the quantity of free mineral acid present is not too large) the whole of the metal as orange-red amorphous sulphide of antimony, SbS_3 [Sb_2S_3]. From alkaline solutions, it is not thrown down, or at least but imperfectly; neutral solutions also are only imperfectly precipitated. The tersulphide of antimony produced is readily dissolved by potassa or soda and by alkaline sulphides, especially if the latter contain an excess of sulphur; it is but sparingly soluble in ammonia, and, if free from pentasulphide of antimony, almost insoluble in bicarbonate of ammonia. It is insoluble in dilute acids, as also in acid sulphite of potassa. Concentrated boiling hydrochloric acid dissolves it, with evolution of sulphuretted hydrogen gas. By heating in the air, it is converted into a mixture of antimonate of oxide of antimony with tersulphide of antimony. By deflagration with nitrate of soda, it gives sulphate and antimonate of soda. Sulphide of antimony when heated to redness in a current of chlorine, or with a mixture of 5 parts of chloride of ammonium and 1 of nitrate of ammonia, is decomposed, and volatilizes completely. If the operation is performed in a glass tube, chloride of antimony sublimes. If a solution of tersulphide of antimony in potassa or in sulphide of potassium is boiled with oxide of bismuth, sulphide of bismuth is precipitated, and oxide of antimony remains dissolved in the potassa; if the alkaline solution is boiled with oxide of copper, sulphide of copper is formed, and the alkaline solution contains anti-

monate of potassa. On fusing tersulphide of antimony with cyanide of potassium, metallic antimony and sulphocyanate of potassium are produced; if the operation is conducted in a small tube expanded into a bulb at the lower end, or in a stream of carbonic acid gas (see § 132, 12), no sublimate of antimony is produced. If, however, a mixture of tersulphide of antimony with carbonate of soda or with cyanide of potassium and carbonate of soda is heated in a glass tube in a stream of hydrogen gas (compare § 132, 4), a mirror of antimony is deposited in the tube, immediately behind the spot occupied by the mixture.

From a solution of antimonic acid in hydrochloric acid, sulphuretted hydrogen throws down pentasulphide of antimony, SbS_5 [Sb_2S_5], mixed with tersulphide and sulphur. The precipitate dissolves readily when heated with solution of soda or ammonia, but only very sparingly in cold bicarbonate of ammonia; it dissolves in concentrated boiling hydrochloric acid, with evolution of sulphuretted hydrogen gas and separation of sulphur.

6. **Sulphide of ammonium** in solutions of teroxide of antimony produces an orange-red precipitate of sulphide of antimony, which readily redissolves in an excess of the precipitant if the latter contains excess of sulphur. From this solution, acids throw down pentasulphide of antimony, SbS_5 [Sb_2S_5]; the orange colour, however, in that case is usually of a lighter tint, owing to admixture with free sulphur.

7. If a solution of antimony oxide is added to a solution of **hyposulphite of soda** previously mixed with a little aqueous sulphurous acid (whereby it is turned yellow), and the whole heated to boiling, the solution becomes turbid, sulphur separates first, and then the antimony as antimony-vermilion, $2SbS_3,SbO_3$ [Sb_2S_2O].

8. **Potassa, soda, ammonia, carbonate of soda,** and **carbonate of ammonia** throw down a white bulky precipitate of oxide of antimony, from solutions of terchloride of antimony, and of simple salts of teroxide of antimony, also from solutions of tartar emetic or analogous compounds, but far less completely, and generally only after some time: this precipitate redissolves pretty readily in an excess of potassa or soda, but requires the application of heat for its re-solution in carbonate of soda, and is almost insoluble in ammonia.

9. **Metallic zinc** precipitates from all solutions of teroxide of antimony, if they contain no free nitric acid, metallic antimony as a black powder. If a few drops of a solution of antimony, containing some free hydrochloric acid, are put into a platinum capsule (the lid of a platinum crucible), and a fragment of zinc is introduced, hydrogen containing antimoniuretted hydrogen is evolved and antimony separates, staining the part of the platinum covered by the liquid brown or black, even in the case of very dilute solutions: this reaction is recommended as being equally delicate and characteristic. Cold hydrochloric acid fails to remove the stain, heating with nitric acid removes it immediately.

10. If a solution of oxide of antimony in solution of potassa or soda is mixed with solution of **nitrate of silver**, a deep black precipitate, formerly considered to be suboxide of silver, forms along with the grayish-brown precipitate of oxide of silver. On now adding ammonia in excess, the oxide of silver is dissolved, whilst the black precipitate is left (H. Rose). According to Pillitz, this is a variable mixture of antimony and silver, which, perhaps, contains a chemical combination of the two. This exceedingly delicate reaction affords

more especially an excellent means of detecting oxide of antimony in presence of antimonic acid.

11. If a solution of teroxide of antimony is introduced into a flask in which hydrogen gas is being evolved from pure **zinc** and dilute **sulphuric acid**, the zinc becomes oxidized not only at the expense of the oxygen of the water, but also at the expense of that of the oxide of antimony. Antimony separates accordingly in the metallic state, but, in the moment of its separation, a portion of the metal combines with hydrogen, forming antimoniuretted hydrogen, SbH_3 [SbH_3]. If this operation is conducted in a Marsh's arsenic apparatus (§ 132, 10, p. 171), and the hydrogen passing through the jet is ignited after the atmospheric air is completely expelled, the flame appears of a bluish-green tint, which is imparted to it by the antimony separating and burning in the flame.* The white fumes of teroxide of antimony which rise from the flame, condense readily upon cold substances, and are insoluble in water. If, however, a cold substance, such as a porcelain dish, is held in the flame, metallic antimony is deposited upon the surface in a state of the most minute division, forming a deep black and almost lustreless spot. If the middle part of the tube through which the gas is passing is heated to redness, the bluish-green tint of the flame decreases in intensity, and a metallic mirror of antimony of silvery lustre is formed within the tube on both sides of the heated part.

As the acids of arsenic, under the same circumstances, give similar stains consisting of metallic arsenic, it is always necessary to carefully examine the spots produced, in order to ascertain whether they really consist of antimony, or contain any of that metal. With stains deposited on a porcelain dish, the object in view is most readily attained by treating them with a solution of "chloride of soda" (hypochlorite of soda mixed with chloride of sodium, and prepared by adding carbonate of soda in excess, to a solution of chloride of lime and filtering); this immediately dissolves arsenical stains, but leaves those proceeding from antimony untouched, or, at least, dissolves them only after a very protracted action. A mirror within the glass tube, on the other hand, may be tested by heating it whilst the current of hydrogen gas still continues to pass through the tube: if the mirror volatilizes only at a high temperature, and the hydrogen gas then issuing from the tube does not smell of garlic; if it is only with a strong current that the ignited gas deposits spots on porcelain, and the mirror before volatilizing fuses to small lustrous globules distinctly discernible through a magnifying glass—the presence of antimony may be considered certain. Or the metals may be distinguished with great certainty by conducting through the tube a *very slow* stream of dry sulphuretted hydrogen gas, and heating the mirror, proceeding in an opposite direction to that of the current. The antimonial mirror is by this means converted into tersulphide of antimony, which appears of a more or less reddish-yellow colour, and almost black in thick layers. If a feeble stream of dry hydrochloric acid gas is now passed through the glass tube, the tersulphide of antimony, if present in thin layers only, disappears immediately; if the incrustation is somewhat thicker, it takes a short time to

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* By the employment of a platinum jet, the colour of the flame will be rendered very distinct.

volatilize it. The reason for this is, that the tersulphide of antimony decomposes readily with hydrochloric acid, and the terchloride of antimony formed is exceedingly volatile in a stream of hydrochloric acid gas. If the gaseous current is now passed into water, the presence of antimony in the latter may readily be proved by means of sulphuretted hydrogen. By this combination of reactions, antimony may be distinguished with positive certainty from all other metals.

The reaction which hydrogen gas containing antimoniuretted hydrogen exhibits with solution of nitrate of silver and with solid potassa will be found in § 134, 6.

12. If a solution of oxide of antimony in potassa or soda is heated with **aluminium** or with **zinc** and some **magnesium**, hydrogen is evolved and all the antimony is deposited. No antimoniuretted hydrogen is produced in this reaction, affording a means of distinguishing it from arsenic, which, under like conditions, yields arseniuretted hydrogen (Hager, Gatehouse).

13. If a mixture of an antimony compound with **carbonate of soda** and **cyanide of potassium** is exposed on a charcoal support to the **reducing flame of the blowpipe**, brittle globules of metallic antimony are produced, which may be readily recognized by the peculiar reactions that mark their oxidation (compare § 131, 1).

14. In the upper **reducing flame** of the gas lamp (p. 23), compounds of antimony give a greenish-gray colour, and no odour. The metallic **incrustation** is black, sometimes dull, sometimes bright: the incrustation of oxide is white; when moistened with neutral nitrate of silver, and then blown on with ammonia, it gives a black spot (Bunsen).

§ 132.

d. Arsenious Acid, AsO_3 [As_2O_3].

1. Metallic arsenic, when amorphous, is black and lustrous, in the crystalline state it is steel-gray and of brilliant lustre; this it retains in dry air, but loses in moist air, becoming covered with suboxide; the metallic arsenic of commerce, therefore, looks rather dull, with a dim bronze lustre on the planes of crystallization. Arsenic is not very hard, but very brittle; at a dull red heat, it volatilizes without fusion. The fumes have a most characteristic odour of garlic, which is ascribed to the suboxide of arsenic formed. Heated with free access of air, arsenic burns—with a bluish flame at high temperatures—emitting white fumes of arsenious acid, which condense on cold surfaces. If arsenic is heated in a glass tube sealed at the lower end, the greater part of it volatilizes unoxidized; whilst in a current of hydrogen or carbonic acid it volatilizes quite unchanged and recondenses above the heated spot as a lustrous black sublimate (arsenical mirror). This nearest to the heated place is usually glistening and gray (crystalline), whilst farther on it is black and vitreous (amorphous). In contact with air and water, arsenic oxidizes slowly to arsenious acid. When heated with dilute nitric acid, it is converted into arsenious acid, which dissolves only sparingly in excess of the acid; strong nitric acid converts it partially into arsenic acid. It is insoluble in hydrochloric acid and dilute sulphuric acid; concentrated boiling sulphuric acid oxidizes it to arsenious acid, with evolution of sulphurous acid and aqua regia it also yields arsenic acid.

2. Arsenious acid forms either a transparent vitreous or a white porcelain-like mass, or transparent colourless crystals. By trituration, it gives a heavy, white, gritty powder. When heated, it volatilizes in white inodorous fumes; if the operation is conducted in a glass tube, a sublimate is obtained consisting of small brilliant octahedrons and tetrahedrons. Arsenious acid like fatty substances is with difficulty moistened by water; it is sparingly soluble in cold, but more readily in hot water. It is copiously dissolved by hydrochloric acid, as well as by solution of soda and potassa. When boiled with nitrohydrochloric acid, it dissolves as arsenic acid. It is very poisonous.

If a small lump of arsenious acid (*a*) be introduced into the pointed end of a drawn-out glass tube (fig. 35), a fragment of recently ignited charcoal (*b*) pushed down the tube to within a short distance of the arsenious acid, and first the charcoal and then the arsenious acid be heated to redness, a mirror of metallic arsenic will form at *c*, owing to the reduction of the arsenious acid vapour by the red-hot charcoal. If the tube be now cut between *b* and *c* and again heated in an inclined position, with the end *c* turned upwards, the metallic mirror will volatilize, emitting the odour of garlic so characteristic of arsenic. This is both the simplest and safest way of detecting pure arsenious acid.

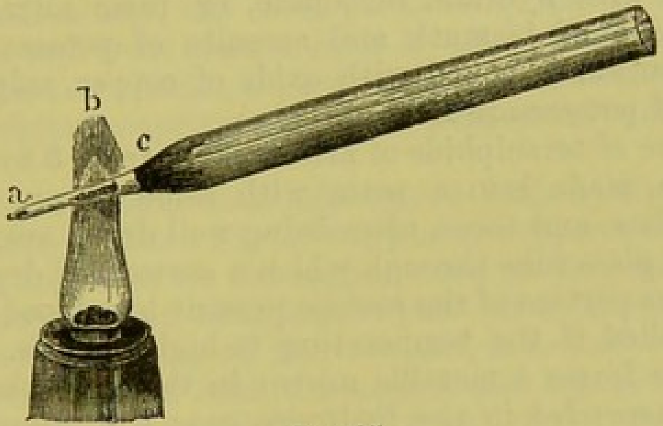

Fig. 35.

3. The arsenites are mostly decomposed by ignition, either into arsenates and metallic arsenic which volatilizes, or into arsenious acid and the base with which it was combined. Of the arsenites, those with alkaline bases are alone soluble in water; the insoluble arsenites are dissolved, or at least decomposed, by hydrochloric acid. Anhydrous terchloride of arsenic is a colourless volatile liquid, fuming in the air; it can be mixed with a small quantity of water, but on adding more water it is decomposed into arsenious acid, part of which separates, and hydrochloric acid, which retains the rest of the arsenious acid in solution. When a solution of arsenious acid in hydrochloric acid is heated and evaporated, chloride of arsenic escapes along with the hydrochloric acid. If the solution is distilled, the distillate contains the arsenic as arsenious acid dissolved in the dilute hydrochloric acid.

4. **Sulphuretted hydrogen** colours aqueous solutions of arsenious acid yellow, but produces no precipitate; neither does it precipitate aqueous solutions of neutral arsenites of the alkalies; on adding a strong acid, however, a bright yellow precipitate of tersulphide of arsenic, AsS_3 [As_2S_3], is at once formed. Sulphuretted hydrogen produces the same precipitate in the hydrochloric acid solution of arsenites insoluble in water; even a large excess of hydrochloric acid does not prevent

complete precipitation. Alkaline solutions are not precipitated. The precipitate is readily and completely dissolved by alkalies, alkaline carbonates and bicarbonates, and also by alkaline sulphides; freshly precipitated sulphide of arsenic is also soluble in the acid sulphites of the alkalies. It is, however, nearly insoluble in hydrochloric acid, even if concentrated and boiling. Boiling nitric acid decomposes and dissolves the precipitate readily.

The deflagration of tersulphide of arsenic with carbonate and nitrate of soda gives rise to the formation of arsenate and sulphate of soda. If the sulphide is heated with a mixture of 5 parts of chloride of ammonium and 1 of nitrate of ammonia, it is completely volatilized, the arsenic being found in the sublimate as chloride of arsenic. When a solution of tersulphide of arsenic in sulphide of sodium or in potassa or soda is boiled with hydrate, carbonate, or basic nitrate of oxide of bismuth, sulphide of bismuth and arsenite of potassa are produced. If a similar solution is boiled with oxide of copper, sulphide of copper and arsenate of potassa are formed.

If a mixture of tersulphide of arsenic with from 3 to 4 parts of carbonate of soda, made into a paste with some water, is spread over fragments of glass, and these, after being well dried, are rapidly heated to redness in a glass tube through which a current of dry hydrogen gas is passed, a large portion of the arsenic present is reduced to the metallic state and expelled if the temperature is high enough. Part of the reduced arsenic forms a metallic mirror in the tube, the remainder is carried away suspended in the hydrogen gas; the minute particles of arsenic impart a bluish tint to the flame when the gas is kindled, and form stains of arsenic upon the surface of a porcelain dish held in the flame. Although this method of reduction gives very accurate results, it does not enable us to distinguish arsenic from antimony with a sufficient degree of certainty, nor to detect arsenic in presence of antimony (compare § 131, 5), and consequently the process described in 12 of this article is generally to be preferred.

5. **Sulphide of ammonium** also gives rise to the formation of tersulphide of arsenic. In neutral and alkaline solutions, however, the tersulphide is not precipitated, but remains dissolved as a double sulphide of arsenic and ammonium. On the addition of an acid to this solution, it is immediately precipitated.

6. **Nitrate of silver** does not affect aqueous solutions of arsenious acid, or at the most produces a trifling yellowish-white turbidity; if a little ammonia is added, however, a yellow precipitate of arsenite of silver, $3AgO,AsO_3$ [Ag_3AsO_3], is at once formed. The same precipitate is produced on adding nitrate of silver to a solution of a neutral arsenite. The precipitate dissolves readily in nitric acid, as well as in ammonia if an alkaline nitrate be present, and is not insoluble in nitrate of ammonia; if, therefore, a small quantity of the precipitate is dissolved in a large amount of nitric acid, and the latter is afterwards neutralized with ammonia, the precipitate does not make its appearance again, as it remains dissolved in the nitrate of ammonia formed. If an ammoniacal solution of arsenite of silver is heated to boiling, metallic silver separates, the arsenious acid being converted into arsenic acid.

7. **Sulphate of copper** gives no precipitate in aqueous solutions of arsenious acid, but under the conditions just described for silver, it gives a yellowish-green precipitate of arsenite of copper; this dissolves in

potassa or soda, forming a blue liquid from which red cuprous oxide separates on boiling (comp. 8).

8. If to a solution of arsenious acid in an excess of solution of soda or potassa, or to a solution of an alkaline arsenite mixed with potassa or soda, a few drops of a very dilute solution of **sulphate of copper** are added, a clear blue liquid is obtained, which when boiled deposits a red precipitate of cuprous oxide, leaving arsenate of potassa in solution. This reaction is exceedingly delicate, provided too much of the solution of sulphate of copper is not used. Even should the red precipitate be so exceedingly minute as to escape detection on looking across the tube, yet it will always be discernible with great distinctness on looking down the test-tube. Of course this reaction, although really of great importance in certain instances as a confirmatory proof of the presence of arsenious acid, and more particularly also as a means of distinguishing that acid from arsenic acid, is yet entirely inapplicable for the direct detection of arsenic, since grape sugar and other organic substances also precipitate cuprous oxide from salts of oxide of copper under like conditions.

9. If a solution of arsenious acid mixed with hydrochloric acid is heated with a perfectly clean slip of **copper** or copper-wire, an iron-gray metallic film is deposited on the copper, even in *very dilute* solutions; when this film increases in thickness, it peels off in black scales. If the coated copper, after washing off the free acid, is heated with solution of ammonia, the film peels off from the copper, and separates in the form of minute spangles (Reinsch). Let it be borne in mind that these are not pure arsenic, but consist of an arsenide of copper, Cu_5As [Cu_5As_2]. If the substance, either simply dried or oxidized by ignition in a current of air (which is attended with escape of some arsenious acid), is heated in a current of hydrogen, there escapes relatively but little arsenic, alloys richer in copper being left behind (Fresenius, Lippert). It is only after the presence of arsenic in the alloy has been fully demonstrated that this reaction can be considered a decisive proof of the presence of that metal, as antimony and other metals under the same circumstances are also precipitated upon copper; sulphurous acid also may produce a black stain on the copper (see p. 193).

10. If an acid or neutral solution of arsenious acid, or any of its compounds, is placed in contact with **zinc**, water, and dilute **sulphuric acid** or **hydrochloric acid**, arseniuretted hydrogen, AsH_3 [AsH_3], is formed, in the same manner as compounds of antimony under like conditions give antimoniuretted hydrogen. (Compare § 131, 10.) This reaction affords a most delicate test for the detection of even the most minute traces of arsenic.

The operation is conducted in the apparatus illustrated by fig. 36, or in one of similar construction.[*] *a* is the evolution flask, *b* a bulb intended to receive the water carried over with the current of gas, *c* a tube filled with cotton wool and small lumps of chloride of calcium for drying the gas.[†] This tube is connected with *b* and *d* by pieces of india-rubber tube which have been boiled in solution of soda; *d* should have an inner diameter of 7 mm. (fig. 37), and must be made of difficultly

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[*] The author uses the very convenient form of Marsh's apparatus recommended by Otto in his excellent "Lehrbuch der Chemie."

[†] A bulb-tube containing sulphuric acid may also be used for drying the gas (Lyttkens, Lenz).

fusible glass free from lead. In experiments requiring great accuracy the tube should be drawn out as shown in fig. 36. The experiment is commenced by evolving in *a* a moderate and uniform current of hydrogen from pure granulated zinc and pure sulphuric acid diluted with 3 parts of water; the addition of a few drops of chloride of platinum will be found useful. When the evolution of hydrogen has proceeded for some time, so that it may safely be concluded that the air has been completely expelled from the apparatus, the gas is kindled at the open end of the tube *d*. It is advisable to wrap a piece of cloth round the flask before applying a light to the gas, so as to guard against accidents in case of an explosion. It is necessary first to ascertain whether the zinc and the sulphuric acid are quite free from arsenic. This is done by holding a porcelain dish in the flame so that the flame spreads over the surface of the porcelain: if the hydrogen contains arseniuretted hydrogen, brownish or brownish-black stains of arsenic will appear on the porcelain; if there are no such stains, the zinc and sulphuric acid may be considered as free from arsenic. In very accurate experiments, however, the part of the tube *d* shown in fig. 36 must be heated to redness for some time; no arsenical coating should make its appearance in the narrowed part of the tube.

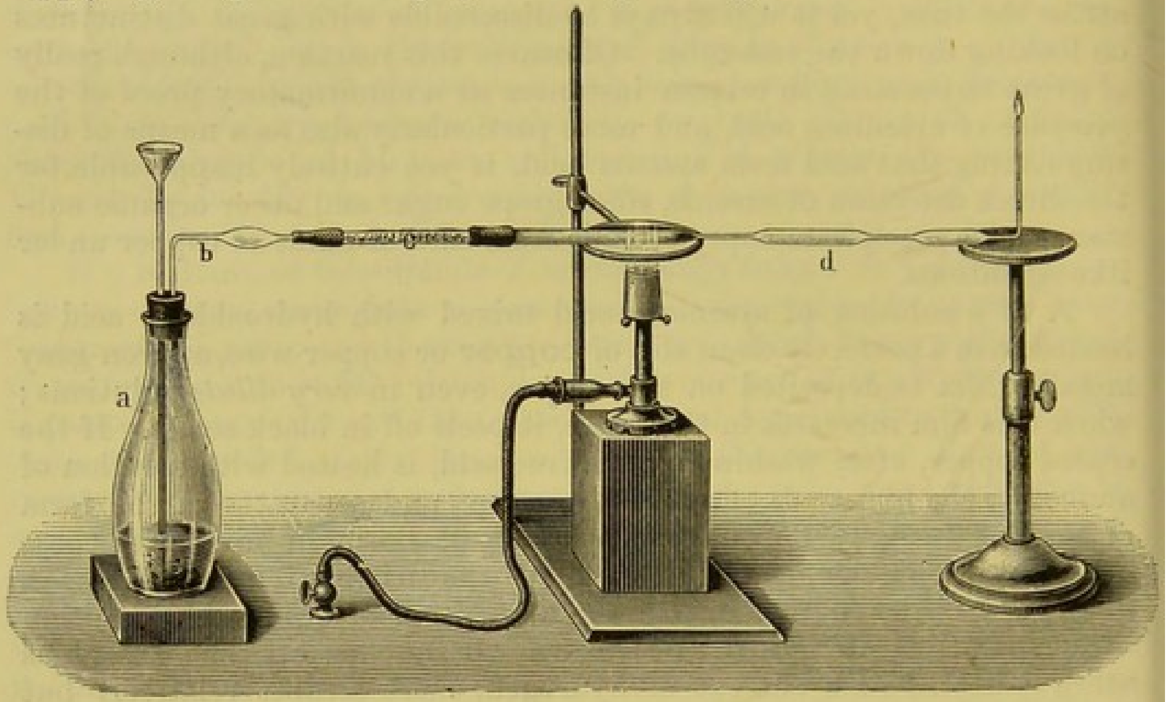

Fig. 36.

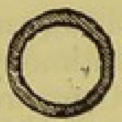

Fig. 37.

Having ascertained in this way that the reagents employed are free from arsenic, the solution to be tested for arsenic is poured through the funnel tube into the flask, and afterwards some water to rinse the tube. Only a very little of the solution should be poured in at first, as in cases where the quantity of arsenic present is considerable, and too much of the solution is poured into the flask at once, the gas is often evolved with such violence as to stop the further progress of the experiment.

If the solution contains an oxygen compound of arsenic, or arsenic in combination with a salt radicle, arseniuretted hydrogen is evolved along with the hydrogen, and imparts a bluish tint to the flame, owing to the combustion of the arsenic in the arseniuretted hydrogen. At the same time, white fumes of arsenious acid are produced, which condense upon cold objects. If a porcelain plate is now introduced into the flame, the separated and not yet reoxidized arsenic condenses upon the plate as a black stain, in a similar manner to antimony (see § 131, 10). The stains formed by arsenic, however, are more of a brownish-black tint, and bright metallic lustre; the antimonial spots, on the other hand, are of a deep black, and dull. The arsenical, moreover, may be distinguished from the antimonial stains by solution of "chloride of soda" (hypochlorite of soda and chloride of sodium, compare § 131, 11); this will at once dissolve the arsenical stains, leaving antimonial stains unaffected, or removing them only after a considerable time.

If the part of the tube *d* shown in fig. 36 is heated, a brilliant arsenical mirror makes its appearance in the narrow portion of the tube behind the heated part; this mirror is darker and of a less silvery-white hue than that produced by antimony under similar circumstances; it is moreover distinguished from the latter by the facility with which it may be volatilized in a current of hydrogen gas without previous fusion, and by the characteristic arsenical garlic odour emitted by the escaping (unkindled) gas. If the gas is kindled whilst the mirror in the tube is being heated, the flame will deposit arsenical stains on a porcelain plate even with a very slight current of gas.

The reactions and properties just described are amply sufficient to enable us to distinguish between arsenical and antimonial stains and mirrors; but they will often fail to detect arsenic with positive certainty in presence of antimony. In cases of this kind, the following process will serve to set at rest all possible doubt as to the presence or absence of arsenic:—

The long tube through which the gas to be tested in passing is heated to redness in several parts, so as to produce strong metallic mirrors; a very feeble current of dry sulphuretted hydrogen gas is then passed through the tube, and the metallic mirrors are heated, proceeding from the outer towards the inner border. If arsenic alone is present, yellow tersulphide of arsenic is formed in the tube; if antimony alone is present, orange-red or black tersulphide of antimony is produced; but if the mirror consists of both metals, the two sulphides appear side by side, the sulphide of arsenic as the more volatile lying invariably before the sulphide of antimony. If dry hydrochloric acid gas is now passed through the tube containing the sulphide of arsenic or the sulphide of antimony, or both sulphides together, without applying heat, no alteration will take place if sulphide of arsenic alone is present, even though the gas be passed through the tube for a considerable time. If sulphide of antimony alone is present, this will entirely disappear, as already stated, § 131, 11, and if both sulphides are present, the sulphide of antimony will immediately volatilize, whilst the yellow sulphide of arsenic will remain. If a small quantity of ammonia solution is now drawn into the tube, the sulphide of arsenic is dissolved, and may thus be readily distinguished from sulphur which may have separated. These combined tests are infallible for the detection of arsenic.

The reaction of hydrogen containing arseniuretted hydrogen with solution of nitrate of silver will be found in § 134, 6.

Marsh was the first who suggested the method of detecting arsenic by the production of arseniuretted hydrogen.

11. On adding a few drops of a solution of stannous chloride to about 5 c.c. of fuming hydrochloric acid, and then a few drops of a solution of arsenious acid or an arsenite, the arsenious acid is reduced, and a brownish-black precipitate of arsenic containing tin is obtained (Bettendorf). This reaction which takes place slowly in the cold but rapidly on heating is very delicate, but only takes place in the presence of excess of fuming hydrochloric acid. If the sp. gr. of the hydrochloric acid which contains the arsenic is less than 1·123, the precipitation is either incomplete or does not take place at all. If it is necessary to frequently test for arsenic by this method, a solution of stannous chloride in the most concentrated hydrochloric acid (38 per cent.) should be kept made up (oxide of antimony is not reduced under similar circumstances).

12. If arsenites, or arsenious acid, or tersulphide of arsenic are fused with a mixture of 3 parts of dry **carbonate of soda** and 1 of **cyanide of potassium**, the whole of the arsenic is reduced to the metallic state, and so is the base also, if easily reducible; the eliminated oxygen converting part of the cyanide of potassium into cyanate of potassa. In the reduction of tersulphide of arsenic, sulphocyanate of potassium is formed. If the operation is performed in a convenient apparatus, all the arsenic in arsenious acid or in tersulphide of arsenic is volatilized and deposited as a mirror. With arsenites, however, a mirror is only obtained when the base remains either altogether unaffected, or is reduced to a metallic arsenide which loses its arsenic partly or totally on being strongly heated. This method of reducing arsenic compounds with cyanide of potassium is to be particularly recommended on account of its simplicity and neatness, as well as for the accuracy of the results attainable by it, even in cases where only very minute quantities of arsenic are present. It is more especially adapted for directly obtaining arsenic from tersulphide of arsenic, and is in this respect superior in simplicity and accuracy to all other methods hitherto suggested. Formerly, when glass tubes were free from arsenic, the experiment could be performed quite safely in a glass tube with a small bulb blown at the lower end, or, better still, in a tube drawn out to a long point, through which a slow stream of carbonic anhydride was passed; at present, however, as almost all commercial glass tubing contains arsenic,* the reduction must be performed in such a manner that the fused mixture of potassium cyanide and sodium carbonate shall not come in contact with the glass. The apparatus devised by L. v. Babo and the author, described in the earlier edition, has in consequence been somewhat modified, and is constructed as shown in fig. 38. *a*, *b*, is a Kipp's apparatus for the preparation of carbonic anhydride,† containing marble and pure dilute hydrochloric acid; *c*, a wash-bottle, containing pure concentrated sulphuric acid for drying the carbonic anhydride; *d*, a tube of hard glass free from lead, and which may be made of a piece of combustion tube; the tube is shown half its natural size in fig. 39, and must be sufficiently large in the bore to admit of the insertion of a porcelain boat (represented in fig. 40 of the natural size) containing the mixture to be fused.

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* Compare W. Fresenius, *Der Arsengehalt des Glases als eine Fehlerquelle bei der Nachweisung von Arsen*, Zeit. anal. Chem., 22, 397.

† Instead of Kipp's any other apparatus for giving off carbonic anhydride in which the stream of gas can be accurately regulated by a tap will do equally well.

When the apparatus is arranged and filled with carbonic anhydride, the arsenic sulphide or arsenite, completely dried, is rubbed up in a warm porcelain mortar with 12 parts of a carefully dried mixture of 3 parts of sodium carbonate and 1 part of potassium cyanide completely free from arsenic (§ 46 and § 54); the mixture is then transferred to the porcelain boat, fig. 40, which is inserted into the reduction tube in the position shown at *d*, fig. 38. The tube is then connected with the wash-bottle, a gentle stream of carbonic anhydride is allowed to pass by opening the tap *e* (fig. 38), and the mixture in the boat is most carefully dried by gently warming both the boat and the tube beyond with a burner. When every trace of water has disappeared from the tube, the stream of gas is reduced until one bubble about passes through the sulphuric acid per second. The front of the broad part of the tube just before it narrows is then heated to redness with a gas flame *f*, and as soon as it is red hot, the boat itself is also heated by means of the lamp *g*, moderately at first, so that the fused mass shall not spirt, and finally strongly and continuously until all the arsenic is expelled. Should any of the arsenic have collected in the wider part of the tube, it is heated and driven forward to the narrow neck. Almost the whole

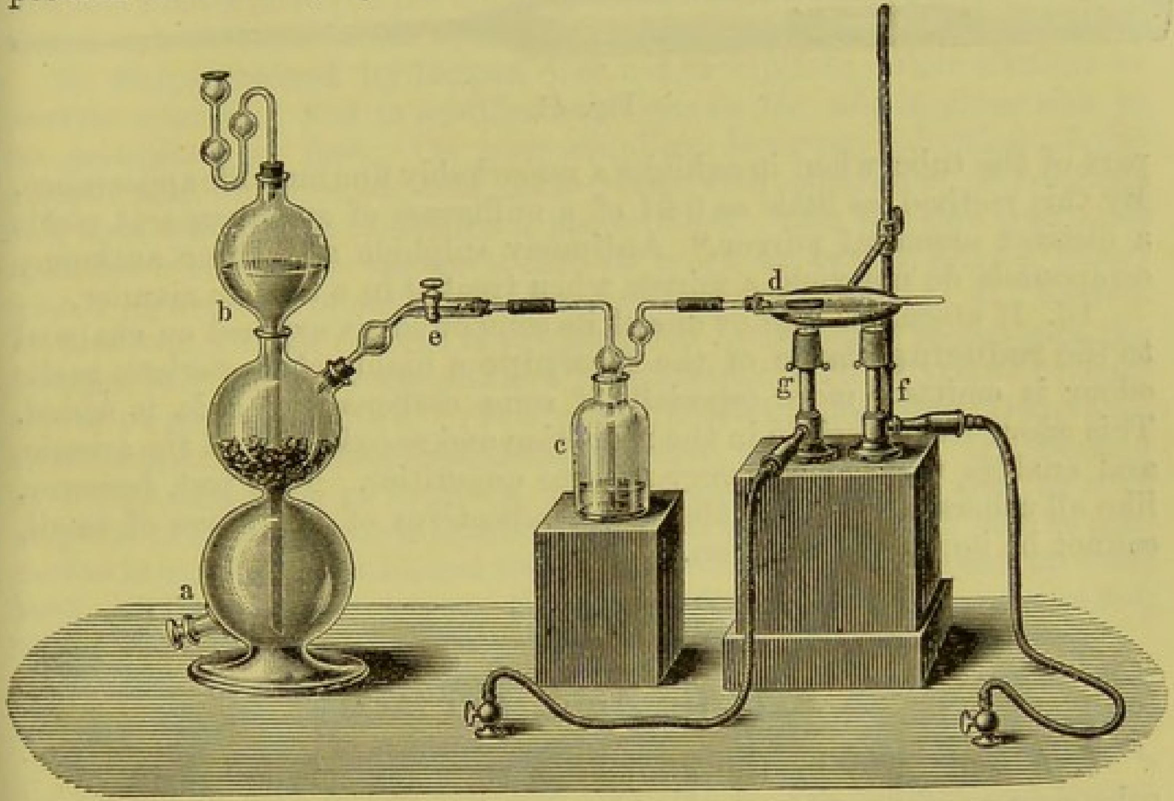

Fig. 38.

Fig. 39.

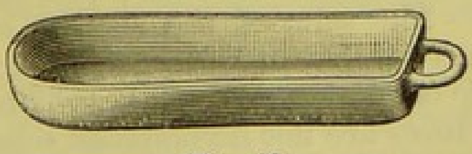

Fig. 40.

of the reduced arsenic is then found as a metallic mirror (fig. 41) beyond that portion of the tube heated to redness by the lamp *f*, fig. 38, which must not be removed during the operation. A small quantity escapes, however, through the narrow portion of the tube and gives rise to a garlic-like odour. Finally the tube may be sealed at the narrow end and the mirror heated cautiously and driven into the wider

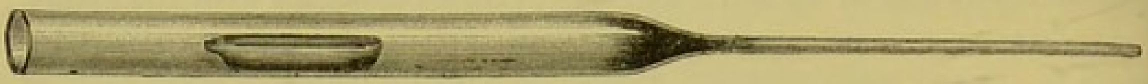

Fig. 41.

part of the tube, when it exhibits a remarkably fine metallic appearance. By this method as little as 0·01 of a milligram of arsenious acid yields a distinct arsenical mirror.* Antimony sulphide and other antimony compounds do not yield a mirror when treated in a similar manner.

13. If arsenious acid or one of its compounds is exposed on charcoal to the **reducing flame** of the **blowpipe** a highly characteristic garlic odour is emitted, more especially if some carbonate of soda is added. This odour has its origin in the reduction and re-oxidation of the arsenic, and enables us to detect very minute quantities. This test, however, like all others based upon the mere indications of the sense of smell, cannot be implicitly relied on.

§ 133.

e. **Arsenic Acid,** AsO_5 [As_2O_5].

1. Arsenic acid in the anhydrous state (arsenic anhydride) is a colourless or white, vitreous, fusible mass, dissolving slowly in cold water, but more rapidly in hot. When heated to redness, it is decomposed into oxygen and arsenious acid. Crystallized from its aqueous solution at a low temperature, it forms a hydrate of arsenic acid, $3HO,AsO_5 + aq$ [$2H_3AsO_4 + H_2O$], in the form of deliquescent, transparent, colourless prisms, which lose their water of crystallization at 100° C.

By heating at 180°, hydrate of pyroarsenic acid, $2HO,AsO_5$ [$H_4As_2O_7$], is obtained; at 206°, hydrate of metarsenic acid, HO,AsO_5 [$HAsO_3$]; and at a little below redness, the anhydride. All the hydrates are soluble in water, forming normal arsenic acid. Arsenic acid acts as a poison.

2. The arsenates correspond with the hydrated acids in composition. There are, therefore, distinct salts of arsenic, pyroarsenic and metarsenic acids. The salts of arsenic acid correspond with those of phosphoric acid, forming normal, monobasic, or bibasic salts accordingly as they contain 3 equivalents of the base and no basic water, 2 equivalents of the base and 1 equivalent of basic water, or 1 equivalent of the base and 2 of basic water. The salts of the alkalies and the acid salts of the alkaline earths are soluble in water; all the other arsenates are soluble in hydrochloric or nitric acids. The anhydrous salts of arsenic acid containing fixed bases are not decomposed when heated to redness.

A solution of arsenic acid or of an arsenate in hydrochloric acid may

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* Compare W. Fresenius, *Ueber die richtige Ausführung und die Empfindlichkeit der Fresenius-Babo'schen Methode zur Nachweisung des Arsens*, Zeit. anal. Chem. **20**, 531.

be boiled for a long time without losing chloride of arsenic, provided too much hydrochloric acid is not present. But when the residual liquid contains about half its volume of hydrochloric acid of specific gravity 1·12, traces of terchloride of arsenic begin to escape with the hydrochloric acid. On the other hand, when arsenic acid is heated with concentrated hydrochloric acid, chloride of arsenic and chlorine escape. If arsenic acid is distilled with diluted (20 per cent.) hydrochloric acid and ferrous chloride, the arsenic is found in the distillate as arsenious acid.

3. **Sulphuretted hydrogen** does not precipitate either alkaline or neutral solutions; and in acidified solutions *in the cold* it gives rise to no precipitate at first. On long standing, however, reduction of the arsenic acid to arsenious acid takes place with separation of sulphur, and then tersulphide of arsenic is precipitated. This reaction continues until the whole of the arsenic is thrown down as tersulphide, mixed with 2 equivalents of sulphur (Wackenroder, Ludwig, H. Rose). If, however, a rapid current of sulphuretted hydrogen is passed into the acidified solution of arsenic acid at a temperature of 70°, a yellow precipitate of pentasulphide of arsenic, AsS_5 [As_2S_5], is produced (Bunsen), or else a mixture of pentasulphide, tersulphide, and sulphur. If a solution of arsenic acid, or of an arsenate, is mixed with sulphurous acid, or with sulphite of soda and some hydrochloric acid, the sulphurous acid is converted into sulphuric acid, and the arsenic acid reduced to arsenious acid; heat accelerates the reaction. If sulphuretted hydrogen is now added, the whole of the arsenic is immediately thrown down as tersulphide.

4. **Sulphide of ammonium** converts the arsenic acid in neutral and alkaline solutions of arsenates into pentasulphide of arsenic; this remains in solution as a salt of pentasulphide of arsenic and sulphide of ammonium. On adding an acid to the solution, this salt is decomposed, and pentasulphide of arsenic is precipitated. The separation of this precipitate proceeds more rapidly than is the case when acid solutions of arsenates are precipitated with sulphuretted hydrogen. It is promoted by heat. The precipitate formed is pentasulphide of arsenic, and not a mixture of arsenic tersulphide with sulphur.

5. **Nitrate of silver** in solutions of arsenic acid and of the arsenates of the alkalies produces a highly characteristic reddish-brown precipitate of arsenate of silver, $3AgO,AsO_5$ [Ag_3AsO_4]; this is readily soluble in dilute nitric acid and in ammonia, and also to some extent in nitrate of ammonia. If the precipitate is dissolved in a little nitric acid and dilute ammonia is poured on to the solution, precipitation takes place at the surface of contact of the two liquids, forming a coloured ring. The addition of acetate of soda increases the delicacy of the reaction. If, however, a little of the precipitate is dissolved in a large proportion of nitric acid, neutralization with ammonia often fails to reproduce the precipitate. The ammoniacal solution of arsenate of silver does not deposit silver when boiled (difference between arsenic and arsenious acids).

6. **Sulphate of copper** produces no precipitate in an aqueous solution of arsenic acid. On adding an alkali, a greenish-blue precipitate of arsenate of copper is formed; this is soluble in excess of potassa or soda to a pale blue liquid. No cuprous oxide is formed on boiling.

7. If a dilute solution of arsenic acid mixed with some hydrochloric acid is heated with a clean slip of **copper**, the metal remains perfectly clean (Werther, Reinsch); but if to 1 volume of the solution

2 volumes of concentrated hydrochloric acid are added, a gray film is deposited on the copper, as in the case of arsenious acid. The reaction is under these circumstances equally delicate as with arsenious acid (Reinsch).

8. If a solution of arsenic acid, or of an arsenate soluble in water, is added to a clear mixture of **sulphate of magnesia**, **chloride of ammonium**, and a sufficient quantity of **ammonia**, a crystalline precipitate of arsenate of ammonia and magnesia,

$$2MgO,NH_4O,AsO_5 + 12aq \; [MgNH_4AsO_4,6H_2O],$$

separates immediately from concentrated solutions; from dilute solutions only after some time. If a small portion of the precipitate is dissolved on a watch-glass in a drop of nitric acid, a little nitrate of silver added, and the solution touched with a glass rod dipped in ammonia, brownish-red arsenate of silver is formed. Or if a small portion of the precipitate is dissolved in hydrochloric acid, and sulphuretted hydrogen is passed into the warm solution, a yellow precipitate is formed. (Differences between arsenate and phosphate of magnesia and ammonia.)

9. If a small quantity of a solution of arsenic acid or of an arsenate is added to a few c.c. of a solution of **molybdate of ammonia** in nitric acid, no precipitate is formed in the cold even on long standing. If the mixture be heated, however, a bright yellow precipitate of arseno-molybdate of ammonia will be formed. This is soluble in ammonia; in the solution thus formed, the magnesia mixture produces the reaction described in 8.

10. With **stannous chloride** and concentrated hydrochloric acid, with **zinc** in presence of sulphuric acid, with **cyanide of potassium**, and before the **blowpipe**, the compounds of arsenic acid behave in the same way as those of arsenious acid. If the reduction of arsenic acid by zinc is effected in a platinum capsule, the platinum does not turn black (difference from antimony).

§ 134.

Recapitulation and Remarks.

Several different methods may be employed for the detection of the metals of the second section of the sixth group in mixtures or solutions which contain several or all of them; no advice can be given as to which is the best, as one or the other method may be preferable according to the proportion in which the metals are present, and as to whether very great accuracy, or rapidity in obtaining the results, is the primary object. The different ways of effecting the detection or separation of tin, antimony, and arsenic, when present together, will be first described, and afterwards the means of distinguishing between the several oxides of the three metals.

1. If the mixture contains sulphide of tin, sulphide of antimony, and sulphide of arsenic, 1 part of it is triturated with 1 part of dry carbonate of soda and 1 of nitrate of soda, and gradually added to 2 parts of nitrate of soda kept in a state of fusion in a small porcelain crucible at a not over-strong heat; oxidation of the sulphides takes place, attended with slight deflagration. The fused mass contains binoxide of tin, arsenate and antimonate of soda, with sulphate, carbonate, nitrate, and nitrite of soda. Care must be taken not to raise the heat to such a degree, or to continue the fusion so long, as to lead to a re-

duction of the nitrite of soda to caustic soda, otherwise stannate of soda would be formed soluble in water. On treating the mass with a little cold water, stannic oxide and antimonate of soda remain undissolved, whilst arsenate of soda and the other salts pass into solution. If the filtrate is acidified with nitric acid, and heat is applied to remove carbonic and nitrous acids, the arsenic acid may be detected and separated, either with nitrate of silver, according to § 133, 5, or with a mixture of sulphate of magnesia, chloride of ammonium, and ammonia, according to § 133, 8, or as arsenomolybdate of ammonia, 9.

The undissolved residue, consisting of stannic oxide and antimonate of soda, after being washed once with cold water and three times with dilute spirits of wine, is treated with some hydrochloric acid in the lid of a platinum crucible, and a gentle heat applied; the mass either completely dissolves, or, if the tin is present in large proportion, a white residue is left. In either case, if a fragment of zinc is added, the compounds will be reduced to the metallic state, and the antimony will be at once detected by its blackening the platinum. If, after the evolution of hydrogen has nearly ceased, the remainder of the zinc is taken away, the chloride of zinc solution carefully decanted, and the contents of the lid heated with a little hydrochloric acid, the tin will dissolve as stannous chloride, whilst the antimony will be left in the form of black flakes. The tin may then be tested for in the solution by mercuric chloride, or by a mixture of ferric chloride with ferricyanide of potassium, and the antimony, after dissolving it in a little tartaric and nitric acid, with sulphuretted hydrogen. As this method of detecting arsenic, tin, and antimony in presence of each other is adopted in the systematic course of analysis, the principle only upon which it is based is here explained, the details of the process being given in § 192.

2. If the mixed sulphides, after being freed from the greater part of the adhering water, by laying the filter containing them on blotting paper, are treated with fuming hydrochloric acid, at a gentle heat, the sulphides of antimony and tin dissolve, whilst the sulphide of arsenic is left almost completely undissolved. By treating this with ammonia, and evaporating the solution obtained, with addition of a small quantity of carbonate of soda, an arsenical mirror may easily be produced from the residue, by means of cyanide of potassium and carbonate of soda in a stream of carbonic acid gas (§ 132, 12). The solution containing the tin and the antimony may be evaporated in the water-bath after the addition of chloride of sodium, and treated with zinc as in 1.

If a great excess of antimony is present, the latter solution may be mixed with sesquicarbonate of ammonia in excess, and boiled; the greater portion of the antimony will remain in solution, leaving stannic oxide, mixed with a little teroxide of antimony; the tin may now be more readily detected in this residue by the method given in 1 (Bloxam).

3. If the mixed sulphides are digested at a gentle heat with some common solid carbonate of ammonia and water, sulphide of arsenic dissolves, whilst the sulphides of antimony and tin remain undissolved; this separation, however, is not quite complete, as traces of sulphide of antimony are apt to pass into the solution, whilst some sulphide of arsenic remains in the residue. The sulphide of arsenic precipitated from the alkaline solution by hydrochloric acid, therefore, especially if

it consists of a few flakes only, must be washed, treated with ammonia, the solution evaporated, with addition of a small quantity of carbonate of soda, and the residue fused with cyanide of potassium in a stream of carbonic acid, so as to obtain an arsenical mirror. The residue, insoluble in carbonate of ammonia, should be treated as directed in 2.

4. The sulphide of antimony, sulphide of tin, and sulphide of arsenic are dissolved in boiling sulphide of sodium, avoiding unnecessary excess, and oxide of copper is added,* during continuous boiling, in quantity sufficient to desulphurize the sulphides. When the copper sulphide has settled to the bottom as a heavy powder, and the supernatant liquid has become colourless, it is filtered whilst still warm. The solution, which contains sodium arsenate, antimonate, and stannate, on cooling deposits—if much antimony be present—a white, granular precipitate of sodium antimonate. The cooled solution is mixed with one-fourth to one-third of its volume of alcohol to precipitate the sodium antimonate remaining in solution, and after some time this is collected on a filter, and the filtrate, which is turbid at first, is poured back on to the filter several times. The clear filtrate is then heated to drive off the alcohol, and an excess of a concentrated solution of chloride of ammonium is added. If this produces a precipitate, tin is present in large quantity; and if the solution also contains arsenic acid, it will be found in the precipitate, either in part or entirely. Without, however, paying any regard to whether a precipitate is formed by chloride of ammonium or not, some ammonia is added, and sulphuretted hydrogen passed in until the solution is clear or only turbid from the presence of whitish flocks of silica and alumina. The solution, filtered if necessary, is mixed with one-third of its volume of aqueous ammonia, the magnesia mixture described in § 133, 8, is added, and the whole is allowed to remain for an hour, when the arsenic separates as arsenate of ammonia and magnesia. The filtrate from this precipitate is acidified with hydrochloric acid, when the tin separates as sulphide (Berglund). This method is better adapted for the separation of large quantities than for the detection of traces of the respective metals.

5. In the analysis of alloys, stannic oxide, oxides of antimony, and arsenic acid are often obtained together as a residue insoluble in nitric acid. The best way is to fuse this residue with soda in a silver crucible, to treat the mass with water, and add one-third (by volume) of spirit of wine; the solution is then filtered from the undissolved antimonate of soda, and the latter is washed with spirit of wine mixed with a few drops of solution of carbonate of soda. In the presence of much tin, it is advisable to repeat the above treatment on the residue, in order to extract all the tin. The filtrate is acidified with hydrochloric acid, and the tin and arsenic are then precipitated from the hot solution as sulphides. On heating the precipitated sulphides in a stream of gaseous sulphuretted hydrogen, the whole of the tin is left as sulphide, whilst the sulphide of arsenic volatilizes, and may be received in solution of ammonia (H. Rose).

6. For the method of separating antimony and arsenic, and distinguishing between the two metals, by treating with sulphuretted hydro-

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* Copper oxide particularly well adapted for this purpose is obtained by evaporating a solution of nitrate of copper, heating the residue until it begins to decompose, then powdering the mass and continuing to heat it at a moderate temperature with constant stirring until the nitrate is completely decomposed.

gen the mirror produced by Marsh's process, and separating the resulting sulphides by means of hydrochloric acid gas, the reader is referred to § 132, 10. Antimony and arsenic, when mixed together in form of hydrogen compounds, may also be separated in the following ways:—

a. The gases, mixed with the excess of hydrogen, are passed first through a tube containing fragments of glass moistened with a dilute solution of acetate of lead, in order to retain the hydrochloric and hydrosulphuric gases, then in a slow stream through a solution of nitrate of silver. Almost all the antimony in the gas is removed as black antimonide of silver, Ag_3Sb [Ag_3Sb], whilst the arsenic passes into solution as arsenious acid, with reduction of the silver, and may be detected in the solution as arsenite of silver, by cautious addition of ammonia, or—after precipitating the excess of silver by hydrochloric acid—by means of sulphuretted hydrogen. As, however, a little antimony always passes into solution, the precipitated sulphide must not be set down as sulphide of arsenic without further examination, according to § 132, 12. The antimony in the precipitated antimonide of silver, which is often mixed with much silver, may be most readily detected by boiling the precipitate—thoroughly freed from arsenious acid by boiling with water—with tartaric acid and water. This will dissolve the antimony alone, which may then be readily detected by means of sulphuretted hydrogen in the solution acidified with hydrochloric acid (Lassaigne, A. W. Hofmann).

b. The gases mixed with the excess of hydrogen are passed through a rather wide glass tube, 3 or 4 inches of which at least are filled with caustic potassa in small lumps. The potassa decomposes the antimoniuretted hydrogen entirely, becoming coated with a lustrous film of metal. The arseniuretted hydrogen, on the contrary, is not decomposed, and may be detected readily on its exit from the tube by the production of the arsenical mirror (§ 132, 10), or by its action on solution of nitrate of silver (Dragendorff).

c. The gas is passed in a slow current through a mixture of 2 c.c. of a solution of silver nitrate (1 part of silver nitrate and 24 parts of water), 2 c.c. of concentrated nitric acid, and from 8 to 10 c.c. of water. When the black precipitate which is formed subsides, the action may be considered as complete. Bromine water is then added in excess to the flask containing the liquid and precipitate, or hydrochloric acid with sufficient chlorate of potassa to insure an excess of chlorine may be used instead; after a short time, the solution is filtered, tartaric acid, chloride of ammonium, and ammonia in excess are added to the filtrate, and the arsenic which is present as arsenic acid is precipitated as arsenate of ammonia and magnesia (§ 133, 8); after standing for some time, this is filtered off, the filtrate acidified with hydrochloric acid, and the antimony precipitated with sulphuretted hydrogen (E. Reichardt). If the liquid obtained by the methods *a*, *b*, and *c*, to which zinc and dilute sulphuric acid has been added, also contains tin, it will be separated in the metallic form by the continued action of the zinc; on pouring off the solution of zinc, heating the residue with hydrochloric acid, filtering, and adding a solution of mercuric chloride, a precipitate of mercurous chloride will be formed if tin is present.

d. If a solution of an oxide or chloride of arsenic be introduced into an apparatus in which hydrogen is evolved from an alkaline solution, such as aqueous potash and aluminium leaf or wire, and the gas passed through a silver solution, blackening will take place; this is a decisive proof of the presence of arsenic, as antimoniuretted hydrogen is not formed under these circumstances.

e. By acting on paper moistened with a solution of silver nitrate, with arseniuretted or antimoniuretted hydrogen, the wet portion of the paper becomes discoloured; for example, when arseniuretted hydrogen acts on paper moistened with a solution of 1 part of silver nitrate in 1 part of water, it is first coloured lemon-yellow and then black, whilst with a more dilute silver solution it is turned black at once. This reaction, in using which it must be remembered that sulphuretted and phosphoretted hydrogen yield similar colorations, has since it has been admitted into the second edition of the *Pharmacopœia Germanica* undergone a very varied elaboration and examination. A complete collection and critical discussion of these researches has been prepared by H. Beckurts.* It can, however, be merely referred to here.

7. On adding saturated sulphuretted hydrogen water to a solution containing arsenic and antimonic acids, acidified with hydrochloric acid, and then removing the excess of sulphuretted hydrogen by passing a stream of air through the liquid for several minutes, a precipitate is obtained which contains all the antimony as pentasulphide, but no arsenic. The arsenic may afterwards be precipitated by passing hydrogen sulphide through the filtrate heated at 70° (C. Bunsen).

8. Finally, chemists expert in flame reactions may employ Bunsen's† method, by which the presence of the sulphides of the three metals may be detected in the sulphuretted hydrogen precipitate by the flame and blowpipe reactions. H. Hager's methods, chiefly intended for the rapid detection of arsenic in pharmaceutical preparations, partly microscopic, to which he has given the names of Guttural ‡ and Kramatom § methods, can merely be referred to here.

9. Stannous and stannic oxides may be detected in presence of each other, by testing one portion of the solution for the stannous oxide with mercuric chloride, chloride of gold, or a mixture of ferricyanide of potassium with ferric chloride, and another portion for the stannic oxide, by pouring it into a concentrated hot solution of sulphate of soda. For the last test, the solution must not contain much free acid.

10. Oxide of antimony in presence of antimonic acid may be identified by the reaction described in § 131, 10; antimonic acid in presence of oxide of antimony, by heating the oxide, which must be free from other compounds, with hydrochloric acid and iodide of potassium (§ 131, 2 and 3).

11. Arsenious acid and arsenic acid in the same solution may be distinguished by means of nitrate of silver. If the precipitate contains but little arsenate and much arsenite of silver, it is necessary, in order to identify the former, to add cautiously and drop by drop exceedingly dilute nitric acid, which dissolves the yellow arsenite of silver first. A still better method of detecting small quantities of arsenic acid in presence of arsenious acid is to precipitate the solution with a mixture of sulphate of magnesia, chloride of ammonium, and ammonia (§ 133, 8), by which means an actual separation of the two acids is effected. Arsenious acid may be recognized in presence of arsenic acid by the

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* Pharm. Centralhalle, 1884, No. 17 *et seq.*

† Zeit. anal. Chem., **5**, 378.

‡ Pharm. Centralhalle, 1884, 277.

§ *Ibid.*, 1884, 265.

immediate precipitation of the acidified solution with sulphuretted hydrogen in the cold; also by the reduction of oxide of copper in alkaline solution; also by the separation of metallic silver on boiling the ammoniacal solution of the silver salts. To ascertain the degree of sulphuration of a sulphide of arsenic in a sulphur salt, the alkaline solution of the salt under examination is boiled with hydrated oxide of bismuth, the sulphide of bismuth formed is separated by filtration, and the filtrate tested for arsenious and arsenic acids. To distinguish between the tersulphide and pentasulphide of arsenic, the sulphur which may be present is first extracted by means of bisulphide of carbon, the residue dissolved in ammonia, and nitrate of silver added in excess; the sulphide of silver is then filtered off, and nitric acid cautiously added, when arsenite or arsenate of silver will be precipitated. In the last two methods, it should be noted that a portion of the arsenic is contained in the sulphide of bismuth or sulphide of silver as the case may be (Waitz).

Special Reactions of the rarer Oxides of the sixth group.

§ 135.

a. Oxide of Iridium, IrO_2 [IrO_2].

Iridium is found not only in combination with platinum and other metals in platinum ores, but more especially as a native alloy of osmium and iridium. Alloyed with platinum, it has of late been employed for crucibles, &c. Iridium resembles platinum, but it is brittle; it fuses with extreme difficulty; its sp. gr. is 22·4. In the compact state, or reduced at a red heat by hydrogen, it dissolves in no acid, not even in aqua regia (difference between iridium and gold and platinum); reduced in the moist way, say by formic acid, or if largely alloyed with platinum, it dissolves in aqua regia as bichloride, $IrCl_2$ [$IrCl_4$]. **Acid sulphate of potassa** in a state of fusion will oxidize, but not dissolve it (difference between iridium and rhodium). It is oxidized by fusion with **soda**, with access of air, or by fusion with nitrate of soda, forming sesquioxide of iridium, Ir_2O_3 [Ir_2O_3]; the compound of sesquioxide of iridium with soda dissolves partially in water; on heating it with aqua regia, it gives a deep-black solution of bichloride of iridium, $IrCl_2$ [$IrCl_4$], and chloride of sodium.

If iridium in powder is mixed with chloride of sodium, the mixture heated to incipient redness, and treated with **chlorine**, iridiochloride of sodium is formed, which yields a deep reddish-brown solution with water. **Potassa,** added in excess, colours the solutions greenish, a little brownish-black iridiochloride of potassium being precipitated at the same time. If the solution is heated, and exposed to the air for some time, it acquires at first a reddish tint, which changes afterwards to azure blue (characteristic difference between iridium and platinum); if the solution is now evaporated to dryness, and the residue treated with water, a colourless liquid is obtained, leaving a blue deposit of binoxide of iridium. **Sulphuretted hydrogen** in the first place decolorizes solutions of bichloride of iridium, the sesquichloride, Ir_2Cl_3 [Ir_2Cl_6], being formed, with separation of sulphur; finally brown sulphide of iridium is precipitated. **Sulphide of ammonium** produces the same precipitate, which redissolves readily in excess of the precipitant. **Chloride of potassium** precipitates iridiochloride of potassium as a dark-brown powder, insoluble in concentrated solutions of chloride of potassium. **Chloride of ammonium** from concentrated solutions precipitates iridiochloride of ammonium in the form of a dark-red powder, consisting of microscopic octahedrons, insoluble in concentrated solutions of chloride of ammonium. Ammonium and potassium iridiochloride are turned olive-green by **nitrite of potassa,** especially in hot solution, owing to the formation of ammonium or potassium iridiosesquichloride,

$$2(KCl,IrCl_2)+KO,NO_3=3KCl,Ir_2Cl_3+NO_4$$
$$[2K_2IrCl_6+2KNO_2=6KIr_2Cl_7+2NO_2],$$

which crystallizes out on cooling. On heating or evaporating the green solution with excess of nitrite of potassa, it turns yellow, and when boiled deposits a white precipitate which is almost insoluble in water and hydrochloric acid. (This reaction may be taken advantage of to separate iridium from platinum, Gibbs.) If the iridiochloride of ammonium is dissolved in water by boiling, and **oxalic acid** is added, a reduction of the bichloride to sesquichloride takes place, so that the solution remains clear on cooling (difference between iridium and platinum, C. Lea). If chloride of iridium solution is boiled with **stannous chloride**, excess of potassa added, and the mixture boiled again, a fawn-coloured precipitate is produced. **Ferrous sulphate** decolorizes the solution, but does not produce a precipitate. **Zinc** precipitates black metallic iridium. On suspending oxide of iridium in a solution of **sulphite of potassa**, saturating with **sulphurous acid**, and boiling with renewal of the evaporating water until all the free sulphurous acid is expelled, the whole of the iridium is converted into insoluble sulphite of iridium oxide (any oxide of platinum which may be present will remain dissolved as sulphite of protoxide of platinum and potassa, C. Birnbaum). When compounds of iridium are ignited with **carbonate of soda** in the upper oxidizing flame, they yield the metal; this when elutriated out is gray, devoid of lustre, and without ductility.

b. Oxides of Molybdenum.

Molybdenum is not widely distributed in nature, and is found only in moderate quantities, more especially as sulphide of molybdenum and as molybdate of lead (yellow lead ore). Since molybdate of ammonia has come into use as a means of detecting and determining phosphoric acid, molybdenum has acquired considerable importance in practical chemistry. Molybdenum is tin-white and hard, when heated in the air it oxidizes, it is soluble in nitric acid and very difficult to fuse. The protoxide, MoO [MoO], and sesquioxide, Mo_2O_3 [Mo_2O_3], are black, the oxide, MoO_2 [MoO_2], is dark-brown or dark-violet. When heated in the air or treated with nitric acid, the metal and oxides are all converted into molybdic acid, MoO_3 [MoO_3]; this is a white porous mass, which in water separates into fine scales, and dissolves to a slight extent; it fuses at a red heat; in closed vessels, it volatilizes only at a very high temperature, in the air it volatilizes easily at a red heat and sublimes in transparent laminæ and needles. On igniting it in a current of hydrogen, it is first converted into the binoxide, and afterwards by strong and long-continued heating into the metal. The non-ignited molybdic acid dissolves in acids. The solutions are colourless; the hydrochloric solution is soon coloured by contact with **zinc**, and immediately on addition of **stannous chloride**, the colour being brown, green, or blue according to the proportion of reducing agent and the concentration of the solution. Digested with **copper**, the sulphuric acid solution turns blue, the hydrochloric acid solution brown; the reaction often requires some time. Ferrous sulphate solution acidified with sulphuric acid colours it permanently blue. **Ferrocyanide of potassium** produces a reddish-brown precipitate in solutions acidified with hydrochloric acid. **Infusion of galls** colours solutions of molybdates of the alkalies deep red passing into brown, and on adding hydrochloric acid a brown precipitate or brown coloration is produced. **Sulphuretted hydrogen**, added in small proportion, imparts a blue tint to solutions of molybdic acid; in larger proportion, it produces a brownish-black precipitate; the supernatant liquid appears green at first, but if it be allowed to stand for some time, heated, and sulphuretted hydrogen repeatedly passed into it, the whole of the molybdenum present will ultimately though slowly separate as brownish-black tersulphide of molybdenum. The precipitated tersulphide of molybdenum dissolves in sulphides of the alkali metals; acids precipitate from the sulphur salts the tersulphide, MoS_3 [$\mathbf{MoS_3}$], application of heat promotes the separation. Boiling oxalic acid solution does not attack sulphide of molybdenum (method of separation from sulphide of tin formed in the wet way, the latter being soluble, Clarke). By heating to redness in the air, or by heating with nitric acid, sulphide of molybdenum is converted into molybdic acid. **Sulphocyanate of potassium**, if added to a solution of molybdic acid containing hydrochloric acid, produces no colour until zinc is added, when the liquid becomes crimson; the coloration is due to the formation of a sulphocyanate of molybdenum corresponding to the oxide or sesquioxide. Phosphoric acid does not destroy the colour (difference from sulphocyanate of iron). On shaking the red fluid with ether, the sulphocyanate dissolves and the ether becomes coloured (C. D. Braun).

Molybdic acid dissolves readily in solutions of caustic **alkalies** or of **carbonates of the alkalies**; from the concentrated solutions, **nitric acid** or **hydrochloric acid** throws down molybdic acid, which redissolves in a large excess of the precipitant. The solutions of molybdates of the alkalies are coloured yellow by **sulphuretted hydrogen**, and then on adding an acid they give a brownish-black precipitate. If a solution of molybdic acid in excess of ammonia is boiled for some time with **yellow sulphide of ammonium**, besides the brownish-black precipitate, an intensely red solution is obtained, unless a very large excess of sulphide of ammonium is used. For the deportment of molybdic acid with **phosphoric acid** and ammonia, see § 142, 10.

If a little concentrated **sulphuric acid** is poured on to a piece of platinum foil bent into the shape of a cup, a little powdered molybdic acid or a molybdate added, and the mixture heated until thick vapours are given off, the sulphuric acid when cold acquires an intense blue colour on adding to it a little spirit, or on breathing repeatedly on the platinum foil (v. Kobell, Schön, Maschke). If antimonic acid or much stannic oxide is present, the mixture must be evaporated to dryness with phosphoric acid before it is heated with sulphuric acid.

When molybdic acid is heated on charcoal in the **oxidizing flame**, it volatilizes, coating the charcoal with a yellow, often crystalline, powder, which turns white on cooling. In the **reducing flame**, the acid suffers reduction to the metallic state, the molybdenum being obtained as a gray powder by elutriating the charcoal support. Sulphide of molybdenum in the oxidizing flame gives sulphurous acid and an incrustation of molybdic acid on the charcoal. If molybdic acid or a molybdate is heated for a short time in a platinum spiral with carbonate of soda, the product dissolved in a few drops of warm water, and the solution taken up by strips of filter paper, the molybdic acid in them can be recognized by adding hydrochloric acid and ferrocyanide of potassium, stannous chloride, or sulphide of ammonium and hydrochloric acid (Bunsen).

c. Oxides of Tungsten.

Tungsten is not widely distributed, and is not abundant. The principal tungsten minerals are tungstate of lime and a double tungstate of ferrous oxide and protoxide of manganese called wolfram. As obtained by the reduction of tungstic acid in a current of hydrogen at an intense red heat, it is an iron-gray powder, very difficultly fusible. By ignition in the air, this powder is converted into tungstic acid, WO_3 [$\mathbf{WO_3}$]; whilst if ignited in a current of dry chlorine free from air dark-violet terchloride of tungsten, WCl_3 [$\mathbf{WCl_6}$], sublimes; as a rule, however, this also contains lower chlorides and sometimes oxychloride. When heated with water, this chloride is decomposed with formation of hydrated tungstic acid. Tungsten is insoluble or almost insoluble in acids, even in aqua regia, and also in potassa; it dissolves, however, in the latter if mixed with a hypochlorite. Oxide of tungsten, WO_2 [$\mathbf{WO_2}$], is brown; by intense ignition with free access of air, it is converted into tungstic acid. Tungstic acid is lemon-yellow, dark-orange when hot, fixed, insoluble in water and acids. With water and with bases, it forms two series of compounds, tungstic acid and metatungstic acid. By fusing tungstic acid with acid sulphate of potassa, and treating the fused mass with water, an acid solution is obtained, which contains no tungstic acid; after the removal of this solution, the residue, consisting of tungstate of potassa with a large excess of tungstic acid, completely dissolves in water containing carbonate of ammonia (means of separating tungstic from silicic acid). Tungstates of the alkalies soluble in water are formed readily by fusion with alkaline carbonates, but only with difficulty by boiling with their solutions. In the solution of these tungstates, **hydrochloric acid, nitric acid,** and **sulphuric acid** produce white precipitates, which turn yellow on boiling and are insoluble in an excess of the acids (difference from molybdic acid), but soluble in ammonia; the residue after removal of the acid dissolves, however, by prolonged treatment with water. On evaporating to dryness with an excess of hydrochloric acid, heating the residue at 120°, and treating it with water, the tungstic acid is left undissolved. **Phosphoric acid** produces no precipitate; it rapidly changes the tungstic acid into metatungstic acid, and thus prevents the precipitation by other acids. **Chloride of barium, chloride of calcium, acetate of lead, nitrate of silver,** and **mercurous nitrate** produce white precipitates. **Ferrocyanide of potassium,** with addition of acid, colours the liquid deep brownish-red, and after some time produces a precipitate of the same colour. **Tincture of galls,** with a little acid added, produces a brown precipitate. **Sulphuretted hydrogen** barely precipitates acid solutions. **Sulphide of ammonium** fails to precipitate solutions of tungstates of the alkalies; on acidifying the mixture, light-brown tersulphide of tungsten, WS_3 [$\mathbf{WS_3}$], is thrown down; this is slightly soluble in pure water, but insoluble in water containing salts. **Stannous chloride** produces a yellow precipitate; on acidifying with hydrochloric acid and applying heat, this precipitate acquires a beautiful blue colour (highly delicate and characteristic reaction). If solutions of tungstates of alkalies are mixed with hydrochloric acid, or, better still, with an excess of phosphoric acid, and **zinc** is added, the liquid acquires a beautiful blue colour. The blue coloration produced in the hydrochloric acid solution changes to a fugitive red, and then becomes brownish-black. **Ferrous sulphate** produces an ochreous precipitate, which does not become blue on the addition of acids (distinction from molybdic acid). The metatungstates are mostly soluble in water. Long-continued boiling of their solutions with sulphuric, hydrochloric, or nitric acid causes the precipitation of the ordinary hydrated tungstic acid. **Microcosmic salt** dissolves tungstic acid. The bead, exposed to the oxidizing flame, appears clear, varying from colourless to yellowish; in the reducing flame, it becomes pure blue, and on adding ferrous sulphate blood-red. By mixing with a little **carbonate of soda,** and exposing in the cavity of the charcoal support to the reducing flame, tungsten in powder is obtained, which may be separated by elutriation. If tungstic acid is fused with carbonate of soda on a platinum spiral, the product warmed with a few drops of water, and the solution absorbed by strips of filter paper, these will give the tests for tungstic acid, namely, a yellow coloration when moistened with hydrochloric acid and warmed, and a blue on adding stannous chloride and warming; sulphide of ammonium either alone or after the addition of hydrochloric acid, does not colour the paper, but on warming it it turns blue or green (Bunsen). The tungstates which are insoluble in water may, most of them, be decomposed by digestion with acids. Wolfram, which strongly resists the action of acid, may be fused with carbonated alkali, when water will dissolve out of the fused mass tungstate of the alkali.

d. Oxides of Tellurium.

Tellurium is not widely distributed, and is found in small quantities only in the native state, or alloyed with other metals, or as tellurous acid. It is a white, brittle, but readily fusible metal, which may be sublimed in a glass tube. Heated in the air, it burns with a greenish-blue flame, emitting thick white fumes of tellurous acid. Tellurium is insoluble in hydrochloric acid, but dissolves readily in nitric acid, forming tellurous acid, TeO_2 [TeO_2]. Tellurium in powder dissolves in cold concentrated sulphuric acid, yielding a purple-coloured solution, from which it separates again on adding water. Tellurous acid is white; at a gentle red heat, it fuses to a yellow liquid; and on being strongly ignited in the air it volatilizes, but does not yield a crystalline sublimate. The anhydrous acid dissolves readily in hydrochloric acid, sparingly in nitric acid, freely in solution of potassa, slowly in ammonia, barely in water. The hydrate of tellurous acid is white; it is perceptibly soluble in cold water, and dissolves easily in hydrochloric acid and in nitric acid. On adding water to the solution in acid, a white hydrate is thrown down, and from the nitric acid solution nearly the whole of the tellurous acid separates after some time as a crystalline precipitate, even without addition of water. Caustic **alkalies and carbonates of the alkalies** throw down from the hydrochloric acid solution a white hydrate, which is soluble in an excess of the precipitant. In acid solutions, **sulphuretted hydrogen** produces a brown precipitate, TeS_2 [TeS_2], resembling stannous sulphide in colour; this is very freely soluble in sulphide of ammonium. **Sulphite of soda, stannous chloride,** and **zinc** precipitate black metallic tellurium. If a solution of tellurous acid in excess of potassa or soda is heated with **grape-sugar**, the tellurium separates in the metallic state (Stolba). Tellurous acid produces a white precipitate in a mixture of chloride of magnesium, chloride of ammonium, and ammonia; this is not crystalline (distinction from selenious acid) (Hilger, v. Gerichten). Telluric acid, TeO_3 [TeO_3], is formed by fusing tellurium or tellurites with nitrates and carbonates of the alkalies; the fused mass is soluble in water. The solution remains clear when acidified with hydrochloric acid in the cold; but, on boiling, chlorine is evolved, and tellurous acid formed; the solution is therefore now precipitated by water if the excess of acid is not too great.

If tellurium, its sulphide, or an oxygen compound of the metal is fused with **cyanide of potassium** in a stream of hydrogen, a cyanide of tellurium and potassium is formed. The fused mass dissolves in water, but a current of air throws down the whole of the tellurium from the solution (difference and means of separating tellurium from selenium). If a little water is poured on finely powdered tellurium or an ore of tellurium—telluride of gold, for example—in a porcelain basin, some mercury added, and then a little sodium amalgam, the water is at once coloured a beautiful violet by the telluride of sodium formed (G. Küstel). When tested in the dry way by Bunsen's method (p. 23), the compounds of tellurium give a grayish-blue colour to the upper reducing flame, while at the same time the upper oxidizing flame appears green. The volatilization is not accompanied by any odour. The **incrustation** produced by reduction is black, with a blackish-brown edge, and gives a crimson solution when heated with concentrated sulphuric acid. The incrustation of oxide is white, scarcely visible; stannous chloride colours it black, metallic tellurium being separated. When heated with **carbonate of soda** in the **stick of charcoal**, compounds of tellurium yield telluride of sodium, which when placed on clean silver and moistened produces a black mark, and when treated with hydrochloric acid (in the presence of enough tellurium) emits an odour of telluretted hydrogen with separation of tellurium.

e. Oxides of Selenium.

Selenium is of rare occurrence in nature in the form of selenides of the metals. It is found occasionally in the flue-dust of pyrites-furnaces, and also in Nordhausen oil of vitriol. It resembles sulphur in some respects, tellurium in others. Fused selenium is grayish-black; it volatilizes at a high temperature, and may be sublimed. When heated in the air, it burns, forming selenious acid, SeO_2 [$\mathbf{SeO_2}$], and exhaling a characteristic odour resembling that of decaying horse-radish. Selenium is soluble in bisulphide of carbon; in contact with mercury this forms black selenide of mercury. Concentrated sulphuric acid dissolves selenium without oxidizing it; on diluting the solution, the selenium separates in red flakes. Nitric acid and aqua regia dissolve selenium, forming selenious acid; this is converted at 200° into a yellow gas. Sublimed anhydrous selenious acid forms white four-sided needles, and its hydrate crystallizes in forms resembling those of nitrate of potassa. Both the acid and its hydrate dissolve readily in water to a strongly acid solution. Of the neutral salts, only those with the alkalies are soluble in water; the solutions have alkaline reactions. All selenites dissolve readily in nitric acid, with the exception of the selenites of lead and silver, which are only sparingly soluble. In solutions of selenious acid or of selenites (in presence of free hydrochloric acid), **sulphuretted hydrogen** produces a yellow precipitate of sulphide of selenium (?), which, when heated, turns reddish-yellow; it is soluble in sulphide of ammonium. **Chloride of barium** produces (after neutralization of the free acid, should any be present) a white precipitate of selenite of baryta, which is soluble in hydrochloric acid and in nitric acid. **Stannous chloride** or **sulphurous acid**, with addition of hydrochloric acid, produces a red precipitate of selenium, which is gray if the solution is hot. Metallic **copper** when placed in a warm solution of selenious acid containing hydrochloric acid becomes immediately coated black; if the solution remains long in contact with the copper, it turns light red from separation of selenium (Reinsch). In a mixture of **chloride of magnesium**, chloride of ammonium, and ammonia, selenious acid, generally after some time, produces a colourless crystalline precipitate of selenite of magnesia soluble in acids (Helger, v. Gerichten). Selenic acid, SeO_3 [$\mathbf{SeO_3}$], is formed by heating selenium or its compounds with carbonates and nitrates of the alkalies. The fused mass dissolves in water; the solution remains clear when acidified with hydrochloric acid; when concentrated by boiling, it evolves chlorine, whilst the selenic acid is reduced to selenious acid. By fusing selenium or its compounds with **cyanide of potassium** in a stream of hydrogen, a cyanide of selenium and potassium is obtained, from which the selenium is not separated by exposure to the air (as is the case with tellurium); it is precipitated, however, on long-continued boiling, after addition of hydrochloric acid. When tested according to p. 23, compounds of selenium give a bright blue **colour to the flame**, and by **volatilization** and combustion of the vapour, the above-mentioned odour is emitted. The **incrustation** produced by reduction is brick-red to cherry-red, and gives a dirty green solution with concentrated sulphuric acid. The incrustation of oxide is white, and when moistened with stannous chloride becomes red from separated selenium. In the **charcoal stick** with **carbonate of soda**, selenide of sodium is formed, which when placed on silver and moistened produces a black mark, and when treated with acids yields seleniuretted hydrogen.

B.—Behaviour of the Acids and their Radicles.

§ 136.

The reagents which serve for the detection of the acids are divided, like those used for the detection of the bases, into general reagents, that is, such as indicate the group to which the acid under examination belongs; and special reagents, that is, such as serve to effect the detection and identification of the individual acids. The groups into which we classify the various acids can scarcely be defined with the same degree of precision as those into which the bases are divided.

The two principal groups into which acids are divided are those of the inorganic and the organic acids. This classification is based upon those characteristics which are most useful for the purposes of analysis, quite irrespective of theoretical considerations. We therefore take, as the characteristic mark to guide us in the classification into organic and inorganic acids, the behaviour of the various acids at a high temperature, and call those acids organic acids of which the salts (particularly those which have an alkali or an alkaline earth for base) are decomposed by ignition, with separation of carbon. By fixing on this deportment at a high temperature as the distinctive characteristic of an organic acid, we are enabled to determine at once by a most simple preliminary experiment the class to which the acid belongs. The salts of organic acids with alkalies or alkaline earths are converted into carbonates when heated gently to redness.

Before proceeding to the special study of the several acids considered in this work, a general view of the whole of them is given as in the case of the bases.

I. INORGANIC ACIDS.

First Group:

Division *a.* Chromic acid (sulphurous and hydrosulphurous acids, iodic acid).

Division *b.* Sulphuric acid (hydrofluosilicic acid).

Division *c.* Phosphoric acid, boric acid, oxalic acid, hydrofluoric acid (phosphorous acid).

Division *d.* Carbonic acid, silicic acid.

Second Group:

Chlorine and hydrochloric acid; bromine and hydrobromic acid; iodine and hydriodic acid; cyanogen and hydrocyanic acid, together with hydroferro- and hydroferri-cyanic acids; sulphur and sulphuretted hydrogen (nitrous acid, hypochlorous acid, chlorous acid, hypophosphorous acid).

Third Group:

Nitric acid, chloric acid (perchloric acid).

II. ORGANIC ACIDS.

First Group:

Oxalic acid, tartaric acid, citric acid, malic acid (racemic acid).

Second Group:

Succinic acid, benzoic acid, salicylic acid.

Third Group:

Acetic acid, formic acid (lactic acid, propionic acid, butyric acid).

The acids the names of which are spaced (as chromic acid) are more frequently met with in the examination of minerals, waters, ashes of plants, industrial products, food-stuffs, medicines, &c.; the others are more rarely met with.

I. INORGANIC ACIDS.

§ 137.

First Group.

Acids which are precipitated from Neutral Solutions by Chloride of Barium.

This group is again subdivided into four divisions, viz.:

a. Acids which are decomposed in acid solution by sulphuretted hydrogen, and to which, therefore, attention has been already directed in the testing for bases, viz., chromic acid (sulphurous acid and hyposulphurous acid, the latter because it is decomposed and detected by the mere addition of hydrochloric acid to the solution of one of its salts; and also iodic acid).*

b. Acids which are not decomposed in acid solution by sulphuretted hydrogen, and the baryta compounds of which are insoluble in hydrochloric acid: sulphuric acid (hydrofluosilicic acid).

c. Acids which are not decomposed in acid solution by sulphuretted hydrogen, and the baryta compounds of which dissolve in hydrochloric acid, apparently without decomposition, inasmuch as the acids cannot be completely separated from the hydrochloric acid solution by heating or evaporation: phosphoric acid, boric acid, oxalic acid, hydrofluoric acid (phosphorous acid). (Oxalic acid belongs more properly to the organic group. We consider it, however, here with the acids of the inorganic class, as the property of its salts to be decomposed on ignition without actual carbonization may lead to its being overlooked as an organic acid.)

d. Acids which are not decomposed in acid solution by sulphuretted hydrogen, and the baryta salts of which are soluble in hydrochloric acid with separation of the acid: carbonic acid, silicic acid.

First Division of the First Group of the Inorganic Acids.

§ 138.

Chromic Acid, CrO_3 [CrO_3].

1. Chromic acid is obtained as a scarlet crystalline mass, or in the form of distinct acicular crystals. On ignition, it is resolved into sesquioxide of chromium and oxygen. It deliquiesces rapidly on exposure to the air. It dissolves in water, imparting to the solution a deep reddish-yellow tint, which is visible even in very dilute solutions.

2. The chromates are all red or yellow, and for the most part

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* To this first division of the first group of inorganic acids belong properly also all the oxygen compounds of a distinctly pronounced acid character, which have been discussed already with the Sixth Group of the metallic oxides (acids of arsenic, antimony, selenium, &c.). But as the reactions of these compounds with sulphuretted hydrogen tend rather to confounding them with other metallic oxides than with other acids, it appeared the safer course to class these compounds, which may be said to stand between the bases and the acids, with the metallic oxides.

insoluble in water; some of them are decomposed by ignition. Those with alkaline bases are soluble in water, and when neutral are fixed; the solutions of the neutral alkaline chromates are yellow, those of the alkaline dichromates are reddish-yellow. These tints are visible in highly dilute solutions. The yellow colour of the solution of a neutral salt changes to reddish-yellow on the addition of an acid, owing to the formation of an acid chromate.

3. **Sulphuretted hydrogen** acting on an acidified solution of a chromate produces first a brownish coloration of the fluid, then a green coloration, arising from the salt of sesquioxide of chromium formed; this change of colour is attended with separation of sulphur, which imparts a milky appearance to the liquid,

$$KO,2CrO_3 + 4(HO,SO_3) + 3HS = KO,SO_3 + Cr_2O_3,3SO_3 + 7HO + 3S$$

$$[K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S].$$

Heat promotes this reaction, part of the sulphur being in that case converted into sulphuric acid.

4. **Sulphide of ammonium**, when added in excess to a solution of an acid chromate of an alkali, immediately produces a brownish-gray-green precipitate of hydrated chromate of sesquioxide of chromium; on boiling, the whole of the chromium separates as green hydrated oxide. In a solution of neutral chromate of potassa, at first a dark brownish coloration alone is produced, but the brownish-gray-green precipitate above mentioned soon separates.

5. Chromic acid may also be reduced to sesquioxide by means of many other substances, more particularly by **sulphurous acid**, by heating with concentrated **hydrochloric acid**, or with the dilute acid and alcohol (in which case chloride of ethyl and aldehyde are formed), by metallic **zinc**, by heating with **tartaric acid**, **oxalic acid**, &c. All these reactions are clearly characterized by the change of the red or yellow colour of the solution to the green or violet tint of the salt of sesquioxide of chromium.

6. **Chloride of barium** produces in aqueous solutions of chromates a yellowish-white precipitate of chromate of baryta, BaO,CrO_3 [$BaCrO_4$], soluble in dilute hydrochloric or nitric acid.

7. **Nitrate of silver** produces in aqueous solutions of chromates a dark purple-red precipitate of chromate of silver, AgO,CrO_3 [Ag_2CrO_4], soluble in nitric acid and in ammonia; in slightly acid solutions it produces a precipitate of dichromate of silver, $AgO,2CrO_3$ [$Ag_2Cr_2O_7$].

8. **Acetate of lead** produces in an aqueous or acetic acid solution of a chromate a yellow precipitate of chromate of lead, PbO,CrO_3 [$PbCrO_4$], soluble in potassa or soda, sparingly soluble in dilute nitric acid, insoluble in acetic acid. When heated with alkalies, the yellow neutral salt is converted into basic red chromate of lead,

$$2PbO,CrO_3 \quad [PbCrO_4PbO].$$

9. If a very dilute acid solution of **peroxide of hydrogen*** (about

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* Solution of peroxide of hydrogen may be easily prepared by triturating a fragment of peroxide of barium (about the size of a pea) with some water, and adding it with stirring to a mixture of about 30 c.c. hydrochloric acid and 120 c.c. water. The solution keeps a long time without suffering decomposition. In default of peroxide of barium, impure peroxide of sodium may be used instead; this may be obtained by heating a fragment of sodium in a porcelain capsule until it takes fire, and letting it burn.

6 or 8 c.c.) is covered with a layer of ether (about half a centimetre thick), and a solution containing chromic acid is added, the solution of peroxide of hydrogen acquires a fine blue colour. By repeatedly inverting the test-tube, closed with the thumb, without much shaking, the solution becomes colourless, whilst the ether acquires a blue colour. The latter reaction is particularly characteristic. 1 part of chromate of potassa in 40,000 parts of water suffices to produce it distinctly (Storer); the presence of vanadic acid materially impairs the delicacy of the test (Werther).* The blue coloration is due to perchromic acid, Cr_2O_7 [Cr_2O_7]. After some time, reduction of the chromic acid to sesquioxide takes place, and the ether becomes colourless.

10. If insoluble chromates are fused with **carbonate of soda**, a little chlorate of potassa being added and the fused mass treated with water, a yellow solution is obtained containing an alkaline chromate; on adding an acid, the yellow colour changes to reddish-yellow. The oxides are left either in the pure state or as carbonates.

11. The compounds of chromic acid show the same reactions with **microcosmic salt** and with **borax** in the blowpipe flame, as the compounds of sesquioxide of chromium.

12. Very minute quantities of chromic acid may be detected in aqueous solutions by the following methods: *a.* the solution, slightly acidified with sulphuric acid, is mixed with a little tincture of guaiacum (1 part of the resin to 100 parts of alcohol of 60 per cent.); the mixture acquires an intense blue colour, but this speedily disappears if traces only of chromic acid are present (H. Schiff). *b.* the solution of the alkaline chromate, which must be *as neutral as possible*, is mixed with a dilute decoction of logwood boiled half-a-minute and allowed to stand half-an-hour; a very intense black coloration will be produced; in the presence of exceedingly small quantities of chromic acid, the colour is violet-red (R. Wildenstein).

Chromic acid being reduced by sulphuretted hydrogen to sesquioxide of chromium, this acid is in the course of analysis always found in the examination for bases. The intense colour of the solutions containing chromic acid, the delicate reaction with peroxide of hydrogen, and the characteristic precipitates produced by solutions of salts of lead and of silver, afford ready means for its detection. For the discovery of traces of chromium present in many minerals, for instance, in serpentine, the reactions in 12 may be used after the mineral has been fused with alkaline carbonate and chlorate. For the detection of neutral chromates of the alkalies in the presence of acids, and of acid chromate in the presence of neutral chromate and chromic acid in the presence of acid chromates of the alkalies, compare E. Donath (Zeit. anal. Chem. **18**, 78).

Special reactions of the Rarer Acids of the First Division.

§ 139.

a. Sulphurous Acid, SO_2 [SO_2].

Sulphurous acid is a colourless, uninflammable gas, having the stifling odour of burning sulphur. It dissolves abundantly in water; the solution has the odour of the gas, reddens litmus-paper, and bleaches Brazil-wood paper. It gradually absorbs oxygen from the air, and is converted into sul-

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* Jour. pr. Chem., **83**, 195.

phuric acid. The salts are colourless. Of the neutral sulphites, it is only those with alkaline base which are readily soluble in water; many of the sulphites insoluble or sparingly soluble in water dissolve in an aqueous solution of sulphurous acid, but are reprecipitated on boiling. All the sulphites evolve sulphurous acid when treated with **sulphuric acid.** **Chlorine water** converts sulphites into sulphates, and generally dissolves them. **Chloride of barium** precipitates neutral sulphites, but not free sulphurous acid; the precipitate is soluble in hydrochloric acid. **Sulphuretted hydrogen** decomposes free sulphurous acid, water and pentathionic acid being formed and free sulphur separated. If a piece of clean **copper** wire is added to a solution of sulphurous acid mixed with an equal volume of hydrochloric acid, and the mixture boiled, the copper appears black, as if covered with soot, if much sulphurous acid is present; but only dull if a little is present (H. Reinsch). If a trace of sulphurous acid or of a sulphite is introduced into a flask in which hydrogen is being evolved from **zinc** free from sulphur or **aluminium** and **hydrochloric acid,** sulphuretted hydrogen is immediately evolved along with the hydrogen, and the gas produces a black coloration or a black precipitate in a solution of acetate of lead to which soda has been added in sufficient quantity to redissolve the precipitate formed at first. Sulphurous acid is a powerful reducing agent; it reduces chromic acid, permanganic acid, iodic acid, and mercuric chloride (to subchloride), decolorizes iodide of starch, produces a blue precipitate in a mixture of ferricyanide of potassium and ferric chloride, &c. **Nitrate of silver** added to a solution of sulphurous acid throws down a white precipitate of sulphite of silver soluble in nitric acid. With a hydrochloric acid solution of **stannous chloride,** a yellow precipitate of bisulphide of tin is formed after some time. If an aqueous solution of an alkaline sulphite is carefully neutralized with acetic acid, or bicarbonate of soda is added to it, according as it has an alkaline or acid reaction (excess of the bicarbonate is without effect, but excess of caustic alkali or simple carbonate or of carbonate of ammonia prevents the reaction), and a relatively large amount of solution of **sulphate of zinc** mixed with a very small quantity of **nitroprusside of sodium** be then added, the solution will become red if the quantity of the sulphite present is not too small; when, however, the amount of sulphite is very minute, the coloration makes its appearance only after the addition of some solution of ferrocyanide of potassium. If the quantities are not altogether too minute, a purple-red precipitate will form on the addition of the ferrocyanide of potassium (Bödeker). Hyposulphites of the alkalies do not show this reaction.

b. Hyposulphurous Acid or Thiosulphuric Acid, S_2O_2 [$\mathbf{S_2O_2}$].

This acid does not exist in the free state. Most of its salts are soluble in water. The solutions of most hyposulphites may be boiled without suffering decomposition; hyposulphite of lime, on boiling, is resolved into sulphite of lime and sulphur. When the hyposulphites of the alkalies are heated without access of air, they are decomposed, water, sulphur, and sulphuretted hydrogen volatilizing, whilst a residue is left, consisting of a sulphide and sulphate of the metal. If **hydrochloric acid** or **sulphuric acid** is added to a solution of a hyposulphite, it remains at first clear and inodorous, but after a short time—the shorter, the more concentrated the solution—it becomes more and more turbid, owing to the separation of sulphur, and acquires the odour of sulphurous acid; the application of heat promotes this decomposition. **Nitrate of silver** produces a white precipitate of hyposulphite of silver, soluble in excess of the hyposulphite; after a little while (on heating, almost immediately) this precipitate turns black, being decomposed into sulphide of silver and sulphuric acid. Hyposulphite of soda dissolves chloride of silver; on adding an acid, the solution remains clear at first, but after some time, and immediately on boiling, sulphide of silver separates. **Chloride of barium** produces a white precipitate, which is soluble in much water, more especially hot water, and is decomposed by hydrochloric acid.

Ferric chloride colours the solutions of alkaline hyposulphites reddish-violet (difference from alkaline sulphites); after a time, the liquid loses its colour, especially if heated, ferrous chloride being formed. An acidified solution of **chromic acid** is immediately reduced to the green sesquioxide by hyposulphites; if the solution is not acidified, it becomes brown, and on heating deposits brown chromate of chromium. **Iodide of starch** and an acidified solution of permanganate of potassa are at once decolorized. With **zinc** or **aluminium** and **hydrochloric acid**, the hyposulphites behave like the sulphites.

When, as is often the case, it is required to find sulphites and hyposulphites of the alkalies in presence of alkaline sulphides, solution of sulphate of zinc is first added until the sulphide is decomposed; the sulphide of zinc is then filtered off, and one part of the filtrate is tested for hyposulphurous acid by addition of acid, another portion for sulphurous acid with nitroprusside of sodium, &c.

c. Iodic Acid, IO_5 [I_2O_5].

Iodic acid is a white crystalline powder, the hydrate forms colourless rhombic crystals, both are readily soluble in water, and when moderately heated are decomposed into iodine, oxygen, and—in the case of the hydrate—water. The salts are decomposed by ignition, being resolved either into oxygen and a metallic iodide, or into iodine, oxygen, and a metallic oxide: the iodates with an alkaline base alone dissolve readily in water. **Chloride of barium** throws down from solutions of iodates of the alkalies a white precipitate of iodate of baryta, which is soluble in nitric acid; **nitrate of silver** a white granular-crystalline precipitate of iodate of silver, which dissolves readily in ammonia, but only sparingly in nitric acid. **Acetate of lead** throws down iodate of lead as a white precipitate almost insoluble in water and soluble with difficulty in nitric acid. From solutions of iodic acid, **sulphuretted hydrogen** throws down iodine, which then dissolves in the hydriodic acid formed; sulphur is separated at the same time. If an excess of sulphuretted hydrogen is used, the solution becomes colourless, and a further separation of sulphur takes place, the whole of the iodine being converted into hydriodic acid. Iodic acid combined with bases is also decomposed by sulphuretted hydrogen. **Sulphurous acid** throws down iodine, which by excess of the acid is converted into hydriodic acid. A boiling concentrated solution of **oxalic acid** liberates all the iodine from iodic acid. **Phosphorus**, both ordinary and amorphous (the latter with great energy), reduces iodic acid, whether free or in combination, even in very dilute solution; phosphoric acid is formed and iodine liberated (Pollacci).

SECOND DIVISION OF THE FIRST GROUP OF THE INORGANIC ACIDS.

§ 140.

Sulphuric Acid, SO_3 [SO_3]

1. Anhydrous sulphuric acid is a white feathery crystalline mass which fumes strongly on exposure to the air; hydrated sulphuric acid (which contains rather more water than corresponds with the formula, HO,SO_3 [H_2SO_4]), forms an oily liquid, colourless and transparent like water. Both the anhydrous and hydrated acid char organic substances, and combine with water in all proportions, the process of combination being attended with considerable elevation of temperature, and in the case of the anhydrous acid with a hissing noise.

2. The neutral sulphates are readily soluble in water with the

exception of the sulphates of baryta, strontia, lime, and lead. The basic sulphates of the oxides of the heavy metals which are insoluble in water dissolve in hydrochloric acid or in nitric acid. Most of the sulphates are colourless. The sulphates of the alkalies and alkaline earths undergo no change at a moderate red heat, but are decomposed more or less at a very high temperature; of the other sulphates, some are readily decomposed at a red heat, others resist decomposition altogether.

3. **Chloride of barium** produces, even in exceedingly dilute solutions of sulphuric acid and of the sulphates, a finely pulverulent, heavy, white precipitate of sulphate of baryta, BaO,SO_3 [$BaSO_4$], practically insoluble in dilute hydrochloric or nitric acid. From very dilute solutions, the precipitate separates only after standing for some time. Concentrated acids and concentrated solutions of many salts impair the delicacy of the reaction.

4. **Acetate of lead** produces a heavy white precipitate of sulphate of lead, PbO,SO_3 [$PbSO_4$], which is almost insoluble in water, still less in dilute sulphuric acid, and insoluble in alcohol; it is sparingly soluble in dilute nitric acid, but dissolves completely in hot concentrated hydrochloric acid. It is soluble in a boiling solution of acetate or tartrate of ammonia.

5. The sulphates of the alkaline earths which are insoluble in water and acids are converted into carbonates by fusion with **alkaline carbonates**; sulphate of lead, on the other hand, is reduced to the state of oxide, an alkaline sulphate being simultaneously formed in both cases. The sulphates of the alkaline earths and sulphate of lead are also resolved into insoluble carbonates and soluble alkaline sulphate by digestion or boiling with concentrated solutions of carbonates of the alkalies (comp. §§ 95, 12; 96, 9; 97, 9). In the case of sulphate of baryta, however, repeated boiling with fresh quantities of the solution is necessary in order to decompose it.

6. On fusing sulphates with **carbonate of soda on charcoal** in the inner flame of the blowpipe, or on heating them in the **stick of charcoal** (p. 24) in the lower reducing flame, the sulphuric acid is reduced, and sulphide of sodium formed, which may be readily recognized by the odour of sulphuretted hydrogen produced when the sample and the part of the charcoal into which the fused mass has penetrated is moistened, and an acid added. If the fused mass is transferred to a clean silver plate, or a polished silver coin, and moistened with water, a black stain of sulphide of silver is immediately formed. (Compounds of tellurium and selenium give the same reaction.) As the gas flame contains sulphur compounds, a spirit lamp must be used to effect the fusion.

Remarks.

The characteristic and exceedingly delicate reaction of sulphuric acid with salts of baryta renders the detection of this acid an easier task than that of almost any other. It is simply necessary to take care not to confound with sulphate of baryta precipitates of chloride of barium, and particularly of nitrate of baryta, which are formed when aqueous solutions of these salts are mixed with liquids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from sulphate of baryta, as they redissolve immediately on diluting the acid solution with water. It is a rule that should never be departed from, in testing for sulphuric acid with chloride of barium, to dilute the solution largely; a little hydrochloric acid should also be added, as it counteracts the adverse influence of many salts, citrates of the alkalies, for instance. Where very minute quantities of sulphuric acid are to be detected, the mixture should be allowed to remain for several hours at a gentle heat; the trace of sulphate of baryta formed will in that case be found deposited at the bottom of the vessel. When the least uncertainty exists about the nature of the precipitate produced by chloride of barium in presence of hydrochloric acid, the reaction in 6 will at once set all doubt at rest. In looking for very small quantities of sulphuric acid in the presence of much hydrochloric or nitric acid, the greater part of the latter should first be evaporated off or neutralized. To detect free sulphuric acid in presence of a sulphate, the solution is mixed with a very little cane-sugar, and evaporated to dryness in a porcelain dish at 100°. If free sulphuric acid be present, a black residue will remain, or in the case of very minute quantities, a blackish-green residue. Other free acids do not decompose cane-sugar in this way. This test may also be applied by adding to the solution a very small quantity of cane-sugar, about 0·2–0·3 per cent.; strips of filter-paper about 300 to 400 mm. long are then placed in such a way that they dip into the liquid at one end only; after remaining for twenty-four hours they are taken out, dried, and heated at 100°. If free sulphuric acid is present, the upper edge of the part that was moistened will become brown or black, and very frequently quite brittle (Nessler).

§ 141.

Hydrofluosilicic Acid, HF,SiF_2 [H_2SiF_6].

Hydrofluosilicic acid is a white deliquescent mass melting at 19°, and easily soluble in water. The aqueous solution is very acid, and on evaporation in a platinum vessel volatilizes completely as fluoride of silicon and hydrofluoric acid; when evaporated in glass, it etches the latter. With bases, it forms water, and silico-fluorides of the metals, which are most of them soluble in water, redden litmus-paper, and on ignition are resolved into metallic fluorides and fluoride of silicon. **Chloride of barium** forms a crystalline precipitate with hydrofluosilicic acid (§ 95, 6); chloride of strontium gives no precipitate, but acetate of lead in excess throws down a white precipitate. **Salts of potassa** precipitate transparent gelatinous silico-fluoride of potassium; **ammonia** in excess throws down hydrated silicic acid, with formation of fluoride of ammonium. By heating metallic silico-fluorides with concentrated **sulphuric acid**, dense fumes are emitted in the air, arising from the evolution of hydrofluoric acid and fluoride of silicon. If the experiment is conducted in a platinum vessel covered with glass, the fumes etch the glass (§ 146, 5); the residue contains the sulphates formed.

THIRD DIVISION OF THE FIRST GROUP OF THE INORGANIC ACIDS.

§ 142.

a. Phosphoric Acid, PO_5 [P_2O_5].

1. Phosphorus is a colourless, transparent, waxy solid, of 1·83 specific gravity; it is insoluble in water, somewhat soluble in alcohol and ether, and easily soluble in bisulphide of carbon. Taken internally it acts as a virulent poison. It melts at 44·3°, and boils at 290°, but

volatilizes slightly when boiled with water. Exposed to the action of light under water, phosphorus turns first yellow, then red, and is finally covered with a white crust. If phosphorus is exposed to the air at the ordinary temperature, it exhales a highly characteristic and most disagreeable odour, whilst copious fumes are evolved which are luminous in the dark. These fumes are formed by the oxidation of the vapour of phosphorus, and consist of phosphoric and phosphorous acids, and phosphorus vapour. When the air is moist, ozone, peroxide of hydrogen, and nitrite of ammonia are produced at the same time. Phosphorus very readily takes fire, burning with a luminous flame and forming white fumes of phosphoric acid. By long exposure to light, or by long-continued heating at 250°, phosphorus is converted into a red variety, the so-called amorphous phosphorus. In this state, it does not alter in the air, it is not luminous, its inflammability is much decreased, it has a specific gravity of 2·1, and is insoluble in bisulphide of carbon. Nitric acid and nitrohydrochloric acid dissolve phosphorus pretty readily on heating; the solutions at first contain phosphorous acid as well as phosphoric acid. Hydrochloric acid does not dissolve phosphorus. If phosphorus is boiled with solution of soda or potassa, or with milk of lime, hypophosphites and phosphates are formed, whilst spontaneously inflammable phosphuretted hydrogen gas escapes. If a substance containing unoxidized phosphorus is placed at the bottom of a flask, a slip of paper moistened with solution of nitrate of silver suspended inside the flask by means of a cork loosely inserted into the mouth, and a gentle heat applied (from 30° to 40°), the paper slip will turn black in consequence of the reducing action of the phosphorus vapour, even though only a most minute quantity of phosphorus should be present. If, after the termination of the reaction, the blackened part of the paper is boiled with water, the undecomposed portion of the silver salt precipitated with hydrochloric acid, the solution filtered, and the filtrate evaporated as far as practicable on the water-bath, the presence of phosphoric acid in the residue may be shown by means of the reactions described below. (J. Scherer.) It must be borne in mind that the silver salt is blackened also by sulphuretted hydrogen, formic acid, volatile products of putrefaction, &c.; and also that the detection of phosphoric acid in the slip of paper can be of value only when the nitrate of silver and the filtering paper are perfectly free from phosphorus. As regards the behaviour of phosphorus when boiled with dilute sulphuric acid, and in a hydrogen evolution apparatus in contact with zinc and dilute sulphuric acid, see § 227.

2. Anhydrous phosphoric acid is a white, snowlike mass, which rapidly deliquesces when exposed to the air; with water it hisses like a red-hot iron, and is at first only partially dissolved; in time, however, the solution is complete. It forms with water and bases three series of compounds, viz., with 3 equivalents of water or base, ordinary hydrated tribasic phosphoric acid (orthophosphoric acid) or common phosphates (orthophosphates); with 2 equivalents of water or base, hydrate of pyrophosphoric acid or pyrophosphates; with 1 equivalent of water or base, hydrate of metaphosphoric acid or metaphosphates. As the meta- and pyrophosphoric acids are of comparatively rare occurrence, they will be treated less fully in a supplemental paragraph.

3. The hydrate of tribasic phosphoric acid, $3HO,PO_5$ [H_3PO_4], forms colourless transparent crystals, which deliquesce rapidly in the air to a syrupy non-caustic liquid. The action of heat changes it

into hydrated meta- or pyrophosphoric acid, according as 1 or 2 equivalents of water are expelled. When heated in an open platinum dish, the hydrate of common phosphoric acid, if pure, volatilizes completely, although with difficulty, in white fumes.

4. The tribasic phosphates with fixed bases are not decomposed when heated, but are converted into pyrophosphates if they contain 1 equivalent of basic water or ammonia, and into metaphosphates if they contain 2 equivalents. Of the tribasic phosphates, those with alkaline base alone are soluble in water, in the neutral state. The solutions have an alkaline reaction. If pyro- or metaphosphates are fused with carbonate of soda, the fused mass invariably contains the phosphoric acid in the tribasic state.

5. **Chloride of barium** in aqueous solutions of the neutral or basic phosphates of the alkalies, but not in solutions of the hydrate, produces a white precipitate of phosphate of baryta, $2BaO,HOPO_5$ [$BaHPO_4$], or $3BaO,PO_5$ [$Ba_3(PO_4)_2$],[*] which is soluble in hydrochloric and nitric acids, but only sparingly soluble in chloride of ammonium.

6. Solution of **sulphate of lime** in neutral or alkaline solutions of phosphates, but not in solutions of the hydrate, produces a white precipitate of phosphate of lime, $2CaO,HO,PO_5$ [$CaHPO_4$], or $3CaO,PO_5$ [$Ca_3(PO_4)_2$], which as long as it is amorphous dissolves readily in acids, even acetic acid, and is soluble also in chloride of ammonium.

7. **Sulphate of magnesia** produces in concentrated neutral solutions of phosphates of the alkalies a white precipitate of phosphate of magnesia, $2MgO,HO,PO_5 + 14aq$ [$MgHPO_4,7H_2O$], which often separates only after some time; on boiling, a precipitate of basic salt, $3MgO,PO_5 + 7aq$ [$Mg_3(PO_4)_2,7H_2O$], is thrown down immediately. The latter is also formed when sulphate of magnesia is added to a solution of a basic alkaline phosphate. If, however, a mixture of sulphate of magnesia and ammonia with sufficient chloride of ammonium to redissolve the precipitate of hydrate of magnesia is added to a solution of free phosphoric acid or of an alkaline phosphate, a white, crystalline, and quickly subsiding precipitate of basic phosphate of magnesia and ammonia, $2MgO,NH_4O,PO_5 + 12aq$ [$MgNH_4PO_4,6H_2O$], is formed, even in highly dilute solutions. This precipitate is insoluble in ammonia and only very sparingly soluble in chloride of ammonium, but dissolves readily in acids, even acetic acid. Very often, it makes its appearance only after the lapse of some time; stirring promotes its separation (§ 98, 8). The reaction cannot be considered decisive unless arsenic acid is absent (§ 133, 9).

8. **Nitrate of silver** throws down from solutions of neutral and basic alkaline phosphates a light yellow precipitate of phosphate of silver, $3AgO,PO_5$ [Ag_3PO_4], readily soluble in nitric acid and in ammonia. If the solution contains a basic phosphate, the liquid in which the precipitate is suspended has a neutral reaction; whilst the reaction is acid if the solution contains a neutral phosphate. The acid reaction in the latter case arises from the circumstance that the nitric acid receives for the 3 eq. of oxide of silver which it yields to the phosphoric acid, only 2 eq. of alkali and 1 eq. of water.

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[*] A precipitate of the former composition is produced in solutions containing an alkaline phosphate with 2 equivalents of a fixed base or ammonia; whilst precipitates of the latter composition are formed in solutions which contain an alkaline phosphate with 3 equivalents of a fixed base or ammonia.

9. If to a solution containing phosphoric acid and the *least possible excess* of free acid a tolerably large amount of acetate of soda is added, and then a drop of **ferric chloride**, a yellowish-white, flocculent gelatinous precipitate of phosphate of sesquioxide of iron, $Fe_2O_3,PO_5 + 4aq$ [$Fe_2(PO_4)_2,2H_2O$], is formed. An excess of ferric chloride must be avoided, as ferric acetate (of red colour) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect the phosphoric acid in phosphates of the alkaline earths; but it can be considered decisive only when arsenic acid is absent, as the latter gives a similar reaction. To effect the complete separation of phosphoric acid from the alkaline earths, a sufficient quantity of ferric chloride is added to impart a reddish colour to the solution, which is then boiled (whereby the whole of the ferric oxide is thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkaline earths as chlorides. If it is desired to detect, by means of this reaction, phosphoric acid in presence of a large proportion of ferric oxide, the hydrochloric acid solution is boiled with sulphite of soda until the ferric chloride is reduced to ferrous chloride, as indicated by the decolorization of the solution; carbonate of soda is added until the solution is nearly neutral, then acetate of soda, and finally 1 drop of ferric chloride. The reason for this proceeding is, that ferrous acetate does not dissolve phosphate of sesquioxide of iron.

10. If a few c.c. of the solution of **molybdate of ammonia** in nitric acid (§ 52) are poured into a test tube, and a little of a solution containing phosphoric acid in neutral or acid solution is added, a light-yellow finely divided precipitate is formed at once or after a very short time, even in the cold, if the quantity of phosphoric acid is not very small; this precipitate speedily subsides to the bottom of the tube, or is deposited on the sides. With exceedingly minute quantities of phosphoric acid, for example, 0·00002 gram, a few hours must be allowed for the reaction to take place, and it should be aided also by applying a gentle heat, but not higher than 40°. If no other colouring substances are present, the liquid above the precipitate appears colourless. The volume of the solution to be tested should never exceed one-third of that of the reagent, and a yellow coloration merely should never be considered as a proof of the presence of phosphoric acid.

The yellow precipitate contains molybdic acid, ammonia, water, and a little phosphoric acid (about 3 per cent.). As it is insoluble in dilute acids only in presence of an excess of molybdic acid, it should be borne in mind that the addition of phosphoric acid in excess will necessarily prevent its formation. A large amount of hydrochloric acid and certain organic substances, such as tartaric acid, will impede or prevent the precipitation. The precipitate, after subsiding, may be readily recognized even in dark-coloured liquids. By washing it with the solution of molybdate of ammonia with which the precipitation has been effected, dissolving in ammonia, and adding a mixture of sulphate of magnesia, chloride of ammonium, and ammonia, phosphate of magnesia and ammonia is produced.

By conducting the operation in the manner above stated, phosphoric acid cannot well be confounded with any other acid; since arsenic acid *in the cold* gives no precipitate with solution of molybdate of ammonia in nitric acid, although it gives one when heated, and especially when boiled (the supernatant liquid appears yellow); whilst silicic acid shows no reaction with it in the cold, and gives only a strong yellow coloration on heating, and no precipitate.

11. If a finely powdered substance containing phosphoric acid (or a metallic phosphide) is intimately mixed with 5 parts of a flux consisting of 3 parts of carbonate of soda, 1 part of nitrate of potassa, and 1 part of silicic acid, the mixture fused in a platinum spoon or crucible, the fused mass boiled with water, the solution thus obtained decanted, carbonate of ammonia added to it, the liquid boiled again, and the silicic acid which is thereby precipitated filtered off, the filtrate now holds in solution an alkaline phosphate, and may accordingly be tested for phosphoric acid as directed in 7, 8, 9, or 10.

12. On igniting and pulverizing a substance containing phosphoric acid, placing it in a tube of the thickness of a straw and sealed at one end, adding a fragment of magnesium wire about 2 lines long (or a small piece of sodium), which should be covered by the sample, and then heating, a vivid incandescence will be observed and phosphide of magnesium (or of sodium) will be formed. When the black contents of the tube are crushed and moistened with water they exhale the characteristic odour of phosphuretted hydrogen. (Winkelblech, Bunsen.)

13. **Albumin** is not precipitated by solution of hydrate of tribasic phosphoric acid, or by a solution of a tribasic phosphate mixed with acetic acid.

§ 143.

a. **Pyrophosphoric acid.** The solution of the hydrate, $2HO,PO_5$ $[H_4P_2O_7]$, is converted by boiling into solution of the hydrate of orthophosphoric acid. The solutions of the salts bear heating without undergoing decomposition, but when boiled with a strong acid the phosphoric acid is converted into the tribasic state. If the salts are fused with carbonate of soda in excess, tribasic phosphates are produced. Of the neutral pyrophosphates, only those with alkaline bases are soluble in water; the acid salts, such as NaO,HO,PO_5 $[Na_2H_2P_2O_7]$, are converted into metaphosphates, NaO,PO_5 $[NaPO_3]$, by ignition. **Chloride of barium** does not precipitate the free acid, but from solutions of the salts it throws down white pyrophosphate of baryta, $2BaO,PO_5$ $[Ba_2P_2O_7]$, soluble in hydrochloric acid. **Nitrate of silver** throws down from a solution of the hydrate, especially on addition of an alkali, a white, earthy-looking precipitate of pyrophosphate of silver, $2AgO,PO_5$ $[Ag_4P_2O_7]$, which is soluble in nitric acid and in ammonia. **Sulphate of magnesia** precipitates pyrophosphate of magnesia, $2MgO,PO_5$ $[Mg_2P_2O_7]$. The precipitate dissolves in excess of the pyrophosphate, as well as in an excess of the sulphate of magnesia. Ammonia fails to precipitate it from these solutions; on boiling the solution, it separates again (means of detecting pyrophosphoric acid in presence of phosphoric acid). A concentrated solution of **luteo-cobaltic chloride** added to an alkaline pyrophosphate produces an immediate precipitation of pale reddish-yellow spangles. (This distinguishes pyrophosphoric acid from phosphoric and metaphosphoric acids, C. D. Braun.) **Albumin** is not precipitated by solution of the hydrate nor by solutions of the salts mixed with acetic acid. **Molybdate of ammonia**, with addition of nitric acid, gives no precipitate at first. After a time yellow phosphomolybdate of ammonia separates, the pyrophosphoric acid being changed into orthophosphoric acid.

β. **Metaphosphoric acid.** Five sorts of monobasic phosphates (metaphosphates) are known, and the hydrates corresponding with most of these have also been obtained. The several reactions by which these may be distinguished will not be given here, but it may be remarked that the monobasic phosphoric acids differ from the bibasic and tribasic phosphoric acids in that the solutions of the hydrates of the monobasic acids precipitate albumin at once, whilst the solutions of their salts do so after addition of acetic acid. Those hydrates and salts which are precipitated by nitrate of silver yield white precipitates. A mixture of sulphate of magnesia, chloride of ammonium, and ammonia gives no precipitate with the monobasic phosphoric acids or their salts, or if a precipitate is produced it dissolves in chloride of ammonium. All monobasic phosphates, when fused with carbonate of soda, yield tribasic phosphate of soda.

§ 144.

b. Boric Acid or Boracic Acid, BO_3 $[B_2O_3]$.

1. Boric acid, in the anhydrous state, is a colourless, fixed vitreous substance, fusible at a red heat; the hydrate of boric acid, HO,BO_3 $[HBO_2]$, is a porous, white mass; in the crystalline state, $HO,BO_3 + 2aq$ $[HBO_2,H_2O]$, it forms small scaly laminæ. It is soluble in water and in spirit of wine; on evaporating the solutions, a large proportion of the boric acid volatilizes along with the aqueous or alcoholic vapour. The solutions redden litmus-paper, and impart to turmeric-paper a faint brown-red tint, which becomes deeper on drying. The borates are not decomposed by ignition; those with alkaline bases alone are readily soluble in water. The solutions of borates of the alkalies are colourless, and all of them, even those of the acid salts, exhibit an alkaline reaction.

2. **Chloride of barium** produces in solutions of borates, if not too dilute, a white precipitate of borate of baryta, which is soluble in acids and ammoniacal salts. The formula of this precipitate, when thrown down from solutions of neutral borates, is $BaO,BO_3 + 2aq$ $[BaB_2O_4,2H_2O]$; when thrown down from solutions of acid borates, $3BaO,5BO_3 + 6aq$ $[Ba_3B_{10}O_{18},6H_2O]$ (H. Rose).

3. **Nitrate of silver** in concentrated solutions of neutral borates of the alkalies produces a white precipitate, inclining slightly to yellow from admixture of free oxide of silver, $AgO,BO_3 + HO$ $[2AgBO_2,H_2O]$; in concentrated solution of acid borates, a white precipitate of $3AgO,4BO_3$ $[Ag_6B_8O_{15}]$ is produced. With dilute solutions of borates, nitrate of silver gives a brown precipitate of oxide of silver (H. Rose). All these precipitates dissolve in nitric acid and in ammonia.

4. If dilute **sulphuric acid** or **hydrochloric acid** is added to very concentrated, hot solutions of alkaline borates, the boric acid separates on cooling, in the form of shining crystalline scales.

5. If **alcohol** is poured on to free boric acid, or a borate to which a sufficient quantity of concentrated sulphuric acid has been added to liberate the boric acid, and then ignited, the flame appears of a very distinct yellowish-green colour, especially on stirring the mixture; this tint is imparted to the flame by the boric acid which volatilizes with the alcohol. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, igniting the alcohol, allowing it to burn for a short time, then extinguishing the flame, and afterwards rekindling it. At the first flickering of the flame its borders will now appear green, even if the quantity of boric acid is so minute that it imparts no colour to the flame when treated in the usual manner. *Concentrated sulphuric acid must be used, and not too little of it.* As salts of copper also

impart a green tint to the flame of alcohol, any copper which may be present must first be removed by means of sulphuretted hydrogen. The presence of metallic chlorides also may lead to mistakes, as the chloride of ethyl formed in that case colours the borders of the flame bluish-green.

6. If a solution of boric acid, or of a borate with an alkali or an alkaline earth for base, is mixed with hydrochloric acid to slight, but distinct, acid reaction, and a slip of **turmeric-paper** is dipped into it, and then dried on a watch-glass at 100°, the part which has been moistened with the solution shows a peculiar red tint (H. Rose).

This reaction is very delicate; care must be taken not to confound the characteristic red coloration with the blackish-brown colour which turmeric-paper acquires when moistened with rather concentrated hydrochloric acid, and then dried; nor with the brownish-red coloration which ferric chloride, or a hydrochloric acid solution of molybdate of ammonia or of zirconia, gives to turmeric-paper, more particularly on drying. By moistening turmeric-paper reddened by boric acid with a solution of an alkali or an alkaline carbonate, the colour is changed to bluish-black or greenish-black; but a little hydrochloric acid will at once restore the brownish-red colour (A. Vogel, H. Ludwig).

7. If a substance containing boric acid is reduced to a fine powder, moistened with a few drops of water, mixed with 3 parts of a flux composed of $4\frac{1}{2}$ parts of **bisulphate of potassa** and 1 part of finely pulverized **fluoride of calcium**, free from boric acid, and the paste exposed on the loop of a platinum wire in the outer mantle of the Bunsen gas flame, or at the apex of the inner flame of the blowpipe, fluoride of boron escapes, which imparts to the flame—though only for a few instants—a green tint (Turner). With readily decomposible compounds, the reaction may be obtained by simply moistening the sample with hydrofluosilicic acid, and holding it in the flame. The delicacy of this reaction may be increased by intimately mixing the substance to be examined with silica and fluor spar, adding a small piece of marble, and heating the mixture in a test tube with concentrated sulphuric acid; the evolved gases should be led into a Bunsen flame by means of a glass tube fitted with a platinum mouthpiece (Kämmerer).

8. On heating a dry substance containing boric acid to redness with half or an equal volume of **silicofluoride of ammonium** * in a closed tube, a sublimate of ammonium borofluoride is obtained, which, when heated in a Bunsen flame, tinges it green; with turmeric-paper, its aqueous solution yields the reaction mentioned in 6. If the substance to be tested contains a free acid, a slight excess of sodium carbonate must be added (Stolba).

9. Boric acid or borates, even in very small quantity, if fused with carbonate of soda on the loop of a platinum wire, and then placed in the flame of the **spectrum apparatus**, give a spectrum of four well-marked lines of equal width, equidistant from each other. B_1 is brilliant yellowish-green (coinciding with Baγ), B_2 is brilliant light-green (coinciding with Baβ), B_3 is pale bluish-green (nearly coinciding with the blue barium line), B_4 is blue, very pale, not quite reaching Srδ (Simmler).

If a finely powdered substance containing boric acid is mixed to a

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* This salt may be prepared by cautiously neutralizing hydrofluosilicic acid with ammonia, filtering, and evaporating in a platinum dish.

paste with glycerin and placed in the flame of a Bunsen burner, a green flame is obtained well fitted for spectrum analysis (M. W. Iles).

§ 145.

c. Oxalic Acid, $C_4O_6 = \bar{O}$ $[C_2O_3]$.

1. The hydrate of oxalic acid, $2HO,C_4O_6$ $[H_2C_2O_4]$, is a white powder; the crystallized acid, $2HO,C_4O_6 + 4aq$ $[H_2C_2O_4,2H_2O]$, forms colourless rhombic prisms. Both dissolve readily in water and in spirit of wine. When rapidly heated in open vessels, part of the hydrated acid undergoes decomposition, whilst another portion volatilizes unaltered. The fumes of the volatilizing acid are very irritating, and provoke coughing. If the hydrate is heated in a test-tube, part of it sublimes unaltered.

2. The whole of the oxalates undergo decomposition at a red heat, the oxalic acid being converted into carbonic acid and carbonic oxide. The oxalates of the alkalies and of baryta, strontia, and lime are in this process converted into carbonates (if pure, and if gently heated, almost without separation of charcoal). Oxalate of magnesia is converted into pure magnesia even by a very gentle red heat. The oxalates with metallic bases leave either the pure metal or the oxide behind, according to the reducibility of the metallic oxide. The alkaline oxalates, and also some of the oxalates with metallic bases, are soluble in water.

3. **Chloride of barium**, in neutral solutions of alkaline oxalates, produces a white precipitate of oxalate of baryta, $2BaO,C_4O_6 + 2aq$ $[BaC_2O_4,H_2O]$; this is very sparingly soluble in water, more readily in water containing chloride of ammonium, acetic acid, or oxalic acid, freely in nitric acid and in hydrochloric acid; ammonia reprecipitates it from the latter solutions unaltered.

4. **Nitrate of silver**, in solutions of oxalic acid and of alkaline oxalates, produces a white precipitate of oxalate of silver, $2AgO,C_4O_6$ $[Ag_2C_2O_4]$, which is readily soluble in concentrated hot nitric acid, and also in ammonia, but dissolves with difficulty in dilute nitric acid, and is very sparingly soluble in water.

5. **Lime water** and all the soluble **salts of lime**, including solution of **sulphate of lime**, produce, even in highly dilute solutions of oxalic acid or of oxalates of the alkalies, a white finely pulverulent precipitate of oxalate of lime, $2CaO,C_4O_6 + 2aq$ $[CaC_2O_4,H_2O]$, and occasionally $2CaO,C_4O_6 + 6aq$ $[CaC_2O_4,3H_2O]$; this dissolves readily in hydrochloric acid and in nitric acid, but is almost insoluble in oxalic acid and in acetic acid, and practically insoluble in water. The presence of salts of ammonia does not interfere with the formation of these precipitates. Addition of ammonia considerably promotes the precipitation of free oxalic acid by salts of lime. In *very* dilute solutions, the precipitate is only formed after some time.

6. If hydrated oxalic acid or an oxalate, in the dry state, is heated with excess of **concentrated sulphuric acid**, the latter withdraws from the oxalic acid its constitutional water or base, and it then decomposes into carbonic acid and carbonic oxide, $C_4O_6 = 2CO + 2CO_2$ $[C_2O_3 = CO + CO_2]$, which escape with effervescence. If the quantity operated on is not too small, the carbonic oxide may be kindled; it burns with a blue flame. If the sulphuric acid acquires a dark colour

in this reaction, it shows that the oxalic acid contained some foreign organic substance.

7. If oxalic acid or an oxalate is mixed with finely pulverized **binoxide of manganese** (which must be free from carbonates), a little water added and a few drops of sulphuric acid, a lively effervescence takes place, caused by escaping carbonic acid,

$$2MnO_2 + C_4O_6,2HO + 2HO,SO_3 = 2(MnO,SO_3) + 4CO_2 + 4HO$$
$$[MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O].$$

Free oxalic acid gives this reaction without the addition of sulphuric acid, but less readily.

8. If oxalates of alkaline earths are boiled with a concentrated solution of **carbonate of soda**, and filtered, the oxalic acid is obtained in the filtrate in combination with soda, whilst the precipitate contains the base as carbonate. With oxalates containing oxides of heavy metals as the base, this is not always attended with the desired result, as many of these oxalates—oxalate of protoxide of nickel, for example—will partially dissolve in the alkaline fluid, with formation of a double salt. Metals of this kind should therefore be separated as sulphides.

9. For the detection of oxalic acid as oxalate of lime by means of the microscope, see C. Bischoff (Zeit. anal. Chem. **22**, 633).

§ 146.

d. Hydrofluoric Acid, HF [HF].

1. Anhydrous hydrofluoric acid is a colourless liquid which fumes in the air, boils at 19·4°, and is freely dissolved by water. Aqueous hydrofluoric acid is distinguished from all other acids by the property it has of dissolving silica, and also of dissolving or decomposing the silicates which are insoluble in hydrochloric acid; hydrofluosilicic acid and water are formed in the process of solution,

$$SiO_2 + 3HF = SiF_2,HF + 2HO \quad [SiO_2 + 6HF = H_2SiF_6 + 2H_2O].$$

With metallic oxides, hydrofluoric acid forms metallic fluorides and water.

2. The fluorides of the alkali metals are soluble in water; the solutions have an alkaline reaction. The fluorides of the metals of the alkaline earths are either insoluble or only very sparingly soluble in water. Fluoride of aluminium is insoluble. Most of the fluorides of the heavy metals are very sparingly soluble in water, as the fluorides of copper, lead, and zinc, whilst others dissolve in water without difficulty, as the fluorides of nickel, cobalt, silver, antimony, and tin. Many of the fluorides insoluble or sparingly soluble in water dissolve in free hydrofluoric acid; others do not. Most of the fluorides bear ignition in a crucible without undergoing decomposition.

3. **Chloride of barium** precipitates aqueous solutions of hydrofluoric acid, but much more completely solutions of fluorides of the alkali metals. The bulky white precipitate of fluoride of barium, BaF [BaF_2], is almost absolutely insoluble in water, but dissolves in large quantities of hydrochloric acid or nitric acid; ammonia does not precipitate these solutions, or only very incompletely, owing to the solvent action of the neutral ammonia salts.

4. **Chloride of calcium**, in aqueous solutions of hydrofluoric acid or of fluorides, produces a gelatinous precipitate of fluoride of calcium, CaF [CaF_2], which is so transparent as to induce the belief that the solution has remained clear. The addition of ammonia promotes the

complete separation of the precipitate. The precipitate is practically insoluble in water, and only very slightly soluble in hydrochloric acid and nitric acid in the cold: it dissolves somewhat more largely on boiling with hydrochloric acid. Ammonia produces no precipitate in the solution, or only a very trifling one, as the salt of ammonia formed retains it in solution. Fluoride of calcium is scarcely more soluble in free hydrofluoric acid than in water. It is insoluble in alkaline liquids.

5. If a finely pulverized fluoride, no matter whether soluble or insoluble, is treated in a platinum crucible with just enough **concentrated sulphuric acid** to make it into a thin paste, the crucible covered with the convex face of a watch-glass of hard glass coated with bees'-wax, which has been removed again in some places by tracing lines in it with a pointed piece of wood, the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines will, on removal of the wax, be found to be more or less deeply etched into the glass. (The coating with wax may be readily effected by heating the glass cautiously, putting a small piece of wax upon the convex face, and spreading the fused mass equally over it. The removal of the wax coating is effected by heating the glass gently, and wiping with a cloth.) If the quantity of hydrofluoric acid disengaged by the sulphuric acid is very minute, the etching is often invisible on the removal of the wax; it will, however, in such cases appear when the glass is breathed upon: this appearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess. The impressions which thus appear on breathing on the glass may, however, owe their origin to other causes; therefore, though their non-appearance may be held as a proof of the absence of fluorine, their appearance is not a positive proof of the presence of that element. At all events, they ought only to be considered of value where they can be developed again after the glass has been properly washed with water, dried, and wiped.*

This reaction fails if there is too much silicic acid present, or if the substance is not decomposed by sulphuric acid. In such cases, one of the two following methods is resorted to, according to circumstances.

6. If we have to deal with a fluoride decomposable by sulphuric acid, but mixed with a large proportion of silicic acid, the fluorine in it may be detected by heating the mixture in a test-tube with **concentrated sulphuric acid**, as gaseous fluoride of silicon is evolved under these conditions and forms dense white fumes on coming in contact with moist air. If the gas is passed into water through a bent tube moistened inside, the latter has its transparency more or less impaired, owing to the separation of silicic acid. If the quantity operated upon is rather considerable, hydrated silicic acid separates in the water, and the solution is rendered acid by hydrofluosilicic acid.

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* J. Nicklès states that etchings on glass may be obtained with all kinds of sulphuric acid, and, in fact, with all acids suited to effect the evolution of hydrofluoric acid. The author has tried watch-glasses of Bohemian glass with sulphuric and other acids, but could get no etchings in confirmation of this statement. Still, proper caution demands that before using the sulphuric acid, it should first be positively ascertained that its fumes will not etch glass. Should the sulphuric acid contain hydrofluoric acid, the latter may be easily removed by diluting with an equal volume of water and evaporating in a platinum dish to the original strength.

The following process answers best for the detection of small quantities of fluorine. The substance is heated with concentrated sulphuric acid in a flask closed with a cork having two perforations, in which two tubes are inserted, one reaching to the bottom of the flask, whilst the other terminates immediately inside the cork. Through the longer tube a slow stream of dry air is drawn into the flask, and then, as it reissues through the other tube, into a U-tube furnished with a little bulb at the bottom containing a few drops of water, and connected with an aspirator. The fluoride of silicon which is carried over by the air is decomposed by the water with separation of hydrated silicic acid. In this way very small quantities of fluorine may be easily detected. For more difficultly decomposable substances, bisulphate of potassa is used instead of sulphuric acid, and the mixture, to which some marble is added (to ensure a continuous slight evolution of gas), heated for some time to fusion, in a hard glass tube closed at one end and furnished with a gas-leading tube at the other. The gas evolved in the process first described may also be passed into a test-tube containing about 0·3 gram aniline dissolved in 15 c.c. ether and 15 c.c. alcohol. If fluorine be present, a white, glittering deposit of aniline silicofluoride will be formed. If a few drops of a concentrated solution of soda in absolute alcohol are now added to the compound suspended in the liquid, silicofluoride of sodium will be formed and gradually deposited on the bottom of the tube (W. Knop).

7. Silicates not decomposable by sulphuric acid must first be fused with 4 parts of carbonate of soda and potassa mixture. The fused mass is treated with water, the solution filtered, the filtrate concentrated by evaporation, allowed to cool, transferred to a platinum vessel, hydrochloric acid added to feebly acid reaction, and the liquid allowed to stand until the carbonic acid has escaped. It is then supersaturated with ammonia, heated, filtered into a bottle, chloride of calcium added to the still hot solution, the bottle closed, and allowed to remain. If a precipitate separates after some time, it is collected on a filter, dried, and examined by the method described in 5 (H. Rose).

8. Minute quantities of metallic fluorides in minerals, slags, &c., may also be readily detected by means of the **blowpipe**. For this purpose a piece of thin platinum foil is bent, and inserted in a glass tube as shown in fig. 42, the finely powdered substance mixed with powdered microcosmic salt which has been previously fused on charcoal is introduced, and the blowpipe flame is directed on to the mass, so that the products of combustion may pass into the tube. A metallic fluoride treated in this way yields hydrofluoric acid gas, which is recognized by its pungent odour, by the dimming of the glass tube (which becomes perceptible only after cleaning and drying), and the yellow tint which the acid air issuing from the tube imparts to a moist slip of Brazil-wood paper* (Berzelius, Smithson). When silicates containing metallic fluorides are treated in this manner, gaseous fluoride of silicon is formed, which also imparts a yellow colour to a moist slip of Brazil-wood paper inserted into the tube, and causes silicic acid to be deposited within the tube. After washing and drying

Fig. 42.

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* Prepared by moistening slips of fine printing-paper with decoction of Brazil wood.

the tube, it appears dimmed here and there. A small quantity of a fluoride present in a mineral containing water may generally be detected by heating the substance by itself in a glass tube sealed at one end and inserting a slip of Brazil-wood paper in the tube; the paper will usually turn yellow (Berzelius).

§ 147.

Recapitulation and Remarks.

The baryta compounds of the acids of the third division of the first group are dissolved by hydrochloric acid, apparently without decomposition; alkalies, therefore, as they neutralize the hydrochloric acid, reprecipitate them unaltered. The baryta compounds of the acids of the first division of this group also behave in the same way; these acids, if present, therefore, must be removed before any conclusion regarding the presence of phosphoric acid, boric acid, oxalic acid, or hydrofluoric acid can be drawn from the reprecipitation of a salt of baryta by alkalies. But even leaving this point altogether out of the question, no great value can be attached to this reaction, not even as far as the mere detection of these acids is concerned, and still less as regards their separation from other acids, since if the solution contains any considerable proportion of free acid or of an ammoniacal salt, ammonia fails to reprecipitate from hydrochloric acid solutions the salts of baryta in question, more particularly the borate of baryta and fluoride of barium. Boric acid is well characterized by the coloration it imparts to the alcohol flame, or as fluoride of boron to the flame of a bunsen, and also by its action on turmeric-paper; the latter reaction is more particularly suited for the detection of very minute traces. If oxides of the heavy metals are present, they are most conveniently removed by sulphuretted hydrogen or sulphide of ammonium, or the substance may be tested according to § 144, 8 (p. 202). Before proceeding to concentrate dilute solutions of boric acid, the acid must be combined with an alkali, otherwise a large portion of it will volatilize with the aqueous vapours. Small quantities of boric acid may also be safely and easily detected by the spectroscope. The detection of phosphoric acid in compounds soluble in water is not difficult; the reaction with sulphate of magnesia, &c., is the best for the purpose. The detection of phosphoric acid in insoluble compounds cannot be effected by means of magnesia solution. Ferric chloride (§ 142, 9) is well suited for the detection of phosphoric acid in its salts with the alkaline earths, and particularly for the separation of the acid from the alkaline earths; the nitric acid solution of molybdate of ammonia is specially adapted for the detection of phosphoric acid in minute quantities, or if alumina and ferric oxide are present. It must carefully be borne in mind that both these reactions demand the *strictest* attention to the directions given. If present in combination with oxides of the fourth, fifth, or sixth group, phosphoric acid may be separated by the method given in § 142, 11, or by precipitating the bases with sulphuretted hydrogen or sulphide of ammonium.

Oxalic acid may always be easily detected in aqueous solutions of oxalates of the alkalies, by solution of sulphate of lime. The formation of a finely divided pulverulent precipitate, insoluble in acetic acid, leaves hardly a doubt on the point, as racemic acid alone, which occurs so very rarely, gives the same reaction. In case of doubt, the oxalate of lime may be readily distinguished from the racemate, by simple ignition, with exclusion of air, as the decomposed racemate leaves a considerable proportion of charcoal behind; the racemate dissolves, moreover, in cold solution of potassa or soda, in which oxalate of lime is insoluble. The deportment of the oxalates with sulphuric acid, or with binoxide of manganese and sulphuric acid, also affords a satisfactory means of confirming the results of other tests. In insoluble salts, the oxalic acid is detected most safely by decomposing them by boiling with solution of carbonate of soda, or by sulphuretted hydrogen or sulphide of ammonium (§ 145, 8). The fact should be noted also that there are certain soluble oxalates which are not precipitated by salts of lime; these are more particularly oxalate of sesquioxide of chromium and oxalate of sesquioxide of iron; this is owing to the circumstance that these salts form soluble double salts with oxalate of lime. Hydrofluoric acid is readily detected in salts decomposable by sulphuric acid; but it must be borne in mind that too large a proportion of sulphuric acid impedes the free evolution of hydrofluoric acid gas, and thus impairs the delicacy of the reaction; also that the glass cannot be distinctly etched if, instead of hydrofluoric acid gas, silicon fluoride alone is evolved; in the case of compounds abounding in silica, therefore, the safer way is to try, besides the reaction given in § 146, 5, also the one given in 6. In silicates which are not decomposed by sulphuric acid, the presence of fluorine is often overlooked, because the analyst omits to examine the compound carefully by the method given in 7.

§ 148.

Phosphorous Acid, PO_3 [P_2O_3].

Anhydrous phosphorous acid is a white powder, which can be sublimed, and burns when heated in the air. With a small proportion of water, it forms a thickish liquid, which crystallizes on long standing. Heat decomposes it into hydrated phosphoric acid and phosphuretted hydrogen gas, which is not spontaneously inflammable. It is poisonous, and dissolves freely in water. Of its salts, those with alkaline base are readily soluble in water, all the others sparingly soluble; the latter dissolve in dilute acids. All the salts are decomposed by ignition into phosphates, which are left behind, and hydrogen, or a mixture of hydrogen and phosphuretted hydrogen, which escapes. With **nitrate of silver**, separation of metallic silver takes place, more especially on adding ammonia and warming; with **mercurous nitrate**, under the same circumstances, metallic mercury separates. With **mercuric chloride** in excess, phosphorous acid throws down mercurous chloride after some time, more rapidly on heating. **Chloride of barium** and **chloride of calcium** produce in not over-dilute solutions of phosphorous acid, upon addition of ammonia, white precipitates, soluble in acetic acid. A mixture of **sulphate of magnesia**, chloride of ammonium, and ammonia gives no precipitate unless the solutions are rather concentrated. **Acetate of lead** throws down white phosphite of lead, insoluble in acetic acid. On heating to boiling with **sulphurous acid** in excess, phosphoric acid is formed and sulphur separated. In contact with zinc and dilute **sulphuric acid**, phosphorous acid gives a mixture of hydrogen with phosphuretted hydrogen; this smokes in contact with the air, burns with an emerald-green colour, and precipitates silver and phosphide of silver from solution of nitrate of silver. Nitric acid prevents the formation of phosphuretted hydrogen; if this acid is only present in small quantity, some ferrous chloride is first added, and then after some time the zinc. The gas containing the phosphuretted hydrogen may be allowed to act on pure filter-paper or parchment-paper moistened with silver solution instead of on the silver solution itself (H. Hager). If the amount of phosphorous acid is but small, the silver paper does not blacken until the lapse of some hours. It must be remembered that both sulphuretted hydrogen and arseniuretted hydrogen will blacken the paper.

Fourth Division of the First Group of the Inorganic Acids.

§ 149.

a. **Carbonic Acid,** CO_2 [CO_2].

1. Carbon is a solid, tasteless, inodorous body. The very highest degrees of heat alone can effect its fusion and volatilization (Despretz). All carbon is combustible, and yields carbonic acid when burnt with a sufficient supply of oxygen or atmospheric air. In the diamond, the carbon is crystallized, transparent, pellucid, exceedingly hard, difficultly combustible; as graphite it is opaque, blackish-gray, soft, greasy to the touch, difficultly combustible, and stains the fingers; whilst as charcoal obtained by the decomposition of organic matter it is black, opaque, non-crystalline—sometimes dense, shining, and difficultly combustible, and sometimes porous, dull, and readily combustible.

2. Carbonic acid, at the ordinary temperature and atmospheric pressure, is a colourless gas of far greater density than atmospheric air, so that it may be poured from one vessel into another. It is inodorous, has a sourish taste, and reddens moist litmus-paper; but the red tint disappears again on drying. Carbonic acid is readily absorbed by solution of potassa or soda; it dissolves pretty freely in water.

3. The aqueous solution of carbonic acid has a feebly acid and pungent taste; it imparts a fugitive red tint to litmus-paper, and colours solution of litmus wine-red; it loses its carbonic acid if shaken with air in a half-filled bottle, and more completely still when heated. Some of the carbonates lose their carbonic acid by ignition; those with colourless oxides are white or colourless. Of the neutral carbonates, only those with alkaline bases are soluble in water; their solutions have a very strongly alkaline reaction. Besides the carbonates with alkaline bases, those also with an alkaline earth for base, and some of those with a metallic base, dissolve in water as acid carbonates.

4. The carbonates are decomposed by all free **acids** soluble in water, with the exception of hydrocyanic acid and sulphuretted hydrogen; most of these are decomposed in the cold, but several (magnesite, for instance) require to be heated. The decomposition is attended with effervescence, the carbonic acid being disengaged as a colourless and inodorous gas, which imparts a fugitive reddish tint to litmus-paper. It is necessary to apply the decomposing acid in excess, especially when acting on carbonates with alkaline bases, since the formation of bicarbonates will frequently prevent effervescence if too little of the decomposing acid be added. Substances which it is intended to test for carbonic acid should first be heated with a little water, to prevent any mistake which might arise from the escape of air-bubbles on treating the dry substances with the acid. Where there is reason to apprehend the escape of carbonic acid on boiling the substance with water, lime water should be used instead of pure water. If it is thought desirable to

prove that the escaping gas is really carbonic acid, it should be passed into lime water or baryta water, or a glass rod may be dipped in the latter and held inside the test-tube near the surface of the liquid; a white film will form on the lime or baryta water, as is explained in 5.

5. **Lime water** or **baryta water**, brought into contact with carbonic acid or with soluble carbonates, produces a white precipitate of neutral carbonate of lime, CaO,CO_2 [$CaCO_3$], or carbonate of baryta, BaO,CO_2 [$BaCO_3$]. In testing for free carbonic acid, the reagents ought always to be added in excess, as the acid carbonates of the alkaline earths are soluble in water. The precipitates dissolve in acids with effervescence, and are not reprecipitated from such solutions by ammonia, after the complete expulsion of the carbonic acid by ebullition. As lime water dissolves very minute quantities of carbonate of lime, the detection of exceedingly minute traces of carbonic acid requires the use of a lime water saturated with carbonate of lime by long digestion therewith (Welter, Berthollet).

6. **Chloride of calcium** or **chloride of barium**, in solutions of neutral alkaline carbonates, immediately produces a precipitate of carbonate of lime or of carbonate of baryta; in dilute solutions of bicarbonates, these precipitates are formed only on boiling; with free carbonic acid, these reagents give no precipitate.

7. To detect free carbonic acid in presence of bicarbonates, a solution of 1 part of **rosolic acid** in 500 parts of 80 per cent. alcohol may be employed, to which baryta water has been added until it begins to acquire a red tinge. If 0·5 c.c. of this rosolic acid solution is added to about 50 c.c. of the water to be tested, a spring water for instance, the liquid will be colourless or at most faintly yellowish if it contains free carbonic acid, whereas if there is no free carbonic acid, but only double salts, it will be red (M. v. Pettenkofer).

8. Salzer[*] gives a test for free carbonic acid or bicarbonates in presence of carbonates, founded on the fact that the Nessler ammonia reaction (§ 92, *b*, p. 90) does not take place in presence of free carbonic acid or carbonates.

§ 150.

b. **Silicic Acid,** SiO_2 [SiO_2].

1. Silicic acid is colourless or white, and unalterable and infusible even in the hottest blowpipe flame, but it melts in the flame of the oxyhydrogen blowpipe. It occurs both crystalline and amorphous. It is insoluble in water and acids (with the exception of hydrofluoric acid, which dissolves the amorphous variety easily, the crystalline variety with more difficulty); its hydrate is soluble in water and acids, but only at the moment of its separation. Amorphous silicic acid and the hydrate dissolve in hot aqueous solutions of potassa and soda and their carbonates, but the crystallized acid is insoluble or nearly so in these liquids. If either of the two is fused with a caustic alkali or alkaline carbonate, a basic silicate of the alkali is obtained, which is soluble in water. Aqueous ammonia dissolves gelatinous hydrated silicic acid tolerably freely, the dried hydrate or amorphous silicic acid less readily, and the crystallized acid scarcely at all. The silicates with alkaline bases are alone soluble in water.

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[*] Zeit. anal. Chem., **20**, 227.

2. The solutions of the alkaline silicates are decomposed by all **acids.** If a large proportion of hydrochloric acid is added at once to even concentrated solutions of alkaline silicates, the separated silicic acid remains in solution; but if the hydrochloric acid is added gradually drop by drop, with stirring, the greater part of the silicic acid separates as gelatinous hydrate. The more dilute the solution, the more silicic acid remains dissolved, and in very dilute solutions no precipitate is formed. If the solution of an alkaline silicate, mixed with hydrochloric or nitric acid in excess, is evaporated to dryness, silicic acid separates in proportion as the acid escapes; and on treating the residue with hydrochloric acid and water, the silicic acid remains in the free state (or, if the temperature was restricted to 100°, as hydrate), as an insoluble white powder. In solutions of alkaline silicates not too dilute, chloride of ammonium produces a precipitate of hydrate of silicic acid (containing alkali): heating promotes the separation.

3. Some of the silicates insoluble in water are decomposed by hydrochloric acid or nitric acid, others are not affected by these acids, even on boiling. In the decomposition of the former, the greater portion of the silicic acid separates usually as gelatinous, more rarely as pulverulent hydrate. To effect the complete separation of the silicic acid, the hydrochloric acid solution, with the precipitated hydrate of silicic acid suspended in it, is evaporated to dryness, the residue heated with stirring, at a temperature somewhat above the boiling point of water until no more acid fumes escape, then moistened with hydrochloric acid, heated with water, and the solution containing the bases filtered from the residuary insoluble silicic acid. Of the silicates not decomposed by hydrochloric acid, many, such as kaolin, are completely decomposed by heating with a mixture of 8 parts of hydrated sulphuric acid and 3 parts of water, the silicic acid being separated in the pulverulent form; many others are acted on to some extent by this reagent. Silicates not decomposable by boiling with hydrochloric or sulphuric acid in the open air, at the ordinary atmospheric pressure, may generally be completely decomposed by heating them in a state of fine powder with the acids in sealed glass tubes at 200°–210° in an air or paraffin bath.

4. If a silicate, reduced to a fine powder, is fused with 4 parts of **carbonate of potassa and soda** mixture until the evolution of carbonic acid ceases, and the fused mass is then boiled with water, the greater part of the silicic acid dissolves as alkaline silicate, whilst the alkaline earths, the earths proper (with the exception of alumina and beryllia, which pass more or less completely into the solution), and the heavy metallic oxides are left undissolved. If the fused mass is treated with water, hydrochloric or nitric acid added to the mixture without previous filtration, to strongly acid reaction, and the solution treated as directed in 3, the silicic acid is left undissolved whilst the bases are dissolved. If the powdered silicate is fused with 4 parts of hydrate of baryta, the fused mass digested with water, with addition of hydrochloric or nitric acid, and the acid solution treated as directed in 3, the silicic acid separates, and the bases, especially the alkalies, are found in the filtrate.

5. If **hydrofluoric acid**, in concentrated aqueous solution or in the gaseous state, is allowed to act on silicic acid, fluoride of silicon escapes, $SiO_2 + 2HF = SiF_2 + 2HO$ [$SiO_2 + 4HF = SiF_4 + 2H_2O$]; the dilute acid dissolves silica to hydrofluosilicic acid, $SiO_2 + 3HF = HF{,}SiF_2 + 2HO$ [$SiO_2 + 6HF = H_2SiF_6 + 2H_2O$]. Hydrofluoric acid acting on silicates gives

rise to the formation of silicofluorides, $CaO,SiO_2 + 3HF = CaF,SiF_2 + 3HO$ [$CaSiO_3 + 6HF = CaSiF_6 + 3H_2O$], which when heated with hydrated sulphuric acid are changed to sulphates, with evolution of hydrofluoric acid and fluoride of silicon. If the powdered silicate is mixed with 3 parts of fluoride of ammonium, or 5 parts of fluoride of calcium in powder, the mixture made into a paste with hydrated sulphuric acid, and heat applied (best in the open air) until no more fumes escape, the whole of the silicic acid present volatilizes as fluoride of silicon. The bases present are found in the residue as sulphates, mixed, if fluoride of calcium was used, with sulphate of lime.

6. On mixing 1 part of silica or a silicate in fine powder with 2 parts of powdered cryolite or fluor spar (free from silica) and 4 or 5 parts of concentrated sulphuric acid, heating the mixture moderately in a platinum crucible, but not allowing it to spurt, and then holding close over the surface the loop of a stout platinum wire which has been freshly ignited, and now contains a drop of water, a pellicle of hydrated silicic acid will soon form on the latter from decomposition of the escaping fluoride of silicon (Barfoed).

7. If silicic acid or a silicate is fused with **carbonate of soda** in the loop of a platinum wire, frothing is observed in the bead owing to the evolution of carbonic acid. The bead obtained with pure silicic acid is always clear when hot; with silicates when they are rich in silicic acid (as the felspathic rocks) the bead is also clear, but if they are not it is opaque. The clearness of the cold bead depends on the proportion between silicic acid, soda, and other bases.

8. **Microcosmic salt**, in a state of fusion, dissolves but very little silicic acid. If, therefore, silicic acid or a silicate is fused, in small fragments, with microcosmic salt on a platinum wire, the bases are dissolved, whilst the silicic acid separates and floats about in the clear bead as a more or less translucent mass, exhibiting the shape of the fragment of substance used.

§ 151.

Recapitulation and Remarks.

Free carbonic acid is readily known by its reaction with lime water or baryta water; the carbonates are easily detected by the evolution of an inodorous gas, when they are treated with acids. Many carbonates—magnesite, for example—are not decomposed until they are heated with the acid. If the compounds evolve other gases besides carbonic acid, the gas must be tested with lime water or baryta water. Silicic acid, both in the free state and in silicates, may generally be readily detected by the reaction with microcosmic salt. It differs moreover from all other compounds in the form in which it is always obtained in analyses, by its insolubility in acids (except hydrofluoric acid), and in fusing bisulphate of potassa, and by being entirely soluble in boiling solutions of alkalies and alkaline carbonates; also from many compounds (especially titanic acid) by completely volatilizing when repeatedly evaporated in a platinum dish, with hydrofluoric acid (or fluoride of ammonium) and sulphuric acid.

Second Group of Inorganic Acids.

Acids which are precipitated by Nitrate of Silver, but not by Chloride of Barium: Hydrochloric Acid, Hydrobromic Acid, Hydriodic Acid, Hydrocyanic Acid, Hydroferrocyanic Acid and Hydroferricyanic Acid, Sulphuretted Hydrogen (*Nitrous Acid, Hypochlorous Acid, Chlorous Acid, Hypophosphorous Acid*).

The silver compounds corresponding with the hydrogen acids are insoluble in dilute nitric acid. These acids react with metallic oxides, the metals combining with the chlorine, bromine, iodine, cyanogen, or sulphur, whilst the oxygen of the metallic oxide forms water with the hydrogen of the acid.

§ 152.

a. Hydrochloric Acid, HCl [HCl].

1. Chlorine is a heavy yellowish-green gas of disagreeable and suffocating odour, and has a most injurious action on the respiratory organs; it destroys vegetable colours (litmus, indigo-blue, &c.); it is not inflammable, and supports the combustion of a few substances only. Minutely divided antimony, tin, &c., spontaneously ignite in it, and are converted into chlorides. It dissolves pretty freely in water, forming chlorine water which has a pale yellowish-green colour, smells strongly of the gas, bleaches vegetable colours, is decomposed by the action of light (§ 29), and loses its odour when shaken with mercury, the latter being converted into a mixture of subchloride and metal. Small quantities of free chlorine may be readily detected in a liquid by the red colour imparted to a mixture of sulphocyanate of potassium and protosalt of iron, or—in the absence of nitrous acid—by the blue colour imparted to a mixture of starch paste and iodide of potassium (see § 154, 9).

2. Hydrochloric acid, at the ordinary temperature and pressure, is a colourless gas, which forms dense fumes in the air, is suffocating and very irritant, and is exceedingly soluble in water. The concentrated solution (fuming hydrochloric acid) loses a large portion of its gas when heated.

3. The neutral metallic chlorides are readily soluble in water, with the exception of chloride of lead, chloride of silver, and mercurous chloride; most of the chlorides are white or colourless. Many of them volatilize at a high temperature without decomposition; others are decomposed on ignition, and many of them are fixed at a moderate red heat.

4. **Nitrate of silver**, even in highly dilute solutions containing free hydrochloric acid or metallic chlorides, produces a white precipitate of chloride of silver, $AgCl$ [$AgCl$]; this when exposed to light changes first to violet, then to black; it is insoluble in dilute nitric acid, but dissolves readily in ammonia as well as in cyanide of potassium, or in a boiling solution of sesquicarbonate of ammonia* (H. Hager). It melts without decomposition when heated. (Compare § 115, 7.) The

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* To prepare this, 1 part of transparent commercial carbonate of ammonia is dissolved in 9 parts of water at the ordinary temperature, and to each 10 c.c. of the solution 5 drops of aqueous ammonia, sp. gr. 0·96, are added.

chlorine in solution of green chloride of chromium is incompletely precipitated by nitrate of silver (Peligot), whilst from a solution of oxychloride of molybdenum in sulphuric acid it is not precipitated at all (Blomstrand). In a solution of chloride of gold, nitrate of silver yields an ochreous-yellow precipitate containing gold, silver, and chlorine.

5. **Mercurous nitrate** and **acetate of lead** produce precipitates of mercurous chloride, Hg_2Cl [Hg_2Cl_2], and chloride of lead, PbCl [$PbCl_2$], in solutions containing free hydrochloric acid or metallic chlorides. For the properties of these precipitates, see § 116, 6, and § 117, 7. In a solution of chloride of gold, acetate of lead gives a precipitate of double chloride of lead and gold.

6. If hydrochloric acid is heated with **binoxide of manganese** or **peroxide of lead**, or a chloride with **binoxide of manganese** or **peroxide of lead** and **sulphuric acid**, chlorine is evolved, which may be readily recognized by its odour, its yellowish-green colour, and its bleaching action on vegetable colours. The best way of testing the latter is to expose to the gas a moist slip of litmus-paper, or of paper coloured with indigo solution. No chlorine is evolved when metallic chlorides are heated with *acetic acid* and binoxide of manganese or peroxide of lead.

7. If a metallic chloride is triturated with **chromate of potassa**, the dry mixture treated with concentrated **sulphuric acid** in a tubulated retort, and a gentle heat applied, a deep brownish-red gas is copiously evolved, oxychloride of chromium or chlorochromic acid, CrO_2Cl [CrO_2Cl_2]; this condenses to a liquid of the same colour, and passes into the receiver. If this distillate is mixed with ammonia in excess, a yellow-coloured solution is obtained from the formation of chromate of ammonia,

$$CrO_2Cl + 2NH_4O,HO = NH_4Cl + NH_4O,CrO_3$$

$$[CrO_2Cl_2 + 4NH_4OH = 2NH_4Cl + (NH_4)_2CrO_4 + 2H_2O].$$

On adding an acid, the colour of the solution changes to a reddish-yellow, owing to the formation of acid chromate of ammonia.

8. The chlorine in the metallic chlorides insoluble in water and nitric acid may be detected by fusing them with carbonate of soda and potassa, and treating the fused mass with water, which will dissolve, besides the excess of the alkaline carbonate, the chloride of the alkali metal formed in the process.

9. If **oxide of copper** is dissolved in the outer blowpipe flame in a bead of **microcosmic salt** on a platinum wire in quantity sufficient to make the mass nearly opaque, a trace of a substance containing chlorine added to it while still in fusion, and the bead then exposed to the reducing flame, a flame of a fine blue colour, inclining to purple, will be seen encircling it so long as chlorine is present (Berzelius).

§ 153.

b. Hydrobromic Acid, HBr [HBr].

1. Bromine is a heavy reddish-brown fluid of a very disagreeable chlorine-like odour, which solidifies at a low temperature to a crystalline mass; this melts at −7·05°* and boils at 58·75°* under a pressure of 760 mm.; it volatilizes rapidly even at the ordinary temperature. The vapour is brownish-red. Bromine bleaches vegetable colours like chlorine; it is tolerably soluble in water, but dissolves more readily in alcohol, and

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* Ramsay and Young, Jour. Chem. Soc., Trans., 1886, 453.

very freely in ether, bisulphide of carbon, and chloroform. The solutions are yellowish-red. Bromine is removed from its aqueous solution when this is agitated with ether, bisulphide of carbon, or chloroform.

2. Hydrobromic acid gas, its aqueous solution, and the metallic bromides in their general behaviour are closely analogous to the corresponding chlorides.

3. **Nitrate of silver** added to aqueous solutions of hydrobromic acid or of bromides produces a yellowish-white precipitate of bromide of silver, $AgBr$ [$AgBr$], which changes to gray on exposure to light; this precipitate is insoluble in dilute nitric acid, almost insoluble in a boiling solution of sesquicarbonate of ammonia (H. Hager), and somewhat sparingly soluble in ammonia, but dissolves with facility in cyanide of potassium.

4. **Nitrate of protoxide of palladium**, but not palladious chloride, produces a reddish-brown precipitate of palladious bromide, $PdBr$ [$PdBr_2$], in neutral solutions of metallic bromides. In concentrated solutions, this precipitate is formed immediately; in dilute solutions, it makes its appearance only after the lapse of some time.

5. **Nitric acid** decomposes hydrobromic acid and the bromides, with the exception of bromide of silver and bromide of mercury, when the mixture is heated, and liberates the bromine, the hydrogen or the metal being oxidized. In the case of a solution, the liberated bromine colours it yellow or yellowish-red; whilst with bromides in the solid state or in concentrated solution, the brownish-red (if diluted, brownish-yellow) vapour of bromine escapes at the same time, and, if evolved in sufficient quantity, condenses in the cold part of the test-tube to small drops. In the cold, nitric acid, even the red fuming acid, fails to liberate the bromine in very dilute solutions of bromides, neither is it liberated by solution of nitrous acid in hydrated sulphuric acid, nor by hydrochloric acid and nitrite of potassa.

6. **Chlorine**, in the **gaseous** state or in **solution**, immediately liberates bromine from the solutions of its compounds; the liquid assuming a yellowish-red tint if the quantity of the bromine present is not too minute. A large excess of chlorine must be avoided, as this would cause formation of chloride of bromine, and the colour will be destroyed completely or nearly so. This reaction is made much more delicate if at the same time a liquid is added which dissolves bromine and does not mix with water, such as **bisulphide of carbon** or **chloroform.** The neutral or feebly acid solution is mixed in a test-tube with a little of one of these liquids, sufficient to form a large drop at the bottom; dilute chlorine water is then added drop by drop, and the tube shaken. With appreciable quantities of bromine, for example, 1 part in 1000 parts of water, the drop at the bottom acquires a reddish-yellow tint; with very minute quantities (1 part of bromine in 30,000 parts of water), a pale-yellow tint, which, however, is still distinctly discernible. Ether is *by no means* so well suited for this reaction. A large excess of chlorine water must be avoided, and it must always be ascertained first whether the chlorine water, mixed with a large quantity of water and some bisulphide of carbon or chloroform, and shaken, will leave these reagents quite uncoloured. If this is not the case, the chlorine water must not be used for the purpose. If the solution of bromine in bisulphide of carbon or chloroform (or ether) is mixed with some solution of potassa, the mixture shaken, and heat applied, the yellow colour

disappears, and the solution now contains bromide of potassium and bromate of potassa. By evaporation and ignition, the bromate of potassa is converted into bromide of potassium, and the ignited mass may then be further tested as directed in 7.

7. If bromides are heated with **binoxide of manganese** or **peroxide of lead** and **sulphuric acid**, concentrated or dilute, brownish-red vapours of bromine are given off. The presence of chlorides in large proportion is not favourable to the reaction; dilute solutions must then be used, so that chloride of bromine is not formed. Bromides give off bromine when heated with peroxide of lead and acetic acid, but not with binoxide of manganese and acetic acid (Vortmann). If the bromine be present in very minute quantity only, the colour of these vapours will not be visible; but if the mixture is heated in a small retort, and the evolved vapours are passed through a long glass condenser, the colour of the bromine vapours may generally be seen by looking lengthways through the tube, and the first drops of the distillate are also coloured yellow. The first vapours and the first drops of the distillate should be received in a test-tube containing some starch moistened with water; as,

8. If moistened **starch** is brought into contact with free bromine, more especially in the form of vapour, yellow bromide of starch is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by sealing the test-tube which contains the moistened starch and the first drops of the distillate from 7, and cautiously inverting it, so as to cause the moist starch to occupy the upper part of the tube whilst the liquid occupies the bottom. The presence of even the slightest trace of bromine will then, in the course of from twelve to twenty-four hours, impart a yellow tint to the starch, which, however, disappears again after some time. The test may be made in a simple manner, almost with the same degree of delicacy, by gently heating the liquid containing free bromine, or also the original mixture of bromide, binoxide of manganese, and sulphuric acid, in a very small beaker, covered with a watch-glass to the lower side of which a slip of paper moistened with starch paste and sprinkled with starch powder has been attached.

9. If sulphuric acid is poured over a mixture of a bromide with **dichromate of potassa**, and heat applied, a brownish-red gas is evolved, exactly as in the case of chlorides; this gas, however, consists of pure bromine, and therefore the liquid which passes over does not turn yellow, but becomes colourless when supersaturated with ammonia. Bromine can also be liberated from solutions of bromides, &c., by heating them with dichromate of potassa and sulphuric acid.

10. If a solution of hydrobromic acid or a bromide is mixed with a little **chloride of gold**, a straw colour or dark orange colour is produced owing to the formation of bromide of gold. If iodine is present, it must be removed before the solution of gold is added (Bill).

11. In the metallic bromides which are insoluble in water and nitric acid, the bromine is detected in the same way as the chlorine in the corresponding chlorides.

12. If a substance containing bromine is added to a bead of **microcosmic salt** saturated with **oxide of copper**, and the bead is then ignited in the inner blowpipe flame, the flame is coloured blue, inclining to green, more particularly at the edges (Berzelius).

§ 154.

c. Hydriodic Acid, HI [HI].

1. Iodine is a solid, soft substance of a peculiar odour. It generally occurs in the form of almost black, shining, crystalline scales. It melts at 114·15°[*] and boils at 184·35°[*] under a pressure of 760 mm., being converted into vapour of a beautiful violet-blue colour, which on cooling condenses to a black sublimate. It is very sparingly soluble in water, yielding a pale brown solution, but readily in alcohol or ether, or in an aqueous solution of iodide of potassium. The solutions in alcohol, ether, and iodide of potassium solution are deep red-brown; in bisulphide of carbon and chloroform, reddish-violet. Iodine destroys vegetable colours only slowly and imperfectly; it stains the skin brown; with starch, it forms an intensely dark-blue compound: this is invariably produced when iodine vapour or a solution containing free iodine comes in contact with starch, best with starch paste. It is decomposed by alkalies, by chlorine and bromine, and also by sulphurous acid and reducing agents generally.

2. Hydriodic acid is a gas resembling hydrochloric and hydrobromic acid; it dissolves copiously in water. The colourless hydrated hydriodic acid speedily becomes reddish-brown in contact with the air; water and free iodine are formed, and the latter dissolves in the hydriodic acid.

3. The iodides correspond also in many respects with the chlorides. Of the iodides of the heavy metals, however, many more are insoluble in water than is the case with the corresponding chlorides. Many iodides have characteristic colours, such as iodide of lead and subiodide and iodide of mercury.

4. **Nitrate of silver** in aqueous solutions of hydriodic acid or of iodides produces a yellowish-white precipitate of iodide of silver, AgI [AgI], which blackens on exposure to light; this precipitate is insoluble in dilute nitric acid, very sparingly soluble in aqueous ammonia of 5 per cent., insoluble in a boiling solution of sesquicarbonate of ammonia (H. Hager), but dissolves readily in cyanide of potassium.

5. **Protochloride of palladium** and **nitrate of protoxide of palladium** produce, even in very dilute solutions of hydriodic acid or metallic iodides, a brownish-black precipitate of palladious iodide, PdI [PdI_2], which dissolves to a trifling extent in saline solutions (chloride of sodium, chloride of magnesium, &c.), but is insoluble or nearly so in dilute cold hydrochloric and nitric acids.

6. A solution of 1 part of **sulphate of copper** and 2½ parts of **ferrous sulphate** throws down cuprous iodide, Cu_2I [Cu_2I_2], from neutral aqueous solutions of the iodides as a dirty white precipitate. The addition of a little ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent. Instead of the mixture of sulphates, sulphate of copper can be used, mixed with a sufficient excess of sulphurous acid or bisulphite of soda.

7. Pure **nitric acid**, free from nitrous acid, decomposes hydriodic acid or iodides only when acting on them in its concentrated form, especially on the application of heat. But **nitrous acid** and **hyponitric acid** decompose hydriodic acid and iodides with the greatest facility

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[*] Ramsay and Young, Jour. Chem. Soc., Trans., 1886, 453.

even in the most dilute solutions. Colourless solutions of iodides therefore acquire immediately a brownish-red colour on addition of some red fuming nitric acid, or of a mixture of this with concentrated sulphuric acid, or better still, on adding a solution of nitrous acid in hydrated sulphuric acid, or of nitrite of potassa and some sulphuric or hydrochloric acid. From somewhat concentrated solutions, the iodine separates in the form of black scales, whilst nitric oxide and iodine vapour escape.

8. As the blue coloration of iodide of starch remains visible in much more highly dilute solutions than the yellow colour of solution of iodine in water, the delicacy of the reaction described in 7 is considerably increased by first mixing the liquid to be tested for iodine with some thin, tolerably clear **starch paste**, then adding a few drops of dilute sulphuric acid, to make the fluid strongly acid, and finally one of the reagents mentioned in 7. A single drop of the solution of nitrous acid in sulphuric acid on a glass rod is sufficient to produce the reaction most distinctly. The author therefore strongly recommends this reagent, which was first proposed by Otto. Red fuming nitric acid must be added in somewhat larger quantity, in order that the reaction may take place satisfactorily; this reagent, therefore, is not well adapted to detect very minute quantities of iodine. The reaction with nitrite of potassa also is extremely delicate. The solution to be tested is mixed with dilute sulphuric acid or with hydrochloric acid to distinctly acid reaction, and a drop or two of a concentrated solution of nitrite of potassa is then added; in cases where the quantity of iodine present is very minute, the fluid turns reddish, instead of blue. An excess of the reagent containing nitrous acid does not materially impair the delicacy of the reaction. As iodide of starch dissolves in hot water forming a colourless liquid, the solutions must be cold; the colder they are, the more delicate the reaction. To attain the highest degree of delicacy, cool the fluid with ice, let the starch deposit, and place the test-tube upon white paper to observe the reaction (compare also § 157).

9. **Chlorine gas** and **chlorine water** also decompose iodine compounds, setting the iodine free; but if the chlorine is used in excess, the liberated iodine combines with it, forming a colourless chloride of iodine. If a little chlorine water, therefore, is added to a dilute solution of the metallic iodide, mixed with starch paste, it at once acquires a blue tint, but becomes colourless again on adding more chlorine water. As it is difficult not to exceed the proper limit, especially when the quantity of iodine present is but small, chlorine water is not well adapted for the detection of minute traces of iodine.

10. If a solution containing hydriodic acid or an iodide is mixed with **chloroform** or **bisulphide of carbon**, so as to leave a few drops undissolved, and one of the agents by which iodine is liberated (a drop of a solution of hyponitric acid in sulphuric acid—hydrochloric acid and nitrite of potassa—chlorine water, &c.) is added, the mixture vigorously shaken, and then allowed to remain at rest, the chloroform or bisulphide of carbon, coloured a deeper or lighter violet-red by the iodine dissolved in it, subsides to the bottom. This reaction is exceedingly delicate. If a solution containing free iodine is shaken with **petroleum**, **benzene**, or **ether**, the first two are coloured red, and the ether more of a reddish-brown or yellow. Iodine colours ether much more intensely than an equal quantity of bromine.

11. If metallic iodides are heated with **concentrated sulphuric**

acid, or with dilute **sulphuric acid** and **binoxide of manganese** or **peroxide of lead**, or with dilute **sulphuric acid** and **chromate of potassa**, or with **ferric chloride** or **sulphate**, iodine separates; this may be known by the colour of its vapour, or in the case of very minute quantities, by its action on a slip of paper coated with starch paste.

12. The iodides which are insoluble in water and nitric acid when fused with **carbonate of soda and potassa** mixture behave in the same manner as the corresponding chlorides.

13. A bead of **microcosmic salt** saturated with **oxide of copper**, touched with a substance containing iodine, and ignited in the inner blowpipe flame, imparts an intense green colour to the flame.

§ 155.

d. Hydrocyanic Acid, HC_2N or HCy [HCN].

1. Cyanogen, C_2N [C_2N_2], is a colourless gas of sp. gr. 1·8 having a peculiar penetrating odour; it burns with a crimson flame, and is pretty soluble in water.

2. Hydrocyanic acid (prussic acid) is a colourless, volatile, inflammable liquid, the odour of which remotely resembles that of bitter almonds; it is miscible with water in all proportions; in the pure state it speedily suffers decomposition. It is extremely poisonous. Its aqueous solution does not redden litmus-paper.

3. The cyanides of the alkalies and alkaline earths are soluble in water; the solutions smell of hydrocyanic acid. They are readily decomposed by acids, even by carbonic acid. Cyanides of potassium and sodium are not decomposed by fusion if air is excluded; when fused with oxides of lead, copper, antimony, tin, &c., they reduce these oxides, and are at the same time converted into cyanates; on fusion with metallic sulphides, these cyanides are converted into sulphocyanates. Only a few of the cyanides with heavy metals are soluble in water; all of them are decomposed by ignition, the cyanides of the noble metals being converted into cyanogen gas, and metal or a paracyanide of the metal, the cyanides of the other heavy metals into nitrogen gas and metallic carbides. Many of the cyanides with heavy metals are not decomposed by dilute oxygen acids, and only with difficulty by concentrated nitric acid. By heating and evaporation with concentrated sulphuric acid, all cyanides are decomposed; hydrochloric acid decomposes a few of them; sulphuretted hydrogen decomposes many cyanides.

4. The cyanides have a great tendency to combine with each other; hence most of the cyanides of the heavy metals dissolve in cyanide of potassium. The compounds formed are either:

a. True double salts, such as KCy + NiCy [$2KCN, Ni(CN)_2$]. From solutions of such double salts, acids, by decomposing the cyanide of potassium, precipitate the metallic cyanide which was combined with it. —Or,

b. Simple haloid salts, compounds of the first order, in which a metal, potassium, for example, is combined with a compound radicle consisting of cyanogen and another metal (iron, cobalt, manganese, chromium). Ferrocyanide and ferricyanide of potassium, $K_2C_6N_3Fe$ or K_2Cfy [$K_4FeC_6N_6$], and $K_3C_{12}N_6Fe_2$ or K_3Cfdy [$K_6Fe_2C_{12}H_{12}$], are compounds of this kind. From solutions of compounds of this nature, dilute acids do not separate metallic cyanides in the cold. If the potassium is displaced by hydrogen, peculiar hydrogen acids are formed which must not be confounded with hydrocyanic acid.

In the first place, the reactions of hydrocyanic acid and the simple cyanides will be considered, and subsequently, in separate sections, those of hydroferrocyanic and hydroferricyanic acid.

5. **Nitrate of silver** produces, in solutions of free hydrocyanic acid and of cyanides of the alkali metals, white precipitates of cyanide of silver, AgC_2N [$AgCN$], which are readily soluble in cyanide of potassium, but dissolve with some difficulty in ammonia, and are insoluble in dilute nitric acid; these precipitates are decomposed by ignition, leaving metallic silver with some paracyanide of silver. If free hydrocyanic acid is being tested for, the delicacy of the reaction is increased if the solution is first supersaturated with ammonia, nitrate of silver then added, and finally nitric acid to acid reaction.

6. If a solution of **ferrous sulphate** and a few drops of **ferric chloride** are added to a solution of free hydrocyanic acid, no alteration takes place; but if a few drops of a solution of **potassa** or **soda** is now added so as to render the solution alkaline, a bluish-green precipitate forms, which consists of a mixture of prussian-blue and hydrate of ferrosoferric oxide. If hydrochloric acid is added after an interval of five minutes (best after previous application of heat), the hydrate of ferrosoferric oxide dissolves, whilst the prussian-blue (p. 130, 6) remains undissolved. If only a very minute quantity of hydrocyanic acid be present, the liquid will merely appear green on the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates. The same final reaction is observed when a mixture of protosalt and persalt of iron is mixed with the solution of an alkaline cyanide, and hydrochloric acid is then added.

7. If a liquid containing a little hydrocyanic acid or cyanide of potassium (with free hydrocyanic acid, a drop or two of a dilute solution of potassa or soda should be added) be mixed with sufficient **yellow sulphide of ammonium** to impart a yellowish tint to the solution, the mixture warmed in a porcelain dish on the water-bath until it has become colourless, and the excess of sulphide of ammonium is decomposed or volatilized, and the whole finally evaporated to dryness, the liquid will contain sulphocyanate of the alkali. This is dissolved in a little water, acidified with a drop or two of hydrochloric acid, allowed to stand a few minutes, and then ferric chloride is added. A blood-red coloration is then produced by the sulphocyanate. If the colour is violet or the red coloration disappears rapidly, more ferric chloride must be added (Liebig, Almén). This reaction is exceedingly delicate. The following equation expresses the conversion of hydrocyanic acid into sulphocyanate:

$$NH_4S_5 + 2KCy = 2KCyS_2 + NH_4S$$

$$[(NH_4)_2S_5 + 4KCN = 4KCNS + (NH_4)_2S].$$

If an acetate is present, the reaction takes place only on adding more hydrochloric acid. To discover the cyanogen *in insoluble compounds* by converting it into sulphocyanate of iron, proceed as follows:—Fuse some hyposulphite of soda in the loop of a platinum wire until the water of crystallization is driven off and the mass swells up, dip it in the substance, heat for a little time, removing it from the flame as soon as the sulphur begins to burn, and then dip the mass in a few drops of ferric chloride mixed with a little hydrochloric acid. A permanent blood-red colour will be produced. If the substance is heated too long, the reaction fails, as the sulphocyanate of sodium formed is again destroyed. This method is well suited to distinguish chloride, bromide, or iodide of silver from cyanide of silver (A. Fröhde).

8. On mixing a moderately concentrated solution of an alkaline cyanide with a little **picric acid** solution (1 of picric acid to 250 of water), and boiling, the fluid appears dark-red from formation of picrocyamate (isopurpurate) of potassa, the coloration increasing in intensity by standing. If the solution of the alkaline cyanide is very dilute, no more picric acid must be added than is sufficient just to colour the liquid lemon-yellow. After boiling, the red coloration frequently does not make its appearance until the solution has cooled and stood some time. This reaction of C. D. Braun's is not so delicate as those described in 6 and 7, but it can be used to detect cyanide in presence of ferrocyanide of potassium, as the latter does not yield picrocyamate of potassa.

9. On saturating filter-paper with freshly prepared **tincture of guaiacum** containing 3 or 4 per cent. of the resin, allowing the alcohol to evaporate, moistening the paper with solution of **sulphate of copper** containing $\frac{1}{4}$ per cent. of the salt, and then exposing it to air in which a trace of hydrocyanic acid is present, it becomes blue from a separation of active oxygen;

$$3CuO + 2HCy = Cu_2Cy,CuCy + 2HO + O$$

$$[3CuO + 4HCN = Cu_2(CN)_2,Cu(CN)_2 + 2H_2O + O]$$

(Pagenstecher, Schönbein). This reaction is very delicate, but not characteristic of hydrocyanic acid, as air containing ammonia, nitrous acid, ozone, bromine, iodine, or hypochlorous acid also blues the paper. It is still less satisfactory when used for testing solutions, as not only do hydrocyanic acid and cyanides impart a blue colour to a mixture of tincture of guaiacum with very dilute sulphate of copper solution, but soluble chlorides, bromides, iodides, fluorides, &c., produce the same effect.

10. If a very dilute solution of **iodide of starch** is mixed with a trace of hydrocyanic acid, or, after addition of dilute sulphuric acid, with a trace of an alkaline cyanide, the blue colour will disappear immediately, or after a short time, the iodine and the hydrocyanic acid being transformed into iodide of cyanogen and hydriodic acid (Schönbein). This is a very delicate reaction, but cannot be relied on without further tests, as many other substances decolorize iodide of starch.

11. None of the above methods can be used to detect cyanogen in cyanide of mercury. To detect cyanogen in that compound the solution must be treated with sulphuretted hydrogen; the cyanide of mercury is then decomposed, sulphide of mercury is precipitated, and the solution contains free hydrocyanic acid. The cyanogen in solid cyanide of mercury is most readily detected by heating it in a glass tube. (Compare 3.) On heating a solution of cyanide of mercury in a retort with hydrochloric acid, or with chloride of sodium and oxalic acid, or with chloride of sodium and dilute sulphuric acid, the distillate will contain a large proportion of the cyanogen as hydrocyanic acid.

α. Hydroferrocyanic Acid, $H_2FeC_6N_3 = H_2Cfy$ [$H_4FeC_6N_6$].

Hydroferrocyanic acid is colourless, crystalline, and easily soluble in water. Its solutions have a strongly acid reaction. Some of the ferrocyanides, as those containing metals of the alkalies and alkaline earths, are soluble in water, but the greater part of them are insoluble. All the ferrocyanides are decomposed by ignition; where they are not quite anhydrous, hydrocyanic acid, carbonic acid, and ammonia escape, otherwise nitrogen and occasionally cyanogen. In solutions of hydroferrocyanic acid or of soluble ferrocyanides, **ferric chloride** produces a blue precipitate of ferrocyanide of iron (prussian-blue, comp. p. 130, 6); **sulphate of copper** gives a brownish-red precipitate of ferrocyanide of copper (see p. 147, 9); **nitrate of silver** a white precipitate of ferrocyanide of silver, $Ag_2FeC_6N_3 = Ag_2Cfy$ [$Ag_4FeC_6N_6$], which is insoluble in nitric acid and in ammonia if treated with it for a short time in the cold, but dissolves in cyanide of potassium. If boiled with aqueous ammonia, it is converted into ferrocyanide of silver and iron, whilst cyanide of silver and cyanide of ammonium pass into solution. If a not too dilute solution of an alkaline ferrocyanide be mixed with **hydrochloric acid**, and some **ether** poured on the top of the mixture, hydroferrocyanic acid will separate in the crystalline form where the two liquids meet. Ferrocyanides of the alkali-metals in aqueous solution are not decomposed by **carbonic acid**; this distinguishes them from cyanides of the alkali metals. Insoluble ferrocyanides are decomposed by boiling with solution of soda, ferrocyanide of sodium being formed, and the oxides thrown down, unless they are soluble in soda. On heating ferrocyanides, such as prussian-blue, with **ammoniacal silver solution**, oxide of iron separates, and the solution when acidified with nitric acid yields a precipitate of cyanide of silver (Werth). If ferrocyanides are heated with a mixture of 3 parts concentrated **sulphuric acid** and 1 part water, until the free acid is expelled, they are decomposed, and the cyanogen is driven off in the form of hydrocyanic acid; the metals remain behind as sulphates. On projecting metallic cyanides into fusing **nitrate of potassa**, the cyanogen is converted into carbonic acid and nitrogen, and the metals are converted into oxides, which remain in the crucible.

β. Hydroferricyanic Acid, $H_3Fe_2C_{12}N_6 = H_3Cfdy$ [$H_6Fe_2C_{12}N_{12}$].

Hydroferricyanic acid and many of the ferricyanides are soluble in water; like the ferrocyanides, all ferricyanides are decomposed by ignition. In the aqueous solutions of hydroferricyanic acid and its salts, **ferric chloride** produces no blue precipitate; but **ferrous sulphate** produces a blue precipitate of ferricyanide of iron (see p. 129, 8); **sulphate of copper** a yellowish-green precipitate of ferricyanide of copper, Cu_3Cfdy [$Cu_3Fe_2C_{12}N_{12}$], insoluble in hydrochloric acid; **nitrate of silver** an orange-coloured precipitate of ferricyanide of silver, Ag_3Cfdy [$Ag_6Fe_2C_{12}N_{12}$], which is insoluble in nitric acid, but dissolves readily in ammonia and in cyanide of potassium. Aqueous solutions of the ferricyanides of the alkali metals are not altered by **carbonic acid**, but **sulphuretted hydrogen** decomposes them; sulphur separates, and hydroferrocyanic acid and a ferrocyanide of the alkali metal is formed. Free hydroferricyanic acid or a solution of ferricyanide of potassium acidified with hydrochloric acid undergoes an analogous decomposition. The insoluble ferricyanides are decomposed by boiling with solution of **soda**, the metallic oxides being thrown down; in the filtrate from them either ferricyanide of sodium alone is found, or a mixture of ferro- with ferricyanide of sodium. Ferricyanides when heated with an **ammoniacal silver solution** are decomposed in a manner similar to the ferrocyanides. On being heated with a mixture of 3 parts concentrated **sulphuric acid** and 1 part water, and also on fusion with **nitrate of potassa**, the ferricyanides are decomposed like the ferrocyanides.

§ 156.

e. Sulphuretted Hydrogen or Hydrosulphuric Acid,

HS [H_2S].

1. Sulphur is a solid, brittle, friable, tasteless substance, insoluble in water. It occurs occasionally in the form of yellow or brownish crystals, or crystalline masses of a yellow or brownish colour, and occasionally in that of a yellow or yellowish-white or grayish-white powder. It melts at 118°, and at a higher temperature it is converted into brownish-yellow vapours, which in cold air condense to a yellow powder, and on the sides of the vessel to drops. Heated in the air, it burns with a bluish flame forming sulphurous acid, which is recognized at once by its suffocating odour. Concentrated nitric acid, nitrohydrochloric acid, and a mixture of chlorate of potassa and hydrochloric acid dissolve sulphur gradually, with the aid of a moderate heat, converting it into sulphuric acid; it dissolves in boiling solution of soda to a yellow liquid, which contains sulphide of sodium and hyposulphite of soda; it is insoluble in cold ammonia, but in warm ammonia it dissolves to a small extent. Bisulphide of carbon dissolves the ordinary variety of sulphur with ease, but there is also a modification which is insoluble in it. A hydrogen flame brought in contact with sulphur, or with sulphides or sulphates, becomes of a beautiful blue colour.

2. Sulphuretted hydrogen, at the ordinary temperature and pressure, is a colourless inflammable gas, soluble in water, readily recognized by its odour of rotten eggs; it transiently imparts a red tint to litmus-paper. When ignited, it burns with a blue flame yielding water and sulphurous acid. Sulphuretted hydrogen (the uses and properties of which have been already given, p. 49) is decomposed by chlorine, bromine, iodine, ferric chloride, permanganic acid, chromic acid, nitrous acid, and other oxidizing agents, with separation of sulphur.

3. Of the sulphides, only those with alkalies and alkaline earths are soluble in water. These, as well as the sulphides of iron, manganese, and zinc, are decomposed by dilute mineral acids, with evolution of sulphuretted hydrogen, which may be readily detected by its odour, and by its action on solution of lead (see 4). The decomposition of the higher sulphides is attended with separation of sulphur in a finely divided state; the white precipitate may be readily distinguished from similar precipitates by its behaviour when heated. Part of the sulphides of the metals of the fifth and sixth groups are decomposed by concentrated and boiling hydrochloric acid, with evolution of

sulphuretted hydrogen, whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur with mercury, gold, and platinum resist the action of both acids, more or less, but dissolve in nitrohydrochloric acid. On the dissolution of sulphides in nitric acid and in nitrohydrochloric acid, sulphuric acid is formed, and in most cases sulphur is simultaneously separated. Many metallic sulphides, more especially those of a higher degree of sulphuration, give a sublimate of sulphur when heated in a tube sealed at one end. All sulphides are decomposed by fusion with nitrate of potassa and carbonate of soda; on extracting the melt with water, the sulphur is found in solution as alkaline sulphate.

4. If sulphuretted hydrogen, in the gaseous state or in solution, is brought into contact with **nitrate of silver** or **acetate of lead**, black precipitates of sulphide of silver or sulphide of lead are formed. In cases, therefore, where the odour fails to afford sufficient proof of the presence of sulphuretted hydrogen, it can be detected by these reagents with certainty. If the sulphuretted hydrogen is present in the gaseous form, the air suspected to contain it is tested by placing in it a small slip of paper moistened with solution of acetate of lead and a little ammonia; if sulphuretted hydrogen is present, the slip becomes covered with a brownish-black shining film of sulphide of lead. To detect a trace of an alkaline sulphide in presence of a free alkali or an alkaline carbonate, the best way is to mix the liquid with a solution of oxide of lead in soda, which is prepared by mixing solution of acetate of lead with solution of soda until the precipitate which forms at first is redissolved.

5. If a liquid containing sulphuretted hydrogen or an alkaline sulphide is mixed with solution of soda, and **nitroprusside of sodium** added, it acquires a fine reddish-violet tint. The reaction is very delicate; but that with solution of oxide of lead in soda is still more sensitive.

6. Very minute traces of sulphuretted hydrogen may be detected in an aqueous solution by adding to it $\frac{1}{50}$th of its volume of fuming hydrochloric acid and a few particles of **paramidodimethylaniline sulphate**,* and, as soon as the latter has dissolved, 1 or 2 drops of a dilute solution of ferric chloride. If sulphuretted hydrogen is present, methylene-blue is formed, which colours the solution to pure blue (H. Caro, E. Fischer).

7. If metallic sulphides are exposed to the **oxidizing flame of the blowpipe**, the sulphur burns with a blue flame, emitting at the same time the well-known odour of sulphurous acid. If a metallic sulphide is heated in a glass tube open at both ends, in the upper part of which a slip of blue litmus-paper is inserted, and the tube is held in a slanting position during the operation, the escaping sulphurous acid reddens the litmus-paper.

8. If a finely pulverized metallic sulphide is boiled in a porcelain dish with solution of **potassa**, and the mixture then heated to incipient fusion of the hydrate of potassa, or if the test specimen is fused in a platinum spoon with hydrate of potassa, and the mass is, in either case, dissolved in a little water, a piece of bright silver (a polished coin) put into the solution, and the latter warmed, a brownish-black film of sulphide of

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* For the preparation of this reagent, see Zeit. anal. Chem., **23**, 226.

silver forms on the metal. This film may be removed afterwards by rubbing the metal with leather and quicklime (v. Kobell).

9. If the powder of a sulphide which is not decomposed by hydrochloric acid, or only with difficulty, be mixed in a small cylinder, or in a wide-necked flask, with an equal volume of finely divided **iron free from sulphur** (ferrum alcoholisatum) and some moderately dilute hydrochloric acid (1 volume of the concentrated acid to 1 volume of water) poured over the mixture, in a layer a few lines thick, sulphuretted hydrogen will escape along with the hydrogen. This may be easily detected by placing a slip of paper moistened with solution of acetate of lead, and dried again, under the cork, so that the bottom is covered by it, the ends of the slip projecting on both sides, and then loosely inserting the cork into the mouth of the flask. Realgar, orpiment, and molybdenite do not show this reaction (v. Kobell).

§ 157.

Recapitulation and Remarks.

Most of the acids of the first group are also precipitated by nitrate of silver, but the precipitates cannot well be confounded with the silver compounds of the acids of the second group, as the former are soluble in dilute nitric acid, whilst the latter are insoluble. The presence of sulphuretted hydrogen interferes more or less with the testing for the other acids of the second group; this acid, if present, must be removed, therefore, before the testing for the other acids can be proceeded with. The removal of the sulphuretted hydrogen, if present in the free state, may be effected by boiling; and if as an alkali sulphide, by the addition of some metallic salt, which will not precipitate any of the other acids, or at least not in an acid solution. Hydrocyanic acid may be detected, even in presence of hydrochloric, hydrobromic, or hydriodic acid, by the equally characteristic and delicate reaction with a solution containing ferrosoferric oxide. Cyanides of the alkali metals may be detected in the presence of alkaline ferro- and ferricyanides by treating the aqueous solution with carbonic acid gas and then distilling; the cyanogen which was combined with the alkali metals then passes over in the distillate as hydrocyanic acid. The ferrocyanogen and ferricyanogen may also be cautiously precipitated by the addition of ferric and ferrous sulphate respectively, and the cyanogen detected in the filtrate according to § 155, 6. Hydriodic acid may be easily detected in the presence of hydrochloric and hydrobromic acids by adding starch or carbon bisulphide and a solution containing nitrous acid. This iodine reaction, however, is affected or altogether prevented by the presence of cyanogen compounds; the recognition of chlorine and bromine is also rendered more or less difficult by the presence of iodine or cyanogen compounds. Therefore, before testing for iodine, any cyanogen present must be either removed or rendered inert, and when bromine or chlorine are tested for, any cyanogen or iodine present must be similarly treated. The separation of the cyanogen may be readily effected by igniting the mixed silver salts: the cyanide of silver is decomposed, whilst the chloride, bromide, and iodide remain unaltered. On fusing the ignited residue with carbonate of soda and potassa, and boiling the fused mass with water, chloride, bromide, and iodide of the alkali metals are obtained in solution. The fused silver compounds may also be readily decomposed with zinc; for this purpose water is poured over them, a little sulphuric acid and a fragment of zinc added, the mixture allowed to remain for some time, and the solution of chloride, bromide, or iodide of zinc filtered off from the separated metallic silver.

The iodine may be separated from the chlorine and bromine by treating the silver compounds with ammonia, but more accurately by precipitating the iodine as cuprous iodide. From bromine alone, iodine may be separated most accurately by palladious chloride, which only precipitates the iodine; it may be separated from chlorine by nitrate of protoxide of palladium.

Bromine in presence of iodine and chlorine may be identified by the following simple operation: The liquid is mixed with a few drops of dilute sulphuric acid, then with some starch-paste, and a little red fuming nitric acid, or, better still, a solution of nitrous acid in sulphuric acid is added, whereupon the iodine reaction at once appears. Chlorine-water is now added drop by drop until that reaction has disappeared, then some more chlorine-water to set the bromine free, which may be separated and identified by means of chloroform or bisulphide of carbon. Or the iodine—liberated in a very dilute solution—may be taken up with chloroform or bisulphide of carbon, the solution filtered through a moist filter, and the bromine detected in the filtrate by means of chloroform or bisulphide of carbon and chlorine water. Or instead of this, chlorine water may be cautiously added immediately after the liberation of the iodine, when the violet-red coloration will gradually fade away, and give place to the brownish-red colour which bromine imparts to these solvents.

For the detection of metallic chlorides in the presence of metallic bromides and iodides, that is to say, to recognize the three halogens in the presence of one another, the freshly precipitated mixed silver salts are washed by decantation, and then boiled for from two to three minutes with 80 to 100 times the volume of an aqueous solution of sesquicarbonate of ammonia (see note, p. 213), allowed to settle, the solution decanted, and the extraction repeated once more by boiling with fresh sesquicarbonate of ammonia solution. The solution contains all the silver chloride (with a trace of silver bromide). The residue of silver iodide and bromide is treated with a 5 per cent. solution of ammonia (sp. gr. = 0·9783); this dissolves all the silver bromide (with a trace of silver iodide), nearly all the silver iodide remaining undissolved (H. Hager). The precipitate thrown down from the ammoniacal solution and the undissolved silver iodide may then be fused with sodium carbonate, the fused mass treated with water, and the filtrates which contain the halogens in an almost pure condition may then be tested further. In order to recognize the chlorine, the sesquicarbonate of ammonia solution is almost neutralized with sulphuric acid (the reaction may be slightly alkaline, but must not be acid), evaporated to dryness, and the residue fused with dichromate of potassa and the melt treated according to § 152, 7. Chlorine may also be detected in the presence of bromine and iodine by the following method:—The solution containing the halogens combined with the alkali or alkaline earthy metals is heated with acetic acid and peroxide of lead until the supernatant liquid is colourless and has no longer the slightest odour of iodine or bromine; in this way the whole of the bromine and part of the iodine are driven off, the remainder of the latter remaining as iodate of lead along with the excess of lead peroxide. This is filtered off, the precipitate washed with boiling water, and the chlorine precipitated from the filtrate by the addition of silver nitrate. (G. Vortmann.)

A. Mitscherlich states that by long practice it is possible to detect chlorine, bromine, and iodine in presence of one another by means of the spectroscope: see Zeit. anal. Chem. 4, 153.*

As regards the iodide of starch reaction, it must be noted that salts (alum, alkaline sulphates, sulphate of magnesia, &c.) diminish its delicacy. It is also found, as regards this and the bisulphide of carbon reaction, that many organic substances, such as albuminoïds (Puchot), resorcin, orcin, phloroglucin (Hlasiwetz), and especially tannin, may entirely prevent the reaction; moreover, when nitrous acid is used to liberate the iodine, the presence of sulphocyanates may occasion mistakes (Nadler), since a reddish colour may be produced even when iodine is not present from formation of pseudosulphocyanogen. On shaking with bisulphide of carbon, the colouring substance is for the most part taken up by it.

Besides the above-mentioned reagents for liberating iodine, many others have been proposed, and may be employed; thus, for instance, iodic acid or an alkaline iodate and hydrochloric acid (v. Liebig); ferric chloride and sulphuric acid, or chloride of platinum, with addition of some hydrochloric acid (Hempel); permanganate of potassa or chromic acid in slightly acidified solution, &c. With respect to these reagents, it should be noted that iodic acid must be used with the greatest caution, as *a*, in presence of reducing substances iodine is set free from the reagent, and *b*, an excess of iodic acid at once stops the reaction. Ferric chloride, with addition of sulphuric acid, does not act immediately in very dilute solutions; but after a time the reaction will take place, revealing the presence of even the minutest trace of iodine; an excess of the reagent interferes but little with the test. Ferric chloride may be used with advantage when iodine is to be liberated in the state of vapour, in the presence of sulphocyanates, for example, or of those organic substances which interfere with the iodide of starch reaction. The solution in that case is heated nearly to boiling, and the escaping fumes are allowed to act on paper smeared with fresh starch paste. Permanganate of potassa acts immediately, even in the most dilute solutions; as, however, a liquid coloured by minute traces of iodide of starch appears reddish, the coloration imparted by the permanganic acid alone may lead to mistakes in the iodide of starch test. From six to twelve hours should therefore always be allowed to elapse before judging of the actual nature of the coloration with this reagent. The method of operating may of course be modified in various ways, so as to increase the delicacy of the starch reaction; interesting particulars upon this point may be found in the papers of Morin† and Hempel.‡

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* Respecting the detection of small quantities of chlorides in the presence of large amounts of iodides, see Dietzell, Zeit. anal. Chem., 8, 453.—Small quantities of chlorine or bromine with large amounts of iodine, Bohlig, *ibid.*, 9, 315.—Small quantities of iodine in the presence of bromine and bromides, Jorissen, *ibid.*, 19, 353.—For the detection of chlorine, bromine, iodine, cyanogen, ferrocyanogen and ferricyanogen, also of chloric, bromic, and iodic acids in a mixture, see Longi, *ibid.*, 23, 70.

† Jour. pr. Chem., 78, 1.

‡ Ann. Chem. Pharm., 107, 102.

§ 158.

Reactions of Rarer Acids of the Second Group.

1. **Nitrous Acid**, NO_3 [N_2O_3].

Nitrous acid, in the free state, at the ordinary temperature, is a brownish-red gas. In contact with water it is converted, for the most part at least, into nitric acid, which dissolves, and nitric oxide, which escapes in part when the quantity of water is not very large, $3NO_3+HO=HO,NO_5+2NO_2$ [$3N_2O_3+H_2O=2HNO_3+4NO$]. The nitrites are decomposed by ignition; most of them are soluble in water. When nitrites or concentrated solutions of nitrites are treated with dilute sulphuric acid, it is not nitrous acid gas which is evolved, but nitric oxide gas, whilst nitric acid is simultaneously formed. Very dilute solutions of nitrites, such, for example, as contain 0·006 gram, or less, of nitrous acid per litre, when acidified with dilute sulphuric acid or acetic acid and distilled, give a distillate which contains almost the whole of the nitrous acid originally present in the solution; in fact, the first 10–20 c.c. which pass over contain the greater portion of it. This affords a means of concentrating the nitrous acid in a small quantity of liquid, and at the same time separating it from substances which interfere with its detection; of course this method is not applicable when substances which decompose nitrous acid, such as sulphuretted hydrogen, are present. In solutions of nitrites of the alkalies, **nitrate of silver** produces a white precipitate, which dissolves in a very large proportion of water, especially when warmed; in neutral solutions, **ferrous sulphate** produces a pale brownish-yellow coloration, but on the addition of acetic acid this changes to brownish-black, from the nitric oxide dissolving in the solution of the sulphate of iron (distinction from nitric acid). **Sulphuretted hydrogen** produces a white precipitate of sulphur, which appears immediately if free nitrous acid is present, but only gradually, after a time, in neutral solutions of nitrites of the alkalies. **Pyrogallic acid** imparts a brown colour to solutions of nitrites acidified with sulphuric acid, even when very dilute (Schönbein). If **cyanide of potassium** be added to an alkaline nitrite, then some neutral solution of **chloride of cobalt** and a little acetic acid, the liquid becomes of a rosy-orange colour from the formation of nitrocyanide of cobalt and potassium (C. D. Braun). A still more delicate reagent for nitrous acid is solution of **iodide of potassium mixed with starch paste, or iodide of zinc*** solution, especially if sulphuric acid is added (Price, Schönbein); water containing one hundred-thousandth part of nitrite of potassa, together with free sulphuric acid, is coloured distinctly blue by this reagent in a few seconds, and a few minutes suffice to produce the same effect in water containing one millionth part of nitrite of potassa. It must be borne in mind, however, that this reaction is trustworthy only when no other substance is present capable of decomposing iodide of potassium, such, for instance, as iodic acid, ferric oxide, &c. By adding **indigo solution** to water until it has lost its transparence from the depth of colour, then hydrochloric acid and a solution of an **alkaline polysulphide** with stirring, until the blue colour just vanishes, and filtering, a clear liquid is obtained which acquires a distinct blue colour on the addition of a solution containing the merest trace of nitrous acid. This reaction is to be recommended if other reducing substances are present which interfere with the action of nitrous acid on an acidified solution of starch and iodide of potassium (Schönbein); but it must not be overlooked that other oxidizing substances reproduce the blue colour. On mixing

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* A stable solution of iodide of zinc may be prepared according to the following directions:—5 grams of starch and 20 grams of chloride of zinc are boiled together with 100 c.c. of water until the starch granules are completely dissolved, the water being renewed from time to time; 2 grams of iodide of zinc are then added, the whole diluted to 1000 c.c. and filtered. The solution must be kept in a closed flask in the dark.

a solution of nitrous acid (for instance, a solution of nitrite of potassa acidified with acetic acid) with **sulphocyanate of potassium**, the liquid is not coloured, but if nitric, hydrochloric, or sulphuric acid be added, a dark-red colour will make its appearance, which vanishes on adding alcohol or on heating for a short time (difference from sulphocyanate of iron). The colouring substance is mostly taken up from the solution on shaking it with bisulphide of carbon. **Permanganate of potassa** has no action on neutral solutions of nitrites, but on adding a dilute acid, the solution becomes decolorized, and with excess of permanganate all the nitrous acid is converted into nitric acid.*

2. Hypochlorous Acid, ClO [Cl_2O].

At the ordinary temperature, hypochlorous acid is a deep yellowish-green gas of a disagreeable, irritating odour, similar to that of chlorine; when heated, it explodes and is decomposed into chlorine and oxygen. It is soluble in water, and the dilute aqueous solution bears distillation. The hypochlorites are usually accompanied by metallic chlorides, as in the case, for instance, in chloride of lime, *eau de Javelle*, &c.; these solutions are changed by boiling, the hypochlorite being resolved into chloride of the metal and a chlorate, attended, in the case of concentrated, but not in that of dilute solutions, with evolution of oxygen. If a solution of chloride of lime is mixed with hydrochloric acid or sulphuric acid in excess, chlorine is disengaged, but on passing a current of carbonic acid into a solution of chloride of lime, hypochlorous acid is set free. **Nitrate of silver** throws down chloride of silver from solution of chloride of lime which has been neutralized with nitric acid, but not so as to smell of chlorine; the hypochlorite of silver, which forms at first, is speedily resolved into chloride of silver and chlorate of silver: $3(AgO,ClO) = AgO,ClO_5 + 2AgCl$ [$3AgClO = AgClO_3 + 2AgCl$]. **Nitrate of lead** produces a precipitate which is at first white, but changes gradually to orange-red, and ultimately to brown, owing to formation of peroxide; **salts of protoxide of manganese** give a brown-black precipitate of hydrate of binoxide of manganese. The action of free hypochlorous acid on **mercury** gives rise to yellowish-brown oxychloride of mercury (chlorine, on the other hand, gives mercurous chloride). If, however, but little hypochlorous acid is present along with much chlorine, so that, after long-continued shaking, the hypochlorous acid cannot be detected by the colour of the precipitate, the latter must be treated with hydrochloric acid; this dissolves the oxychloride and leaves the mercurous chloride; if hypochlorous acid were present in the original solution, the filtrate will contain mercuric chloride. Hypochlorites can be detected still more readily than the free acid, by shaking the solution with mercury; yellow mercuric oxide is formed which gradually becomes red, and, on continuing the shaking, adheres to the sides of the bottle. Chlorous acid and chloric acid in combination with bases have no action on mercury (Wolters). A solution of **permanganate of potassa** is not decolorized. Solutions of **litmus and indigo** are decolorized by solutions of hypochlorites even when alkaline, but still more rapidly and completely on adding an acid. If a solution of arsenious acid in hydrochloric acid is coloured blue with solution of indigo, and a solution of chloride of lime is added, with active stirring, decolorization will take place only after the whole of the arsenious acid has been converted into arsenic acid.

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* The following reagents have also been proposed for the detection of small amounts and especially of very minute traces of nitrous acid:—Diamidobenzoic acid (P. Griess, Zeit. anal. Chem., **10**, 92); diphenylamine (E. Kopp, *ibid.*, **11**, 461); phenol and mercurous nitrate (P. C. Plugge, *ibid.*, **14**, 131); metadiamidobenzene (P. Griess, *ibid.*, **18**, 127); sulphanilic acid in combination with naphthylamine (P. Griess, *ibid.*, **18**, 597); rosaniline (A. Jorissen, *ibid.*, **21**, 210); paramidobenzene-azodimethylaniline (Meldola, Ber. deutsch. chem. Ges., **17**, 256, and Zeit. anal. Chem., **24**, 98).

3. Chlorous Acid, ClO_3 [Cl_2O_3].

Chlorous acid is a yellowish-green gas of a peculiar and very disagreeable odour, which explodes at 57°, being resolved into chlorine and oxygen. It is soluble in water, and the solution is intensely yellow, even when very dilute. Most of the chlorites are soluble in water; the solutions are readily decomposed, chlorides and chlorates being formed. **Nitrate of silver** gives a white precipitate of chlorite of silver, which is soluble in much water. A solution of **permanganate of potassa** is immediately decomposed by free chlorous acid, a brown precipitate separating after some time. Tincture of **litmus** and solution of **indigo** are instantly decolorized, even if mixed with arsenious acid in excess. If a slightly acidified dilute solution of a ferrous salt is mixed with a dilute solution of chlorous acid, the liquid transiently acquires an amethyst tint, and does not assume the yellowish colour of salts of sesquioxide of iron until the lapse of a few seconds (Lenssen).

4. Hypophosphorous Acid, PO [P_2O].

The concentrated solution of hypophosphorous acid is of syrupy consistence, and resembles that of phosphorous acid (see § 148), with which it also has this in common, that when it is heated without access of air it is resolved into hydrate of phosphoric acid and non-spontaneously inflammable phosphuretted hydrogen gas. Almost all hypophosphites are soluble in water; all are resolved by ignition into the corresponding phosphate, and phosphuretted hydrogen, which in most cases is spontaneously inflammable; the latter is partly resolved into phosphorus and hydrogen. **Chloride of barium, chloride of calcium,** and **acetate of lead** give no precipitate with solutions of hypophosphites (difference from phosphorous acid). **Nitrate of silver** with hypophosphites gives a precipitate of hypophosphite of silver, which is white at first, but turns black even at the ordinary temperature, and still more rapidly on heating, metallic silver being separated. With **chloride of mercury** in excess, hypophosphorous acid precipitates mercurous chloride slowly in the cold, more rapidly on heating. With **zinc** and **dilute sulphuric acid**, hypophosphorous acid gives hydrogen mixed with phosphuretted hydrogen. (Compare § 148, Phosphorous Acid).

Third Group of Inorganic Acids.

Acids which are not precipitated either by Salts of Baryta or by Salts of Silver: Nitric Acid, Chloric Acid (*Perchloric Acid*).

§ 159.

a. Nitric Acid, NO_5 [N_2O_5].

1. Anhydrous nitric acid crystallizes in six-sided prisms. It fuses at 29·5°, and boils at about 45° (Deville). The pure hydrate is a colourless (if it contains hyponitric acid it is red) exceedingly corrosive fluid of sp. gr. 1·522, which boils at 86°, and emits fumes in the air; it quickly destroys organic substances, and colours many nitrogenous matters intensely yellow.

2. All the neutral salts of nitric acid are soluble in water; some only of the basic nitrates are insoluble. All nitrates are decomposed at bright red heat. Those with alkaline bases yield oxygen at first, and are converted into nitrites; afterwards they give off oxygen and nitrogen. Those with other bases yield oxygen and nitrous or hyponitric acid; many (containing water) give off hydrated nitric acids.

3. If a nitrate is thrown on to **red-hot charcoal**, or if charcoal or some organic substance—paper, for instance—is brought into contact with a melted nitrate, deflagration takes place, that is, the charcoal burns at the expense of the oxygen of the nitric acid, with vivid scintillation.

4. If a nitrate is mixed with **cyanide of potassium** in powder and a small quantity of the mixture heated on platinum foil, a vivid deflagration ensues, attended with distinct ignition and detonation. Even very minute quantities of nitrates may be detected in this way.

5. If a nitrate is mixed with **copper filings**, and the mixture heated in a test-tube with concentrated sulphuric acid, the air in the tube acquires a yellowish-red tint, owing to the nitric oxide, which is formed on the oxidation of the copper by the nitric acid, combining with the oxygen of the air to hyponitric acid. The coloration may be observed most distinctly by looking lengthways through the tube.

6. If a solution of a nitrate is mixed with an equal volume of concentrated **sulphuric acid**, free from nitric and hyponitric acids, the mixture allowed to cool, and a concentrated solution of **ferrous sulphate** cautiously added to it so that the liquids do not mix, the surface of contact of the two solutions shows at first a purple, afterwards a brown colour, or, in cases where only a very minute quantity of nitric acid is present, a reddish colour. On mixing the liquids a little, the brown zone becomes darker. In this process, the nitric acid is decomposed by the protoxide of iron, three-fifths of its oxygen combining with the protoxide to form sesquioxide, whilst the nitric oxide produced combines with the remaining undecomposed ferrous salt, and forms with it a peculiar compound, which dissolves in water with a brownish-black colour. The presence of large quantities of chlorides considerably diminishes the delicacy of this reaction. A similar reaction is observed in presence of selenious acid; but on mixing the liquids and allowing it to stand, red selenium separates (Wittstock).

7. If some hydrochloric acid is boiled in a test-tube, 1 or 2 drops of very dilute **solution of sulphate of indigo** added, and the mixture boiled again, the fluid remains blue (provided the hydrochloric acid is free from chlorine). If a nitrate, solid or in solution, is now added to the light-blue liquid, and the mixture heated again to boiling, the colour disappears owing to the decomposition of the indigo blue. This is a most delicate reaction, and the addition of chloride of sodium renders it even more sensitive. It must be borne in mind, however, that several other substances also cause decoloration of solution of indigo—free chlorine especially.

8. If a little **brucine** is dissolved in pure concentrated sulphuric acid,[*] and a small quantity of a liquid containing nitric acid added to the solution, the latter immediately acquires a magnificent red colour at the point where the two solutions mix; this reaction is extraordinarily delicate. The colour soon passes into reddish-yellow. Chloric acid gives the same reaction.

9. One part of **phenol** (carbolic acid) is dissolved in 4 parts of

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[*] The ordinary pure concentrated sulphuric acid of commerce usually gives a rose colour with brucine, due to the presence in it of a small quantity of oxides of nitrogen. Such acid can, however, be readily purified by diluting it with water until it has a sp. gr. of 1·4—best in a platinum dish—and then heating it to boiling for some time.

strong sulphuric acid, and 2 parts of water added. When a drop or two of this solution is added to a solid nitrate (for example, the residue obtained by evaporating a few drops of well-water containing nitrates) a reddish-brown colour is produced, from the formation of a nitro-compound; on adding a drop or two of strong ammonia, the colour turns to yellow, sometimes passing through a green shade. This is a very delicate reaction (H. Sprengel). This test may also be made by adding 1 or 2 drops of the liquid to be examined to some pure concentrated sulphuric acid, and then introducing a crystal of phenol and warming a little, or by rendering the liquid to be tested strongly acid with hydrochloric acid, adding some phenol, and heating to about 80° or 90°; if nitric acid is present, a dark coloration always appears which is usually red or brown, but is occasionally green (H. Hager).

10. An admirable reagent for the detection of nitric acid may be prepared by pouring pure concentrated sulphuric acid on some crystals of **diphenylamine**, adding a little water, and mixing the solution thus formed with more concentrated sulphuric acid; the solution should contain about 1 milligram of diphenylamine in 10 c.c. About 0·5 c.c. of the solution thus prepared is placed in a watch-glass or the inverted lid of a porcelain crucible, and a drop of the liquid to be examined is then allowed to fall in the midst of the reagent; if nitric acid be present, a magnificent blue coloured ring will be formed as the two solutions mix (E. Kopp). This exceedingly delicate test may also be applied by adding a few drops of a solution of diphenylamine sulphate to the liquid to be tested, and then adding pure concentrated sulphuric acid so that two layers are formed. The blue coloration gradually turns to a green, and finally disappears. The interpretation of this reaction requires caution, as nitrous acid, chloric acid, hypochlorous acid, bromic, iodic, vanadic, chromic, permanganic, and molybdic acids, as also ferric salts, hydrogen peroxide, and barium peroxide, all yield blue colorations (Laar).

11. On adding a few drops of a solution of sulphate of **paratoluidine** to a solution containing a nitrate, and then an equal volume of concentrated sulphuric acid, taking care that the two do not mix, a red zone is formed at the surface of contact, gradually changing to dark yellow.* This is not so delicate as the brucine or diphenylamine reaction, but is useful for the detection of nitric acid in the presence of small quantities of nitrous acid, as the latter at first exhibits a yellowish or brownish-yellow coloration, which does not turn red until after some time (Longi). Chloric acid and other oxidizing compounds produce a similar coloration.

12. Very minute quantities of nitric acid may be detected by reducing the nitric acid first to nitrous acid. This may be effected either in the moist or in the dry way; in the former, by heating the solution containing the nitric acid or the nitrate for some time with finely-divided **zinc**, best with **zinc amalgam**, and then filtering (Schönbein); in the dry way, by fusing the substance with carbonate of soda at a moderate heat, extracting the mass, when cold, with water, and filtering. On adding either of the filtrates to a solution of iodide of potassium

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* Aniline oil, containing a mixture of aniline and paratoluidine, may also be used in this reaction instead of the paratoluidine. C. D. Braun recommended this method in 1867 (Zeit. anal. Chem., **6**, 72). The details, however, differ somewhat from those given by Longi.

mixed with starch paste and dilute sulphuric acid, the fluid acquires a blue colour from the iodide of starch formed (comp. § 158, 1).

13. If a nitrate is mixed with caustic potash solution, some **aluminium** or **zinc** and **iron filings** added, and the whole gently warmed, ammonia is evolved, and may easily be detected by the methods given in § 91, 3.

§ 160.

b. **Chloric Acid**, ClO_5 $[Cl_2O_5]$.

1. Chloric acid, in its most highly concentrated solution, is a colourless or slightly yellowish oily fluid, with a feeble odour, resembling that of nitric acid. It first reddens litmus, then bleaches it. Dilute chloric acid is colourless and inodorous.

2. All chlorates are soluble in water. When heated to redness, the whole of their oxygen escapes and metallic chlorides remain; or else the chlorine and oxygen of the chloric acid are evolved and an oxide remains (chlorates of the earths).

3. When heated with **charcoal** or an organic substance, the chlorates deflagrate, and this with far greater violence than the nitrates.

4. If a mixture of a chlorate with **cyanide of potassium** is heated on platinum foil, deflagration takes place, attended with strong detonation and ignition, even though the chlorate be present only in very small quantity. This experiment should be made with minute quantities only.

5. If the solution of a chlorate is coloured light blue with **solution of indigo**, a little dilute sulphuric acid added, and a small quantity of aqueous sulphurous acid or a solution of sulphite of soda dropped cautiously into the blue fluid, the colour of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric acid of its oxygen, setting free chlorine or a lower oxide of it, which then decolorizes the indigo. An excess of sulphurous acid must be avoided, or sulphuric and hydrochloric acids would be formed.

6. If chlorates are heated with moderately dilute **hydrochloric acid**, the two acids mutually decompose one another, forming water, chlorine, and hypochloric acid, ClO_4 $[ClO_2]$. The test-tube in which the experiment is made becomes filled with a greenish-yellow gas of a very disagreeable odour, resembling that of chlorine, and the hydrochloric acid acquires a greenish-yellow colour. If the hydrochloric acid is coloured blue with indigo solution, the presence of very minute quantities of chlorates will suffice to destroy the indigo colour at once.

7. If a little chlorate is added to a few drops of **concentrated sulphuric acid** in a watch-glass, chloric acid is at first set free, but is at once decomposed into hydrate of perchloric acid, hypochloric acid, and water,

$$6(HO,ClO_5) = 2(HO,ClO_7) + 4ClO_4 + 4HO$$
$$[6HClO_3 = 2HClO_4 + 4ClO_2 + 2H_2O].$$

The hypochloric acid imparts an intensely yellow tint to the sulphuric acid, and may also be recognized by its characteristic, unpleasant odour. The application of heat must be avoided in this experiment, and the quantities operated with should be very small, or the decomposition may take place with such violence as to cause an explosion, as the greenish-yellow gaseous hypochloric acid decomposes at 60°.

8. Chloric acid behaves like nitric acid with **brucine** (Luck), **diphenylamine, paratoluidine,** and **phenol,** dissolved in concentrated **sulphuric acid,** or at all events the reactions are so similar that the two acids cannot be distinguished with certainty by these reagents. Chloric acid may, however, be distinguished from nitric acid by its action on phenol in hydrochloric acid solution (comp. § 159, 9), inasmuch as the chloric acid produces an orange-red turbidity.

9. If a dilute solution of an alkaline chlorate is boiled with a **copper-zinc couple,*** it is completely reduced to chloride with separation of oxide of zinc (Thorpe and Eccles). If a solution of a chlorate be acidified with dilute sulphuric acid, and **zinc** added, the liberated chloric acid is reduced to hydrochloric acid by the nascent hydrogen.

§ 161.

Recapitulation and Remarks.

Of the reactions given for the detection of nitric acid, those with ferrous sulphate and sulphuric acid, with copper filings and sulphuric acid, and also those based upon the reduction to nitrites or ammonia, give the surest results; with regard to deflagration with charcoal, detonation with cyanide of potassium, decolorization of solution of indigo, and the delicate reaction with brucine, diphenylamine, and paratoluidine, we have seen that these reactions take place with both chlorates and nitrates, so that they are decisive only when no chloric acid is present. The presence of free nitric acid in a liquid may be detected by evaporating to dryness in a porcelain dish on the water-bath, having first thrown in a few quill-cuttings; yellow coloration of these indicates the presence of nitric acid (Runge). The best way to ascertain whether chloric acid is present or not (in the absence of other oxygen compounds of chlorine) is to ignite the substance, with addition of carbonate of soda, dissolve the mass, and test the solution with nitrate of silver. If a chlorate is present, this is converted into a chloride by ignition, and nitrate of silver will then produce a precipitate of chloride of silver; this process, however, is not so simple if a chloride is present with the chlorate. In presence of a chloride, the chlorine must be removed first by adding nitrate of silver to the solution as long as a precipitate continues to form, and filtering; pure carbonate of soda is then added to the filtrate, and the mixture evaporated and ignited. It is, however, generally unnecessary to adopt this circuitous method, as the reactions with concentrated sulphuric acid, and with indigo and sulphurous acid, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid, even in presence of nitrates. The best way of detecting nitric acid in presence of a large proportion of chloric acid is to mix the substance with carbonate of soda in excess, evaporate, ignite the residue gently, but sufficiently long to convert the chlorate into chloride, and then test the residue for nitric acid, or for nitrous acid. To detect nitric acid in the presence of nitrous acid, pure urea is added to the aqueous solution, and this is then gradually poured into a solution of urea in dilute sulphuric acid; the nitrous acid is at

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* Gladstone and Tribe's copper-zinc couple is prepared by treating thin zinc foil with a 1 per cent. solution of sulphate of copper until the zinc is covered with a black deposit of reduced copper. When washed and dried, it is ready for use.

once decomposed, with evolution of nitrogen and carbonic acid. If iodide of potassium and starch paste are added to the solution when the reaction is over, it remains colourless; but on introducing a fragment of zinc, a blue coloration (§ 159, 12) will be produced if nitric acid be present (Piccini).*

§ 162.

Perchloric Acid (ClO_7).

Anhydrous perchloric acid is unknown, but the hydrate, HO,ClO_7 [$HClO_4$], is a colourless, caustic fluid, which fumes strongly in the air, and decomposes and explodes with great violence when kept for some time, or when dropped on wood-charcoal, wood, or paper. The compound with 2 equiv. of water, HO,ClO_7+2HO [$HClO_4,H_2O$], crystallizes in needles. Both the hydrate and the crystals dissolve in water with great development of heat. On distilling the dilute solution, water passes over first, then dilute acid, and finally concentrated acid. All perchlorates are soluble in water, most of them freely; they are all decomposed by ignition, those with alkaline bases leaving chlorides behind, with disengagement of oxygen. **Salts of potassa** produce, in not too dilute solutions, a white crystalline precipitate of perchlorate of potassa, KO,ClO_7 [$KClO_4$], sparingly soluble in water, insoluble in spirit of wine. **Baryta salts** and **silver salts** are not precipitated. Concentrated sulphuric acid does not decompose perchloric acid in the cold, and only with difficulty on heating (difference from chloric acid). Hydrochloric acid, nitric acid, and sulphurous acid do not decompose aqueous solutions of perchloric acid or perchlorates; solution of indigo, therefore, previously added to it, is not decolorized (difference from all other acids of chlorine). The alkaline perchlorates are not reduced by the copper-zinc couple (distinction from chloric acid, § 160, 9).

II. ORGANIC ACIDS.

First Group.

The hydrates of the acids of the first group are decomposed entirely or partially by ignition.† The acids are decomposed by boiling with concentrated nitric acid.‡ Their lime salts are insoluble or sparingly soluble in water. The solutions of their neutral alkali salts are not precipitated by ferric chloride: Oxalic Acid, Tartaric Acid (*Racemic Acid*), Citric Acid, Malic Acid.

§ 163.

a. Oxalic Acid, C_4O_6 [C_2O_3] = $\bar{O}$.

The reactions of this acid have been already given § 145.

b. Tartaric Acid, $2HO,C_8H_4O_{10}$ [$H_2C_4H_4O_6$].

1. The hydrate of tartaric acid forms colourless crystals of an agreeable acid flavour, which are persistent in the air, and soluble

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* For the detection of nitric acid in the presence of nitrous acid, see also Longi (Zeit. anal. Chem., **23**, 352); for the detection of nitric acid in solutions containing metallic iodides and bromides, chlorates, bromates, and iodates, see Longi (*ibid.*, **23**, 149); and for the detection of chloric acid in presence of hydrochloric, hydrobromic, hydriodic, hydrocyanic, hydroferrocyanic and hydroferricyanic acid, as well as bromic and iodic acids, see Longi (*ibid.*, **23**, 70).

† Hydrate of oxalic acid, when cautiously heated, partially sublimes unaltered.

‡ The decomposition of oxalic acid by boiling nitric acid into carbonic acid and water is but slow.

in water and in spirit of wine, it is, however, but little soluble in ether (100 : 0·4 according to E. Bourgoin). When heated at 100°, tartaric acid loses no water; at 170° it melts, and at a higher temperature it becomes carbonized, emitting a very peculiar and highly characteristic odour, resembling that of burnt sugar. Aqueous solutions of tartaric acid, as also those of almost all tartrates, turn the plane of polarization of light towards the right. There is also another tartaric acid—lævotartaric acid—which is lævorotary, and differs also from ordinary tartaric acid in its crystalline form. Their reactions, however, are identical.

2. The tartrates with alkaline base are soluble in water; also some others, as tartrate of alumina and ferric tartrate. When evaporated on the water-bath to a syrupy consistence, the solution of ferric tartrate deposits a pulverulent basic salt. Those tartrates which are insoluble in water dissolve in hydrochloric or nitric acid. Many tartrates which are insoluble or only sparingly soluble in water form readily soluble double salts with the tartrates of the alkalies. The tartrates are decomposed when heated to redness, charcoal being separated, and the same peculiar odour being emitted as when free tartaric acid is carbonized.

3. If to a solution of tartaric acid, or to that of an alkaline tartrate, solution of **ferric oxide** or **alumina** be added in not too large proportion, and then ammonia or potassa, there will be no precipitation of the ferric oxide or alumina, since the double tartrates formed are not decomposed by alkalies. Tartaric acid (also citric acid, malic acid, &c.) likewise prevents the precipitation of many other oxides by alkalies.

4. With **salts of potassa**, more particularly the acetate, free tartaric acid yields a sparingly soluble precipitate of bitartrate of potassa. A similar precipitate is formed when acetate of potassa and free acetic acid are added to a solution of a neutral tartrate. The acid tartrate of potassa dissolves readily in alkalies and mineral acids, but tartaric acid and acetic acid do not increase its solubility in water. The separation of the bitartrate of potassa is greatly promoted by shaking, or by rubbing the sides of the vessel with a glass rod; the delicacy of the reaction is increased by concentrating the solution of the tartaric acid; the addition of an equal volume of alcohol also increases the delicacy of the reaction. In the presence of boric acid, fluoride of potassium must be used instead of acetate of potassa; this forms borofluoride of potassium, and prevents the production of the soluble compound of boric acid, tartaric acid, and potassa (Barfoed).

5. **Chloride of calcium** added in excess * throws down from solutions of neutral tartrates a white precipitate of tartrate of lime, $2CaO,C_8H_4O_{10} + 8aq$ [$CaC_4H_4O_6,4H_2O$]. The presence of ammoniacal salts retards the formation of this precipitate for a more or less considerable space of time. Agitation or rubbing the sides of the vessel promotes the separation of the precipitate; this is crystalline, or at all events becomes so after some time. It is soluble in a cold not very dilute solution of potassa or soda, pretty free from carbonic acid, forming a clear liquid. When this solution is boiled, the dissolved tartrate

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* Tartrate of potassa or soda dissolves tartrate of lime (as well as certain other salts insoluble in water, such as phosphate of lime, sulphate of baryta, &c.). Hence enough of the reagent must be added to completely decompose the alkaline tartrate.

of lime separates again in the form of a gelatinous precipitate, which redissolves on cooling.

6. **Lime water** added in excess* to solutions of neutral tartrates—and also if added to a solution of free tartaric acid until the reaction is alkaline—produces a white precipitate which is flocculent at first, but afterwards becomes crystalline. So long as this precipitate remains flocculent, it is readily dissolved by tartaric acid as well as by solution of chloride of ammonium; but the tartrate of lime separates again from this solution after the lapse of several hours, and is deposited in the form of small crystals upon the sides of the vessel.

7. **Solution of sulphate of lime** produces no precipitate when added in excess* to a solution of tartaric acid; in solutions of neutral tartrates of the alkalies, it produces a trifling precipitate after the lapse of some time.

8. If a solution of ammonia is poured on to even a very minute quantity of tartrate of lime, a small fragment of crystallized **nitrate of silver** added, and the mixture slowly and gradually heated, the sides of the test-tube become covered with a bright coating of metallic silver. If, instead of a crystal, solution of nitrate of silver be used, or if the heat be applied too rapidly, the reduced silver will separate in a pulverulent form (A. Casselmann).

9. **Acetate of lead** produces a white precipitate in solutions of tartaric acid or its salts. The washed precipitate, $2PbO,C_8H_4O_{10}$ [$PbC_4H_4O_6$], dissolves readily in nitric acid, and in ammonia free from carbonic acid.

10. **Nitrate of silver** does not precipitate free tartaric acid; but in solutions of neutral tartrates it produces a white precipitate of tartrate of silver, $2AgO,C_8H_4O_{10}$ [$Ag_2C_4H_4O_6$]; this dissolves readily in nitric acid, and in ammonia; on boiling the solution, it turns black, owing to reduction of the silver.

11. If some **ferrous chloride** or **sulphate** be added to a solution containing free tartaric acid or the tartrate of an alkali, then one or two drops of **peroxide of hydrogen**, and lastly excess of caustic potash or soda, a beautiful violet colour will be produced (distinction from citric acid and other organic acids). Other oxidizing agents—such as chlorine water, hypochlorite of soda, acidified solution of permanganate of potassa—may be used instead of peroxide of hydrogen, but care must be taken not to use an excess (Fenton).

12. On heating hydrated tartaric acid or a tartrate with concentrated **sulphuric acid**, the latter acquires a brown colour almost simultaneously with the evolution of gas.

13. If a saturated solution of **dichromate of potassa** is poured on to a crystal of tartaric acid at the ordinary temperature, carbonic acid is evolved, and coloured zones varying from purple-violet to black form round the crystal. This affords a means of detecting crystals of tartaric acid when mixed with citric acid, as the latter only slowly gives a coffee-brown colour (Cailletet).

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* See note p. 236.

§ 164.

c. Citric Acid, $3HO,C_{12}H_5O_{11}$ $[H_3C_6H_5O_7]$.

1. Crystallized citric acid, which separates as the solution cools, has the formula $3HO,C_{12}H_5O_{11} + 2aq$ $[H_3C_6H_5O_7,H_2O]$. It forms transparent, colourless, inodorous crystals of an agreeable, strongly acid taste, readily soluble in water and in spirit of wine, less so in ether (100 : 2·26), and efflorescing slowly in the air. When heated at 130°, the crystallized acid loses its water of crystallization; at a higher temperature it melts, and then carbonizes with evolution of pungent acid fumes, the odour of which may be readily distinguished from that emitted when tartaric acid is decomposed by heat. The aqueous solution of citric acid is optically inactive. If citric acid is heated with nitric acid diluted somewhat, it yields oxalic and mesaconic acids and nitro-derivatives.

2. The citrates with alkaline base, whether neutral or acid salts, are readily soluble in water; solution of citric acid therefore gives no precipitate with acetate of potassa. The compounds of citric acid with such of the metallic oxides as are feeble bases, ferric oxide, for instance, are also freely soluble in water; when evaporated on the water-bath to a syrupy consistence, solution of ferric citrate does not yield any solid salt. Citrates, like tartrates, and for the same reason, prevent the precipitation of sesquioxide of iron, alumina, &c., by alkalies.

3. **Chloride of calcium** gives no precipitate in a solution of free citric acid, even on boiling; but on saturating with potassa or soda a somewhat concentrated solution of citric acid mixed with chloride of calcium in slight excess,* a precipitate of neutral citrate of lime, $3CaO,C_{12}H_5O_{11} + 4aq$ $[Ca_3(C_6H_5O_7)_2,4H_2O]$, is formed immediately; this is insoluble in potassa or soda, easily soluble in an alkaline citrate, somewhat less soluble in chloride of calcium. Chloride of ammonium also dissolves it freely; unless too much chloride of ammonium is present, this solution, when boiled, deposits neutral citrate of lime of the same composition in the form of a white crystalline precipitate; this, however, is no longer soluble in chloride of ammonium. If a solution of citric acid mixed with excess of chloride of calcium is saturated with ammonia, a precipitate will form in the cold only after many hours' standing or on adding its own volume of alcohol; but on boiling the clear solution, neutral citrate of lime of the properties just stated will be at once precipitated. On heating citrate of lime with ammonia and nitrate of silver, the latter is not reduced, or only to a trifling extent.

4. **Lime water** added in excess* produces no precipitate in cold solutions of citric acid or of citrates; but if they are boiled for some time with a tolerable excess of hot prepared lime water, a white precipitate of citrate of lime is formed, of which the greater portion redissolves on cooling.

5. **Acetate of baryta,** added in excess to a solution of an alkaline citrate whether hot or cold, produces an amorphous precipitate of the formula $3BaO,C_{12}H_5O_{11} + 7aq$ $[Ba_3(C_6H_5O_7)_2,7H_2O]$. Baryta water added

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* Alkaline citrates dissolve citrate of lime and also many compounds insoluble in water (phosphate and oxalate of lime, &c.), so that in the reactions in 3 and 4 depending on the separation of citrate of lime, sufficient chloride of calcium or lime must be added to completely decompose all the alkaline citrate present.

in excess to citric acid produces the same precipitate. The precipitate does not make its appearance in dilute solutions, because it is not insoluble in water; if such solutions are heated, however, a precipitate separates which is amorphous at first but soon turns to microscopic needles of the formula $3BaO,C_{12}H_5O_{11} + 5aq$ [$Ba_3(C_6H_5O_7)_2,5H_2O$]. On heating this or the amorphous salt with excess of acetate of baryta for two hours on the water-bath, another very characteristic salt is formed; this consists of well-formed clinorhombic prisms, of the formula $2(3BaO,C_{12}H_5O_{11}) + 7aq$ [$2Ba_3(C_6H_5O_7)_2,7H_2O$]. If the solution is very dilute, the salt does not form until the liquid has been concentrated by evaporation. This is an infallible reaction for citric acid (H. Kämmerer).

6. **Acetate of lead** added in excess to a solution of citric acid produces a white, amorphous precipitate of citrate of lead, which after being washed is readily soluble in ammonia free from carbonic acid. By digestion for several hours with water or acetic acid on a water-bath, the precipitate becomes crystalline, and then has the formula $3PbO,C_{12}H_5O_{11} + 3aq$ [$Pb_3(C_6H_5O_7)_2,3H_2O$]. The microscope does not reveal the presence of well-formed crystals.

7. **Nitrate of silver** added to solutions of neutral citrates of the alkalies produces a white, flocculent precipitate of citrate of silver, $3AgO,C_{12}H_5O_{11}$ [$Ag_3C_6H_5O_7$]. On boiling a rather large quantity of this precipitate with a little water, a gradual decomposition sets in with separation of silver.

8. If citric acid or citrates are heated with concentrated **sulphuric acid**, carbonic oxide escapes at first, then carbonic acid and acetone without any blackening of the sulphuric acid; after boiling for some time, however, the solution becomes dark, and sulphurous acid is evolved.

9. If citric acid (say 0·01 gram) is sealed up in a strong glass tube with excess of ammonia (3 c.c.) so that there is comparatively little free space above the liquid, and then heated at 110° to 120° for six hours, the product acquires an intense blue or green colour when it is poured out into a porcelain dish and exposed to the air. This distinguishes it from oxalic, tartaric, and malic acids, and affords a means of detecting small quantities of citric acid in presence of these acids (Sarandinaki, Sabanin, and Laskowsky).

§ 165.

d. **Malic Acid,** $2HO,C_8H_4O_8$ [$H_2C_4H_4O_5$].

1. Hydrate of malic acid crystallizes with difficulty, forming crusts or tufts of needles, which deliquesce in the air, and are readily soluble in water and in alcohol. The dilute aqueous solution of ordinary malic acid turns the plane of polarization to the right; there is also a synthetically prepared acid which has no action on light, and another that is dextrorotary. If exposed for a long time to a temperature of 140° to 150°, hydrated malic acid is slowly converted, with loss of water, into hydrated fumaric acid, $2HO,C_8H_2O_6$ [$H_2C_4H_2O_4$]; heated in a glass tube or retort at 150°–200°, malic acid is resolved into water, and anhydrous maleic acid, $C_8H_2O_6$ [$C_4H_2O_3$], which volatilize, and fumaric acid, which remains. The anhydrous maleic acid partly unites with the water forming hydrate of maleic acid, $2HO,C_8H_2O_6$ [$H_2C_4H_2O_4$]. By raising the temperature to above 200°,

the fumaric acid is also volatilized, in part without decomposition; the crystalline sublimate thus formed in the upper part of the tube or in the neck of the retort is highly characteristic of malic acid. On heating malic acid with nitric acid, it readily yields oxalic acid, with evolution of carbonic acid.

2. With most bases, malic acid forms salts soluble in water; as the acid malate of potassa is not sparingly soluble in water, acetate of potassa gives no precipitate with solutions of malic acid. Malic acid, like tartaric acid, prevents the precipitation of ferric oxide, &c., by alkalies.

3. If **chloride of calcium**, chloride of ammonium, and ammonia are added in excess to a solution of malic acid or malate of an alkali, the solution remains clear; and even on long boiling no precipitate is formed if the quantity of chloride of ammonium present is not too small (distinction from citric acid). If, however, the solution is mixed with two or three times its volume of spirit of wine, malate of lime, $2CaO,C_8H_4O_8 + 6aq$ [$CaC_4H_4O_5,3H_2O$], separates in white flocks. If the liquid is previously heated nearly to boiling, and hot alcohol is added just sufficient for precipitation, the precipitate is deposited in the form of soft lumps adhering to the sides of the vessel; on cooling, these harden and crumble by pressure to a crystalline powder (Barfoed). When heated with ammonia and nitrate of silver, malate of lime causes no separation of silver or hardly any. Malate of lime is soluble in boiling lime water (distinction and means of separation from citrate of lime, Fleischer).

4. **Lime water** produces no precipitate either in solutions of free malic acid or in solutions of malates; the solution remains perfectly clear even on boiling, provided the lime water was prepared with boiling water.

5. **Acetate of lead** added to a solution of malic acid or of a malate throws down a white precipitate of malate of lead,

$$2PbO,C_8H_4O_8 + 6aq \ [PbC_4H_4O_5,3H_2O].$$

The precipitation is most complete if the solution is neutralized by ammonia, as the precipitate is slightly soluble in free malic acid and acetic acid, and also in ammonia. If the liquid in which the precipitate is suspended is heated to boiling, a portion of the precipitate dissolves, and the remainder fuses to a mass resembling resin melted under water; the hot solution as it cools deposits the salt in plates or needles. To obtain this reaction with small quantities, the solution should be warmed gently at first until the precipitate has shrunk together, the bulk of the liquid then poured off, and the rest heated with the precipitate to boiling. This reaction is distinctly marked only if the malate of lead is tolerably pure; if mixed with other salts of lead—as, for instance, when ammonia is added to alkaline reaction—it is only imperfect, or fails altogether to make its appearance.

6. **Nitrate of silver** added to solutions of neutral malates of the akalies throws down a white precipitate of malate of silver, $2AgO,C_8H_4O_8$ [$Ag_2C_4H_4O_5$], which on long standing, or on boiling turns somewhat gray.

7. On mixing the warm solution of free malic acid with **magnesia** or its carbonate until the acid reaction is destroyed, filtering, evaporating, and adding hot alcohol to the hot solution, malate of magnesia, $2MgO,C_8H_4O_8$ [$MgC_4H_4O_5$], separates as a glutinous mass on

the sides of the vessel; it is hard when cold. Malic acid cannot be distinguished from citric acid by this reaction (Barfoed).

8. When malic acid is heated with concentrated **sulphuric acid**, carbonic acid and carbonic oxide are evolved at first; the mixture then turns brown and ultimately black, with evolution of sulphurous acid.

§ 166.

Recapitulation and Remarks.

Of the organic acids of this group, oxalic acid is characterized by its lime salt being reprecipitated at once on adding ammonia or acetate of soda to its solution in hydrochloric acid, and also by a precipitate being immediately formed on adding solution of sulphate of lime to a solution of the free acid.

Tartaric acid is characterized by the sparing solubility of the acid potassa salt, the solubility of the lime salt in cold solution of soda or potassa, the reaction of the lime salt with ammonia and nitrate of silver, and the peculiar odour which the acid and its salts emit when heated. In the presence of the other acids, it is detected with greatest certainty by means of the reaction with acetate of potassa or fluoride of potassium (§ 163, 4). C. D. Braun's test for distinguishing tartaric acid from the other organic acids by means of cobalthexamine chloride will be found in Zeit. anal. Chem., **7**, 349.

Citric acid is usually recognized by its reaction with lime water, or with chloride of calcium and ammonia in presence of chloride of ammonium, but it is necessary that malic and tartaric acids should be absent or that they should be removed previously; also that a sufficient quantity of lime water or chloride of calcium should be employed. A very safe and characteristic test for citric acid consists in the microscopic appearance of its baryta salt (§ 164, 5) and the formation of the blue or green products mentioned in § 164, 9.

Malic acid would be sufficiently characterized by the behaviour of malate of lead when heated under water, were this reaction more sensitive, and not so easily interfered with by the presence of other acids. The best means of identifying malic acid is to convert it into maleic acid and fumaric acid by heating it in a glass tube; for this purpose, however, it is necessary to have the hydrate of malic acid in a pure state. Malate of lead is sparingly soluble in ammonia free from carbonic acid, whilst the citrate and tartrate of lead dissolve very readily in that reagent; this difference in the behaviour of the lead salts of the acids affords a means of distinguishing between them. Citrate and malate of lime may be separated by means of boiling lime water, which dissolves the latter, but not the former.

If only one of the four acids is present in a solution, lime water will suffice to indicate which of the four is present: malic acid is not precipitated by this reagent, citric acid is precipitated only on boiling, whilst tartaric acid and oxalic acid are thrown down in the cold; the tartrate of lime redissolves on adding chloride of ammonium, the oxalate does not.

If the four acids are present together in a solution, the oxalic acid and tartaric acid are usually precipitated first by chloride of calcium and ammonia in presence of chloride of ammonium. It must be noted, however, that the tartrate of lime requires some time, about two hours, for complete precipitation (it may be separated from the oxalate by means of solution of soda), and also that an alkaline citrate when present in any quantity prevents the complete separation of oxalic acid and still more that of tartaric acid. When alcohol in moderate quantity is cautiously added to the filtrate, the citrate of lime separates (and with it the rest of the oxalate and tartrate of lime); on filtering again and mixing the filtrate with more alcohol, malate of lime is thrown down; the hydrated acid may be prepared from this by dissolving it in acetic acid, adding alcohol, filtering if necessary, mixing the filtrate with acetate of lead, neutralizing with ammonia, washing the precipitate, suspending it in water, treating with sulphuretted hydrogen, filtering, and evaporating the filtrate to dryness. A better method for the detection of malic acid in the presence of the three other acids consists in combining the acids with ammonia, concentrating strongly, neutralizing the liquid with ammonia whilst still warm (to dissolve the acid salts produced in the evaporation), and adding 8 volumes of alcohol of 98 per cent. After twelve to twenty-four hours, the solution of malate of ammonia is filtered from the oxalate, tartrate, and citrate of ammonia which have separated, the malic acid is precipitated with acetate of lead, and the pure hydrated acid is prepared from the precipitate and tested (Barfoed). Where a small quantity of citric acid or malic acid is to be detected in presence of a large proportion of tartaric acid, the best way is to remove the latter first by acetate of potassa, with addition of an equal volume of strong alcohol. The other acids may then be completely precipitated by adding excess of chloride of calcium and ammonia to the filtrate and adding a little more alcohol. Lastly, the malate of lime can be separated from the citrate by treating the mixed lime salts with boiling lime water.

By far the best means of detecting tartaric acid in presence of citric acid, is to heat the suspected mixture with sulphuric acid (1 gram with 10 c.c.) in a water-bath for an hour; with pure citric acid the solution becomes of a lemon-yellow colour merely, whilst if tartaric acid is present it will be brown or red-brown (E. Schmidt, Pusch); the test with chromate of potassa (§ 163, 13) may also be employed.

§ 167.

Racemic Acid, $2HO,C_8H_4O_{10}$ [$H_2C_4H_4O_6$].

The formula of crystallized racemic acid is $2HO,C_8H_4O_{10}+2aq$ [$H_2C_4H_4O_6,H_2O$]. The water of crystallization escapes slowly on exposure to the air, rapidly at 100° (difference between racemic acid and tartaric acid). With solvents, racemic acid behaves like tartaric acid. The reactions of the racemates also are very similar to those of the tartrates; many of them, however, differ from the corresponding tartrates in the amount of water they contain, and in form and solubility. The aqueous solutions of racemic acid and its salts have no action on polarized light (distinction from tartaric acid and metatartaric acid). **Chloride of calcium** added to a solution of free racemic acid or a racemate throws down racemate of lime,

$$2CaO,C_8H_4O_{10}+8aq\ [CaC_4H_4O_6,4H_2O],$$

as a white, crystalline powder; this is reprecipitated from its solution in hydrochloric acid on addition of ammonia, either at once or very quickly (difference between racemic acid and tartaric acid). It dissolves in solution of soda or potassa, but is reprecipitated on boiling (distinction from oxalic acid). **Lime water** added in excess produces immediately a white precipitate insoluble in chloride of ammonium, and in acetic acid (distinction from tartaric acid). **Solution of sulphate of lime** does not immediately produce a precipitate in a solution of racemic acid (difference between racemic and oxalic acid); after ten or fifteen minutes, however, racemate of lime separates (distinction from tartaric acid); in solutions of neutral racemates the precipitate forms immediately. With **salts of potassa**, racemic acid behaves like tartaric acid. On allowing racemate of soda and potassa or of soda and ammonia to crystallize, two kinds of crystals are obtained, which resemble each other as the image reflected by a mirror resembles the object reflected. The one kind of crystal contains ordinary dextrorotary tartaric acid, the other contains lævotartaric acid, that is, an acid which is the same in every respect as tartaric acid, except that it turns the polarized ray to the left. If the two kinds of crystals are mixed and redissolved, the solution again shows all the reactions of racemic acid.

Second Group of Organic Acids.

The Hydrates of the Acids of the Second Group sublime without alteration, or merely split up into the anhydrous acid and water. When heated with nitric acid, they are either left unchanged (Succinic Acid), or merely converted into Nitroderivatives (Benzoic Acid, Salicylic Acid). The Lime Salts are readily soluble in water (Benzoic Acid, Salicylic Acid), or sparingly soluble (Succinic Acid). The solutions of the neutral Alkali Salts are precipitated by ferric chloride (Succinic Acid, Benzoic Acid), or give an intense coloration with it (Salicylic Acid).

The acids of the second group are Succinic Acid, Benzoic Acid, Salicylic Acid.

§ 168.

a. Succinic Acid, $2HO,C_8H_4O_6$ [$H_2C_4H_4O_4$].

1. Hydrate of succinic acid forms colourless, inodorous prisms or tables (rhombic prisms or rhomboid tables). It is easily soluble in hot water or hot alcohol, less readily in the cold solvents, sparingly in ether (100 : 1·265). When heated for a long time at 140°, the hydrated acid volatilizes in part without decomposition, and is partly resolved into water and the anhydrous acid, which sublimes. If heated rapidly, the hydrate melts at 180° and boils at 235°, being mostly resolved into water and the anhydrous acid. The sublimed anhydrous acid forms silky needles. Heated in the air, succinic acid burns with a blue smokeless flame. Pure succinic acid is odourless, and has a feebly acid taste. The officinal acid has an empyreumatic odour, and leaves a somewhat large carbonaceous residue on volatilization. Succinic acid is not destroyed on heating with nitric acid, and may therefore be easily purified from any oil of amber which may be present, by boiling with that acid for half an hour.

2. The succinates are decomposed at a red heat; those which have an alkali or alkaline earth for base are converted into carbonates with separation of charcoal. Most of the succinates are soluble in water. As succinate of soda is almost insoluble in strong alcohol and crystallizes well both as a neutral and acid salt, it may be readily obtained in a pure state from very impure solutions; this method may be utilized for the detection and separation of the acid.* On heating the

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* Compare Meissner and Jolly, Zeit. anal. Chem., 4, 502.

succinates with bisulphate of potassa in a tube, the acid sublimes. The acid may also be obtained from its salts by decomposing them with sulphuric acid, and extracting with warm absolute alcohol; all the succinic acid may also be extracted from a solution by strongly acidifying it up with sulphuric acid and repeatedly shaking it up with ether.

3. If **chloride of calcium**, chloride of ammonium, and ammonia are added to a solution of succinic acid or a succinate, the solution remains clear, and that even on boiling if sufficient chloride of ammonium is present. On adding twice or thrice its volume of alcohol, however, a crystalline precipitate of succinate of lime, $2CaO,C_8H_4O_6 + 6aq$ [$CaC_4H_4O_4,3H_2O$], is produced; often this does not make its appearance until after the lapse of some time.

4. **Chloride of barium** throws down in white crystalline precipitate of succinate of baryta, $2BaO,C_8H_4O_6$ [$BaC_4H_4O_4$], from solutions of succinates of the alkalies, but not from those of succinic acid. Usually this precipitate is not formed until after the lapse of some time: heating promotes its separation. On adding alcohol, it separates quickly even from dilute solutions.

5. **Ferric chloride** which has been carefully neutralized with very dilute ammonia, added until the liquid is dark brown but still clear, produces in solutions of a neutral succinate of the alkalies a brownish pale-red bulky precipitate of basic ferric succinate, $Fe_2O_3,C_8H_4O_6$ [$2Fe_2(C_4H_4O_4)_3,Fe_2O_3$]; one-third of the succinic acid is liberated in this reaction, and retains part of the precipitate in solution if the liquid is filtered off hot. The precipitate is readily soluble in mineral acids; ammonia decomposes it, with separation of a less bulky precipitate of a highly basic ferric succinate, the greater portion of the acid remaining dissolved as succinate of ammonia. Tartrates of the alkalies prevent or interfere with the precipitation of succinic acid as ferric succinate.

6. **Acetate of lead**, when added drop by drop to a solution of free succinic acid, or of an alkaline succinate, produces a white amorphous precipitate which redissolves immediately in excess of succinic acid, of alkaline succinate, or of acetate of lead, but in a short time separates again in the crystalline form. This precipitate consists of neutral succinate of lead, $2PbO,C_8H_4O_6$ [$PbC_4H_4O_4$]; it is almost insoluble in boiling water, succinic acid, and acetate of lead, somewhat more soluble in acetic acid, easily in nitric acid; it is converted into a basic salt by treatment with ammonia.

§ 169.

b. Benzoic Acid, $HO,C_{14}H_5O_3$ [$HC_7H_5O_2$].

1. Pure hydrate of benzoic acid forms inodorous, white scales or needles, or simply a crystalline powder having a feeble aromatic odour. It melts at 121·4°, boils at 250°, and volatilizes without residue; when heated in an open basin at 100°, it volatilizes in considerable quantity. Its vapour causes a peculiar, irritating sensation in the throat, and provokes coughing; if carefully cooled, the vapour condenses in brilliant needles. The vapours burn with a luminous, sooty flame when kindled. The ordinary officinal hydrate of benzoic acid has the odour of benzoin, and leaves a small, carbonaceous residue when heated. Hydrate of benzoic acid dissolves in 588 parts of water at 0°; in 345 at 20°; and in 17 at 100° (Bourgoin). It dissolves easily in

alcohol or ether. Addition of water imparts, therefore, a milky turbidity to a saturated solution of the acid in alcohol. It dissolves in concentrated sulphuric acid forming a colourless solution from which it is thrown down unaltered on addition of water.

2. Most of the benzoates are soluble in water; only those with feeble bases, such as ferric oxide, are insoluble. The soluble benzoates have a peculiar pungent taste. The addition of a **strong acid** to *concentrated* aqueous solutions of benzoates displaces the benzoic acid, which separates as hydrate in the form of a dazzling white, sparingly soluble powder. Benzoic acid is expelled in the same way from the insoluble benzoates by such strong acids as form soluble salts with the bases with which the benzoic acid is combined.

3. **Ferric chloride** which has been carefully neutralized with very dilute ammonia, added until the liquid is dark brown but still clear, when added to solutions of neutral benzoates, throws down all the benzoic acid in combination with ferric oxide. The bulky flesh-coloured precipitate of ferric benzoate,

$$2Fe_2O_3,3(C_{14}H_5O_3) + 15aq\ [Fe_2(C_7H_5O_2)_6,Fe_2O_3+15H_2O],$$

is decomposed by ammonia in the same manner as ferric succinate, but differs from it in that it dissolves in a little hydrochloric acid, with separation of the greater portion of the benzoic acid. The presence of tartrates of the alkalies prevents or interferes with the precipitation of ferric benzoate.

4. **Acetate of lead** does not precipitate free benzoic acid, but it throws down a flocculent precipitate in solutions of alkaline benzoates. The precipitate, $PbO,C_{14}H_5O_3+aq$ $[Pb(C_7H_5O_2)_2,H_2O]$, is insoluble in benzoate of soda, but dissolves in excess of acetate of lead and in acetic acid. The precipitate does not dissolve on heating the solution to boiling, neither is it soluble in ammonia.

5. A mixture of **alcohol, ammonia,** and **chloride of barium,** or **chloride of calcium** added to a solution of benzoic acid or of an alkaline benzoate produces no precipitate (distinction from succinic acid).

§ 170.

c. **Salicylic Acid,** $HO,C_{14}H_5O_5$ $[HC_7H_5O_3]$.

1. Hydrate of salicylic acid crystallizes in colourless and odourless prisms. It is only sparingly soluble in cold, but dissolves more readily in hot water; 1 part of the acid requiring 666 parts of water at 0°, 370 parts at 20°, and 12·6 parts at 100° for solution (Bourgoin). It dissolves very readily, however, in alcohol, ether, amyl alcohol, and chloroform. It melts at 155°, and on cautiously heating may be sublimed unaltered in the form of needles; if heated rapidly to a high temperature, however, it is partially decomposed into carbonic acid and phenol. On boiling an aqueous solution of salicylic acid, it volatilizes in considerable quantity. The aqueous solution has a distinctly acid reaction. On warming hydrated salicylic acid with strong nitric acid, it yields nitrosalicylic acid.

2. Salicylic acid forms two series of salts which are usually, although not correctly, known as neutral and basic salts. Solutions of the salicylates of the alkalies, possibly from the presence of basic salts, become of a brownish colour when heated in the presence of air.

The neutral salicylates are for the most part easily soluble in water; the basic salts are generally either very sparingly soluble or quite insoluble. Most salicylates yield phenol when heated. **Mineral acids** throw down a white precipitate of the hydrated salicylic acid from solution of the salicylates if sufficiently concentrated. Acetic acid yields no precipitate.

3. On adding **ferric chloride** to an aqueous solution of salicylic acid or its salts, it becomes of a deep violet colour. The presence of free acetic acid, however, renders this very characteristic reaction much less delicate, whilst ammonia or hydrochloric acid altogether prevents it.

4. **Lead acetate**, when added to solutions of the neutral salicylates of the alkalies, forms a white precipitate of lead salicylate,

$$PbO,C_{14}H_5O_5 + aq \quad [Pb(C_7H_5O_3)_2,H_2O],$$

soluble in excess of the lead acetate or acetic acid, but insoluble in ammonia. On heating, the precipitate is dissolved, but is deposited again, on cooling, in small crystals.

5. **Chloride of calcium** and **chloride of barium** yield no precipitate in solutions of salicylic acid, even on addition of ammonia or alcohol.

6. On heating a solution of salicylic acid in **methyl alcohol** with half its volume of concentrated sulphuric acid, a compound of aromatic odour is formed and may be separated by distillation. It consists of methyl salicylate, the chief constituent of oil of winter-green. A solution of salicylic acid in ethyl alcohol, when treated in the same way, yields ethyl salicylate possessing a similar odour.

§ 171.

Recapitulation and Remarks.

Benzoic and salicylic acids may be distinguished from succinic acid by the much greater solubility of the last named in water, solutions of benzoates and salicylates yielding precipitates of the hydrates of their respective acids on the addition of mineral acids.

Succinic and benzoic acids may be distinguished from salicylic acid by the fact that they yield a precipitate with ferric chloride, whilst salicylic acid forms no precipitate, but the liquid becomes of a deep violet colour. If the precipitates of the above acids formed with ferric chloride are digested with ammonia, filtered, and the filtrate concentrated and acidified, the benzoic acid is precipitated, whilst the succinic acid remains in solution and may be precipitated as succinate of lime or baryta. Succinic acid may also be separated from salicylic acid by precipitating it as the lime or baryta salt.

To separate any of the three acids from a solution containing other organic substances, it should be rendered strongly acid with sulphuric acid and repeatedly shaken up with ether; on distilling off the ether, the hydrated acids are obtained. To detect the presence of salicylic acid in wine, it is better to shake it up with amyl alcohol instead of ether, in order to avoid extracting tannin. The amyl alcohol solution is then separated, mixed with ordinary alcohol, and tested by adding a small quantity of very dilute ferric chloride solution.

Neither succinic acid, benzoic acid, nor salicylic acid prevents the precipitation of ferric oxide, alumina, &c., by alkalies.

Third Group of Organic Acids.

The Hydrates of the Acids of the Third Group pass over when distilled with water (the hydrate of Lactic Acid with difficulty). The Lime Salts are readily soluble in water. The solutions of the neutral Alkaline Salts are not precipitated in the cold by ferric chloride.

The acids of the third group are Acetic Acid, Formic Acid (*Lactic Acid, Propionic Acid,* and *Butyric Acid*).

§ 172.

a. Acetic Acid, $HO,C_4H_3O_3$ [$HC_2H_3C_2$].

1. The hydrate of acetic acid forms transparent crystalline plates, which melt at 17° to a colourless liquid of a peculiar pungent and penetrating odour, and exceedingly acid taste. It boils at 119°, volatilizing completely in pungent vapours, which burn with a blue flame. It is miscible with water in all proportions, and it is to such mixtures of the acid with water that the name of acetic acid is commonly applied. The hydrate of acetic acid is also soluble in alcohol.

2. The acetates are decomposed at a red heat. The salts of the alkalies, and other salts with the stronger bases, are decomposed at a high temperature, generally with formation of acetone, $C_6H_6O_2$ [C_3H_6O], and carbonic acid, the latter remaining in combination or being evolved in the free state according to the nature of the base. In the case of salts with a feeble base, most of the acetic acid passes off undecomposed; the residue is usually carbonaceous. Almost all the acetates dissolve in water and in alcohol; most of them are readily soluble in water, a few only are sparingly soluble in it. When acetates are distilled with dilute sulphuric acid, the free acetic acid is obtained in the distillate.

3. If **ferric chloride** is added to acetic acid, and the acid is then nearly saturated with ammonia, or if a neutral acetate is mixed with ferric chloride, the liquid acquires a deep red colour, owing to the formation of ferric acetate. On boiling, the solution becomes colourless if it contains an excess of acetate, the whole of the sesquioxide of iron being precipitated as a basic acetate, in the form of brown-yellow flakes. Ammonia added to the solution of ferric acetate throws down the whole of the sesquioxide of iron as hydrate. On adding hydrochloric acid to the red solution of ferric acetate, it turns yellow (distinction from sulphocyanate of iron).

4. Neutral acetates, but not free somewhat dilute acetic acid, with **nitrate of silver,** give a white crystalline precipitate of acetate of silver, $AgO,C_4H_3O_3$ [$AgC_2H_3O_2$], which is very sparingly soluble in cold water. It dissolves more easily in hot water, but, on cooling, separates again in the form of very fine crystals. Ammonia dissolves it readily; free acetic acid does not increase its solubility in water.

5. **Mercurous nitrate** produces in acetic acid, and more readily still in acetates, a white scaly crystalline precipitate of mercurous acetate, $Hg_2O,C_4H_3O_3$ [$Hg_2(C_2H_3O_2)_2$]; this is sparingly soluble in water and acetic acid in the cold, but dissolves without difficulty in excess of

the precipitant. The precipitate dissolves in hot water, but on cooling separates again in the form of small crystals; the mercurous acetate is, however, partially decomposed, a portion of the mercury separating in the metallic state, and imparting a gray colour to the precipitate. If the mercurous acetate is boiled with dilute acetic acid, instead of water, the quantity of metallic mercury which separates is exceedingly minute.

6. **Mercuric chloride** yields no precipitate of mercurous chloride when heated with acetic acid or an acetate.

7. If an acetate is heated with concentrated **sulphuric acid**, hydrate of acetic acid is evolved, which may be known by its pungent odour; if the acetate is heated with a mixture of about equal volumes of concentrated **sulphuric acid** and **alcohol**, acetic ether, $C_4H_5O,C_4H_3O_3$ [$C_2H_5,C_2H_3O_2$], is formed. The odour of this ether is agreeable, very characteristic, and it is most distinct on shaking the mixture when somewhat cooled, and is much less liable to lead to mistakes than the pungent odour of the acid itself.

8. If dilute acetic acid is heated with excess of **oxide of lead**, part of the latter dissolves as basic acetate of lead: the solution has an alkaline reaction; it gives no crystals on cooling.

§ 173.

b. Formic Acid, HO,C_2HO_3 [$HCHO_2$].

1. The hydrate of formic acid is a transparent and colourless, caustic, slightly fuming liquid of a peculiar and exceedingly penetrating odour. It crystallizes at −1° in colourless plates. It is miscible in all proportions with water and alcohol. It boils at 98·5°, and can be distilled without decomposition; the vapour burns with a blue flame.

2. The formates, like the corresponding acetates, leave either carbonates, oxides, or metals behind when ignited; at the same time hydrocarbon, carbonic acid, and water are evolved and carbon separated. All the compounds of formic acid with bases are soluble in water; alcohol also dissolves many of them.

3. Formic acid gives the same reaction with **ferric chloride** that acetic acid does.

4. **Nitrate of silver** gives no precipitate with free formic acid, and decomposes the alkaline formates only in concentrated solutions. The white, sparingly soluble, crystalline precipitate of formate of silver, AgO,C_2HO_3 [$AgCHO_2$], very rapidly becomes darker from separation of metallic silver; complete reduction of the oxide of silver to the metallic state takes place, even in the cold, after the lapse of some time, and immediately on heating the solution with the precipitate. The same reduction of the oxide of silver takes place in a solution of free formic acid, and also in solutions of formates so dilute that the addition of nitrate of silver fails to produce a precipitate; it does not take place, however, in presence of an excess of ammonia. The formic acid deprives the oxide of silver of its oxygen, forming carbonic acid, which is evolved, and water, reduced silver being deposited.

5. **Mercurous nitrate** gives no precipitate with free formic acid, but with solutions of alkaline formates it yields a glistening, white,

sparingly soluble precipitate of mercurous formate, Hg_2O,C_2HO_3 [$Hg_2(CHO_2)_2$]. This rapidly becomes gray, from separation of metallic mercury; after the lapse of some time, reduction is complete, even in the cold, but takes place immediately on heating, carbonic acid and water being formed. As in the case of oxide of silver, this reduction takes place both in solutions of free formic acid and also in solutions so dilute that the mercurous formate remains in solution.

6. If an aqueous solution of formic acid or of an alkaline formate is heated with **mercuric chloride**, mercurous chloride is precipitated even before the boiling point is reached. The presence of free hydrochloric acid or of somewhat considerable quantities of alkaline chlorides prevents the reaction.

7. If formic acid or a formate is heated with concentrated **sulphuric acid**, the formic acid is resolved into water and carbonic oxide; the latter escapes with effervescence and, if kindled, burns with a blue flame. In this reaction, the sulphuric acid removes from the formic acid the water or the oxide necessary for its existence, and thus occasions a transposition of its elements,

$$HO,C_2HO_3 = 2CO + 2HO \ [HCHO_2 = CO + H_2O].$$

If a formate is heated with dilute sulphuric acid in a distilling apparatus, free formic acid is found in the distillate, and may generally be readily detected by its odour. If a formate is heated with a mixture of strong sulphuric acid and alcohol, formic ether is formed, and is characterized by its peculiar odour, resembling that of arrack.

8. When dilute formic acid is heated with excess of **oxide of lead**, the latter partially dissolves. The fluid has an alkaline reaction, and on cooling the solution, which, if necessary, may be concentrated by evaporation, the formate of lead, PbO,C_2HO_3 [$Pb(CHO_2)_2$], separates in brilliant prisms or needles.

§ 174.

Recapitulation and Remarks.

Acetic acid and formic acid may be readily distinguished from the other inorganic acids, inasmuch as they can be distilled over with water, and form with ferric oxide soluble neutral salts which dissolve in water, with a blood-red colour; these are decomposed by boiling. The two acids are distinguished from each other by the odour of their hydrates and ethyl compounds, and by their different reactions with salts of silver and salts of mercury, oxide of lead, and concentrated sulphuric acid. The separation of acetic acid from formic acid is effected by heating the mixture of the two acids with an excess of oxide of mercury or oxide of silver. Formic acid reduces the oxide, and is decomposed, whilst the acetic acid combines with the oxide, and remains in solution.

§ 175.

Rarer Acids of the Third Group of Organic Acids.

1. Lactic Acid, $HO,C_6H_5O_5$ [$HC_3H_5O_3$].

Lactic acid is developed in animal juices, vegetable matters that have turned sour, &c. Pure hydrate of lactic acid is an inodorous syrupy liquid of a purely acid, sharp taste. When it is slowly heated in a retort at 130°, water containing a little hydrated lactic acid distils over, leaving a residue of anhydrous lactic acid, which between 250° and 300° is decomposed into carbonic oxide, carbonic acid, lactide, and other products. Hydrate of lactic acid dissolves freely in water, alcohol, and ether; when the aqueous solution is boiled, a little lactic acid volatilizes with the aqueous vapour. All the lactates are soluble in water and in spirit of wine, the greater part of them, however, but sparingly; they are all insoluble in ether. The preparation of some of these salts and the examination of their form under the microscope supplies the means for the detection of lactic acid; lactate of lime and lactate of zinc are the best suited for this purpose. Lactate of lime may be conveniently prepared from animal or vegetable juices by the following method devised by Scherer:—The liquid, if necessary, is diluted with water, mixed with baryta water, and filtered; the filtrate is distilled with some sulphuric acid (to remove volatile acids), the residue digested several days with strong alcohol, the acid solution distilled with a little milk of lime, filtered warm from the excess of lime and the sulphate of lime, and carbonic acid passed into the filtrate; this is heated once more to boiling, filtered from the precipitated carbonate of lime, the filtrate evaporated, and the residue warmed with strong alcohol; the solution is filtered, and the neutral filtrate allowed to remain for several days to give the lactate of lime time to crystallize. Should the quantity of lactic acid present be insufficient to allow the formation of crystals, the solution is evaporated to a syrupy consistence, mixed with strong alcohol, and the mixture allowed to stand some time; the alcoholic solution is then decanted or filtered into a vessel that can be closed, and a small quantity of ether gradually added; this will cause even minute traces of lactate of lime to separate from the solution. Schultzen and Riess recommend the following method for obtaining lactic acid from urine:—The urine is strongly concentrated, precipitated with 95 per cent. spirit of wine, and after the lapse of twenty-four hours the alcoholic solution is poured off and evaporated to a syrup; this is acidified with dilute sulphuric acid, and exhausted by agitation with ether. The ether is then distilled off, the residue dissolved in water, precipitated with acetate of lead, filtered, and the filtrate treated with sulphuretted hydrogen; lastly, the filtrate from the lead sulphide is repeatedly evaporated on the water-bath to drive off the acetic acid. The lactic acid can then be converted into the desired salt. Under the microscope, lactate of lime appears in tufts of minute needles, pairs of them always being joined at the stalked ends, so as to look like paint-brushes united together. Lactate of zinc, when deposited quickly from its solution, appears under the microscope in the form of spherical groups of needles; on slow evaporation of its solution, lactate of zinc is obtained in crystals resembling clubs truncated at both ends; these crystals gradually increase in size, the two ends becoming smaller in proportion, whilst the middle part expands (Funke).

2. Propionic Acid, $HO,C_6H_5O_3$ [$HC_3H_5O_2$], and
3. Butyric Acid, $HO,C_8H_7O_3$ [$HC_4H_7O_2$].

Propionic acid is formed under a great variety of circumstances; it is chiefly found in fermented liquids. The pure hydrate of the acid is a colourless liquid of powerful acid odour and taste; it boils at 140·5°, and does not solidify even at 21°. It dissolves readily in water, but floats as an oily stratum on aqueous solution of phosphoric acid, or solution of chloride of calcium. It has a peculiar odour recalling both that of butyric acid and of acetic acid. On distilling the aqueous solution, the propionic acid passes over with the distillate.

Butyric acid is frequently found in animal and vegetable matter, and more particularly in fermented liquids of the most varied kinds. The pure hydrate of the acid is a colourless, oily, corrosive, intensely sour liquid, of disagreeable odour, recalling that of rancid butter and of acetic acid; it boils at 163°. It is miscible with water and alcohol in all proportions, but may be separated from the concentrated aqueous solution by chloride of calcium, concentrated acids, &c., in the form of a thin oil. The odour of butyric acid is particularly strong in the aqueous solution; on distilling this, the acid passes over with the aqueous vapour.

Propionic acid and butyric acid are often found associated with formic acid and acetic acid in fermented liquids, in guano, in urine, and in many mineral waters. The following process may be employed for the detection of the several acids:—The substance is diluted sufficiently with water, acidified with sulphuric acid, and distilled; the distillate is then saturated with baryta water, evaporated to dryness, and the residue treated repeatedly with boiling alcohol of 85 per cent. This will leave formate of baryta and part of the acetate undissolved, the remainder of the acetate, together with the propionate and butyrate, being dissolved by the alcohol. The alcoholic solution is evaporated, the residue dissolved in water, decomposed cautiously with sulphate of silver, boiled, filtered, and the liquid (which ought rather to contain a little undecomposed baryta salt than any sulphate of silver) evaporated under the desiccator. The crystals which form first are taken out separately, then the second crop, and finally those which are deposited last, and examined separately to ascertain their nature. Acetate of silver when dissolved in concentrated sulphuric acid gives off the odour of acetic acid, but no oily drops; propionate and butyrate of silver emit the peculiar odour of the acids, and give oily drops, which, however, with minute quantities are visible only under the microscope. In order to distinguish with certainty between propionic and butyric acids, it is indispensable to determine the amount of silver in the separated silver salts, and to fix by this the atomic weight of the acids. If much acetate of baryta has passed into the solution, with a small quantity only of butyrate and propionate, the baryta is first exactly precipitated with sulphuric acid from the aqueous solution of the baryta salts soluble in alcohol, half of the acid fluid is neutralized with soda, the other half added, and the liquid distilled; the distillate, which now contains principally propionic and butyric acids, is saturated with baryta, then decomposed with sulphate of silver, and the remaining part of the process conducted as above.

The following process may be used with advantage for separating propionic acid from acetic acid and formic acid:—The mixture of the three acids is evaporated to dryness with water and excess of lead oxide, the residue ground up with warm water, allowed to remain for twelve hours at the ordinary temperature of the laboratory, and filtered. The filtrate contains all the propionic acid as basic lead salt, together with some formate and acetate of lead; the filtrate is now boiled, when the basic propionate of lead separates, and may be collected on a filter by filtering hot, the formate and acetate of lead remaining dissolved in the filtrate (Linnemann).

PART II.

SYSTEMATIC COURSE
OF
QUALITATIVE CHEMICAL ANALYSIS.

PART II.

SYSTEMATIC COURSE
OF
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PRELIMINARY REMARKS

On the Course of Qualitative Analysis in General, and on the Plan of this Part of the Present Work in Particular.

The knowledge of reagents and of the behaviour of substances with them enables us to ascertain at once whether a simple compound of which the physical properties permit an inference as to its nature is in reality what we suspect it to be. Thus, for instance, a few simple reactions suffice to show that a substance which appears to be calcareous spar is really carbonate of lime, and that another which we hold to be gypsum is actually sulphate of lime. This knowledge usually suffices also to ascertain whether a given substance is present or not in a mixture; for instance, whether or not a white powder contains mercurous chloride. But if our design is to ascertain the chemical nature of a substance entirely unknown to us—if we wish to discover *all the constituents* of a mixture or chemical compound—if we intend to prove that, besides certain substances which we have detected, no other can possibly be present—if consequently a *complete* qualitative analysis is our object, the mere knowledge of the reagents, and of the reactions of different substances with them, will not suffice; the additional knowledge of a systematic course of analysis is required—in other words, the knowledge of the order in which solvents and general and special reagents should be applied, both to effect the speedy and certain detection of every element present, and to prove with certainty the absence of all others. If we do not possess the knowledge of this systematic course, or if, in the hope of attaining our object more rapidly, we adhere to no method, analysis becomes (at least in the hands of a novice) mere guess-work, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which may sometimes prove lucky hits, and at others total failures.

Every analytical investigation must therefore be based upon a definite method, although it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a due attention to circumstances will, on the contrary, generally lead to the adoption of different methods for different cases. All analytical methods, however, agree in this, that the substances to be looked for are in the first place classed into groups, which are then again subdivided, until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order in which reagents are applied, and partly on their selection.

Before we can venture on inventing methods of our own for individual cases, we must make ourselves thoroughly conversant with a course of chemical analysis in general. This system must have been proved by experiment, and must be adapted to every imaginable case, so that, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will be best adapted to a given case.

The exposition of such a systematic course, adapted to all cases, tested by experience, and combining simplicity with the greatest possible security, is the object of the First Section of this part.

The elements and compounds comprised in it are the same which have been considered in Part I., with the exception of those discussed more briefly, and marked by the use of smaller type.

The arrangement is such that, if the course laid down is adhered to, the object will be quickly and certainly attained.

The subdivisions of this systematic course are,—

1. Preliminary Examination;
2. Solution;
3. Actual Examination.

The third subdivision (the Actual Examination) is again divided into the examination of compounds in which but one base and one acid are assumed to be present, and the examination of mixtures or compounds in which all the substances treated in the present work are assumed to be present. With respect to the latter, it should be noted that, where the preliminary examination has not clearly demonstrated the absence of certain groups of substances, the student cannot safely disregard any of the paragraphs to which reference is made in consequence of the reactions observed. In cases where the intention is simply to test a mixture for certain substances, and not to ascertain all the constituents present, it will be easy to select the particular numbers which ought to be attended to.

The construction of a systematic course of analysis which shall be universally applicable requires due provision for every contingency that can possibly arise, but it is self-evident that, although in the system here laid down the various substances comprised in it are assumed to be mixed up together in every conceivable way, they must also be assumed to be free from organic matters, as otherwise many reactions would be hindered or modified.

Although the general analytical course laid down here is devised and arranged in a manner to suit all possible contingencies, yet there are special cases in which it may be advisable to modify it. A preliminary treatment of the substance is also sometimes necessary, before the actual analysis can be proceeded with; the presence of colouring or slimy organic matters more especially requires certain preliminary operations. The Second Section will be found to contain a detailed description of the special methods employed to meet certain cases which frequently occur. Some of these methods show how the analytical process becomes simplified as the number of substances to be looked for decreases.

Lastly, as the intelligent and successful performance of analysis is possible only with an accurate knowledge of the principles whereon the detection and separation of substances depend, an explanation of the general analytical process is given in the Third Section along with numerous additions to the practical operations. As this third section may properly be regarded as the key to the first and second sections, students are strongly recommended to make themselves early and thoroughly acquainted with it. A special section is devoted to this theoretical explanation, as it will be understood better in a connected form than it would have been by explanatory additions to the several paragraphs, which, moreover, might have materially interfered with the perspicuity of the practical process.

In this third section also, the author points out in what residues, solutions, precipitates, &c., which are obtained in the systematic course of analysis, the more rarely occurring elements may be expected to be met with; and also gives instructions how to proceed with a view to ensure the detection of these elements systematically.

SECTION I.

PRACTICAL PROCESS FOR THE ANALYSIS OF COMPOUNDS AND MIXTURES IN GENERAL.

I. PRELIMINARY EXAMINATION.[*]

In the first place, the external properties, such as the colour, shape, hardness, gravity, odour, &c., of the substance should be examined, as from these it is often possible in some measure to infer its nature. If the quantity of the substance is limited, it is as well, before proceeding, to consider how much may safely be spared for the preliminary examination. The habit of economy is in all cases advisable, even when there is plenty of the substance to hand. It should, moreover, be a fixed rule, under all circumstances, never to use up the whole of a substance, but always to keep a portion of it for unforeseen contingencies, and for confirmatory experiments. 1[†]

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[*] Consult also the observations in the Third Section of Part II.

[†] These marginal numbers are simply intended to facilitate reference.

A. THE BODY UNDER EXAMINATION IS SOLID.

§ 176.

I.—It is neither a Metal nor an Alloy.

2 1. The substance is ready for examination, if in powder or in minute crystals; but in the case of larger crystals or solid pieces, a portion must, if practicable, be first reduced to *fine powder*. Bodies of the softer kind may be ground up in a porcelain mortar; those of a harder nature must first be broken into small pieces in a steel mortar, or upon a steel anvil, and the pieces then ground in an agate mortar.

3 2. Some of the powder is put into a glass tube about 60 m.m. long and 5 m.m. wide, sealed at one end or blown out into a small bulb, and is heated at first gently over the spirit lamp or gas lamp, then intensely in the blowpipe flame, or in the gas lamp with chimney. The reactions which take place may lead to many positive or probable conclusions regarding the nature of the substance. The following are the most important of these reactions, to which particular attention ought to be paid; it often occurs that several of them are observed in the case of one and the same substance.

4 *a.* The substance remains unaltered: absence of organic matters, salts containing water of crystallization, readily fusible matters, and volatile substances (except carbonic acid, which often escapes without visible change).

5 *b.* The substance does not melt at a moderate heat, but simply changes colour. From white to yellow, turning white again on cooling, indicates oxide of zinc; from white to yellowish-brown, turning to a dirty pale yellow on cooling, indicates stannic oxide; from white or yellowish-red to brownish-red, turning to yellow on cooling, the substance fusing at a red heat, indicates oxide of lead; from white, or pale yellow, to orange yellow, up to reddish-brown, turning pale yellow on cooling, the body fusing at an intense red heat, indicates oxide of bismuth; from white or yellowish-white to dark brown, remaining dark brown when cold, indicates oxide of manganese (the carbonate, for instance); if it becomes bright reddish-brown on cooling, it indicates oxide of cadmium (carbonate, for example); from bright blue or green to black, points to carbonate of copper; from grayish-white to black indicates ferrous carbonate; from brownish-red to black, turning brownish-red again on cooling, indicates ferric oxide; from yellow to dark orange, the substance melting at an intense heat, indicates neutral chromate of potassa; from bright red to dark red, and then a violet black, turning bright red again on cooling, and yielding a sublimate of mercury when heated to bright redness, indicates oxide of mercury; from bright

red to brown, becoming bright red on cooling, red lead; it leaves yellow fused oxide of lead when very strongly heated.

c. The substance melts without giving off aqueous vapours. If on intense heating, gas (oxygen) is evolved, and a small fragment of charcoal thrown in is energetically consumed, nitrates or chlorates are indicated. 6

d. Aqueous vapours are expelled, which condense on the colder part of the tube: this indicates— 7

(*α*) Substances containing water of crystallization, in which case they will usually fuse readily, and re-solidify after the water has been driven off; many of these swell up considerably as the water passes off: borax and alum, for example;

(*β*) Decomposable hydrates, or salts containing chemically combined water, in which case the substance very often will not fuse;

(*γ*) Anhydrous salts, holding water mechanically inclosed between their lamellæ, in which case the substance decrepitates;

(*δ*) Compounds to which moisture adheres externally;

(*ε*) Salts of ammonia which are decomposed with formation of water, such as nitrate of ammonia, which simultaneously yields nitrous oxide; a glowing chip of wood ignites in the gas.

The liquid condensed in the tube is tested to see if it is acid or alkaline; if alkaline, ammonia is indicated; if acid, a volatile acid (sulphuric, sulphurous, hydrofluoric, hydrochloric, hydrobromic, hydriodic, acetic, &c.) is present.

e. The substance decrepitates without giving off water. This indicates certain anhydrous minerals which possess this property, for instance, heavy spar, zinc blende, galena, spathic iron, plumbocalcite, &c.

f. Gases or vapours escape. Observe whether they have a colour or odour, an acid or alkaline reaction, whether they are inflammable, &c. 8

aa. **Oxygen** indicates oxides of the noble metals, peroxides, chlorates, nitrates, &c. A glowing chip of wood is re-lighted in the evolved gas.

bb. **Sulphurous acid** is produced by the decomposition of sulphites of the heavy metals and of many of the sulphates; also when mixtures of sulphides of the metals with sulphates are ignited; it may be known by its odour and by its acid reaction.

cc. **Hyponitric acid**, resulting from the decomposition of nitrates, especially those of the heavy metals; it may be known by its brownish-red colour, and the odour of the fumes.

dd. **Carbonic acid** indicates carbonates decomposable by heat, or oxalates of reducible metals, such as oxalate of copper. The gas is colourless and odourless, non-inflammable; a drop of lime water on a watch-glass becomes turbid on exposure to the evolved gas.

ee. **Carbonic oxide** indicates oxalates and also formates. The gas burns with a blue flame. In the case of oxalates, the carbonic oxide is generally mixed with carbonic acid—for instance, from oxalate of magnesia—and is therefore more difficult to kindle: in the case of formates, there is marked carbonization. Oxalates evolve carbonic acid when mixed with binoxide of manganese, a little water, and some concentrated sulphuric acid on a watch-glass; formates evolve no carbonic acid under similar circumstances.

ff. **Chlorine, bromine,** or **iodine** indicates decomposable chlorides, bromides, or iodides. The gases are readily recognized by their colour (greenish-yellow, brownish-red, and violet) and odour. Iodine, if evolved in any quantity, forms a black sublimate (compare **9**).

gg. **Cyanogen** and **hydrocyanic acid** indicate cyanides decomposable by heat (such as mercuric cyanide and prussian-blue). Both may be recognized by their odour; and the cyanogen, when tolerably pure, by the crimson flame with which it burns.

hh. **Sulphuretted hydrogen** indicates sulphides containing water (also hyposulphites); the gas may be readily known by its odour.

ii. **Ammonia,** resulting from the decomposition of ammoniacal salts, of cyanides containing water, or of nitrogenous organic matters; in the latter case, browning or carbonization takes place, and usually offensive empyreumatic oils escape with the ammonia.

g. A sublimate is formed. This indicates volatile substances: the following are those more frequently met with:— **9**

aa. **Sulphur.** Given off by mixtures and by many of the metallic sulphides. Sublimes in reddish-brown drops, which on cooling solidify, and turn yellow or yellowish-brown.

bb. **Iodine.** Given off by mixtures, many iodides, iodic acid, &c. Violet vapour, black sublimate, odour of iodine.

cc. **Ammonia salts** give white sublimates; heated with carbonate of soda and a drop of water on platinum foil, they evolve ammonia.

dd. **Mercury** and its compounds. Metallic mercury forms globules; sulphide of mercury is black, but acquires a red tint when rubbed; mercuric chloride fuses before volatilizing; mercurous chloride sublimes without previous fusion, the sublimate, which is yellow whilst hot, turns white on cooling. The red iodide of mercury gives a yellow sublimate.

ee. **Arsenic** and its compounds. Metallic arsenic forms the well-known arsenical mirror; arsenious acid forms small shining crystals; the sulphides of arsenic give sublimates which are reddish-yellow whilst hot, and turn yellow on cooling.

ff. **Oxide of antimony** fuses to a yellow liquid before subliming. The sublimate consists of brilliant needles.

gg. **Chloride of lead.** It melts to a yellow liquid before any sublimate is formed. The sublimate is white, and volatilizes with difficulty.

hh. **Benzoic acid** and **succinic acid.** White crystalline sublimates. The officinal impure acids may be known by the odour of their fumes.

ii. **Salicylic acid.** A white crystalline sublimate. If quickly and strongly heated, it gives off an odour of phenol.

kk. Hydrated **oxalic acid.** White crystalline sublimate, thick irritating vapours in the tube. On heating a small portion on platinum foil with a drop of concentrated sulphuric acid, there is a copious evolution of gas.

h. Carbonization takes place: organic substances. This 10 is always attended with evolution of gases (acetates evolve acetone) and water; the latter has an alkaline or acid reaction. An odour of burnt hair indicates nitrogenous organic matter. If the residue effervesces with acids, whilst the original substance did not show this reaction, organic acids may be assumed to be present in combination with alkalies or alkaline earths. Salts containing readily reducible metallic oxides in combination with organic acids—acetate of copper, for example—often leave the metal behind, and as the carbon is burnt at the expense of the metallic oxide, the residue may contain little or no carbon.

3. A small portion of the substance is placed on a 11 charcoal support (in the cavity scooped out for the purpose), and exposed to the inner blowpipe flame.

As most of the reactions described under 2 (3—10), when the substance is heated in a glass tube, also occur when this method is used, only those phenomena will be noticed which are peculiar to this mode of operation. Evolution of sulphurous acid, when the flame plays upon the sample, generally indicates a sulphide. If the alliaceous odour of arsenic is noticed, this indicates arsenic or an arsenic compound. An odour of ammonia points to certain ammonia compounds, such as carbonate of ammonia. If the charcoal burns vigorously, this usually indicates nitrates or chlorates. Care should be taken to avoid inhaling the vapours of substances which have yielded a sublimate when heated in the glass tube.

Besides those just mentioned, the following reactions will permit of tolerably accurate conclusions being formed as to the nature of the substance.

a. The substance melts, and is absorbed by the 12 charcoal or forms a bead in the cavity, without any incrustation; this indicates more particularly salts of the alkalies.

b. An infusible white residue remains on the charcoal, either at once or after previous melting in its water of crystallization; this indicates more especially baryta, strontia, lime, magnesia, alumina, oxide of zinc (this appears yellow whilst hot), and silicic acid. Amongst these substances, strontia, lime, magnesia, and oxide of zinc are distinguished by strong luminosity in the blowpipe flame; and the alkaline earths, in that they give an alkaline reaction whether uncombined or in the state of sulphides. A drop of nitrate of cobalt solution is added to the ignited white infusible mass, and it is again strongly heated; a change of colour then takes place. The following are characteristic: a brilliant blue indicates alumina or silica; green, oxide of zinc; whilst a violet colour points to phosphate or arsenate of magnesia. It must be noted that a blue coloration more or less marked is produced with phosphates of the alkaline earths. 13

In the case *a* or *b*, the preliminary examination for alkalies and alkaline earths may be completed by examining the colours which the substances impart to flame. For this purpose, a little of the substance is attached to the loop of a fine platinum wire, moistened repeatedly with hydrochloric acid, dried cautiously near the border of the flame, and then held in the fusing zone of the Bunsen gas-flame. The colorations caused by the alkalies make their appearance first, followed—after volatilization of the alkalies—by those of baryta, strontia, and lime. Sometimes it is advisable in the first place to heat the substance in the reducing flame before moistening with hydrochloric acid—as when sulphates are present, for example. For details see § 17, § 92, and § 99.

c. The substance leaves a residue of another colour; or reduction to the metallic state takes place; or an incrustation forms on the charcoal. If no inference can be drawn from the previous experiments, a portion of the powder is mixed with carbonate of soda and a drop of water (if ammonia is evolved, this indicates the presence of an ammonium compound), and is then heated on charcoal in the reducing flame; the residue in the cavity as well as the incrustation on the charcoal must be carefully noticed. If a metallic sulphide or arsenide is present, see **11**. If the substance contains much water of crystallization, it should be heated for a short time on the lid of a porcelain crucible, and powdered, before being mixed with the carbonate of soda. 14

α. If a metallic globule is obtained, without incrustation of the charcoal, this indicates gold or copper; the latter is at once recognized by the green coloration of the flame. The oxides of platinum, iron, cobalt, and nickel are also reduced, but they do not yield a metallic globule. 15

β. An incrustation is formed on the charcoal support either with or without a metallic globule. 16

aa. The incrustation is **white**, at some distance from the test specimen, and is very readily dissipated by heat, emitting a garlic-like odour: arsenic.

bb. The incrustation is **white**, nearer the test specimen than in *aa*, and may be driven from one part of the support to another: antimony. Metallic globules are generally observed at the same time, which continue to evolve white fumes long after heating with the blowpipe jet is discontinued, and on cooling become surrounded with crystals of oxide of antimony; the globules are brittle.

cc. The incrustation is **yellow** whilst hot, but turns white on cooling; it is pretty near the test specimen and is volatilized with difficulty: zinc.

dd. The incrustation is **pale yellow** whilst hot, and turns white on cooling; it surrounds the test specimen closely, and does not volatilize either in the inner or the outer flame: tin. The metallic globules formed at the same time, but only in a strong reducing flame, are bright, readily fusible, and malleable.

ee. The incrustation is **lemon-yellow**, turning sulphur-yellow when cold; heated in the reducing flame, it leaves its place with a blue gleam: lead. Readily fusible, malleable globules are formed at the same time as the incrustation.

ff. The incrustation is **dark orange-yellow** whilst hot, changing to lemon-yellow on cooling; when heated in the reducing flame, it leaves its place without a blue gleam: bismuth. The metallic globules formed are readily fusible and brittle.

gg. The incrustation is **reddish-brown**, in thin layers orange-yellow; it volatilizes without a coloured gleam: cadmium.

hh. The incrustation is **dark-red**, white metallic globules being formed at the same time: silver. Where lead and antimony are present at the same time, the incrustation is crimson.

If, in any case, the reduction to the metallic state is incomplete, the experiment should be repeated, mixing the substance with carbonate of soda and a little cyanide of potassium; the latter considerably facilitates the reduction.

In cases where a reduction to the metallic state takes place, the sample is moistened with water, cut out of the charcoal, ground up in a small agate mortar, and the particles of charcoal washed away with water. The gold will be obtained in yellow, the copper in coppery-red, the silver in nearly white, the tin in grayish-white, the lead in whitish-gray minute flakes or threads, the bismuth as a reddish-gray, the zinc as a bluish-white, the antimony as a gray powder. When copper and tin, or copper and zinc, are present at the same time, yellow alloys are occasionally formed.

γ. If sulphide of sodium is formed, which can be easily recognized by the method given in § 140, 6, this indicates the presence of a sulphate or a sulphite.

4. A small portion is fused with a bead of microcosmic salt (see § 84), and exposed for some time to the outer flame of the blowpipe. 17

a. The substance dissolves readily and in considerable quantity forming a bead which is clear while hot.

α. **The hot bead is coloured:** 18

Blue, when viewed by candlelight inclining to violet—cobalt;

Green, becoming blue on cooling; in the reducing flame, after cooling, red—copper; only, however, if there is plenty of copper in the bead;

Green, particularly fine on cooling, unaltered in the reducing flame—chromium;

Brownish-red, becoming light yellow or colourless on cooling; in the reducing flame red whilst hot, yellow whilst cooling, then greenish—iron;

Reddish to brownish-red, yellow to reddish-yellow or colourless on cooling; not altered in the reducing flame—nickel;

Yellowish-brown, light yellow or colourless on cooling; in the reducing flame almost colourless (especially if a little tin is added), blackish-gray on cooling—bismuth;

Light yellowish to opal, somewhat opaque when cold; in the reducing flame whitish-gray—silver;

Amethyst-red, especially on cooling; colourless in the reducing flame, not quite clear—manganese.

β. **The hot bead is colourless:** 19

aa. It remains clear on cooling: antimony, alumina, zinc, cadmium, lead, lime, magnesia; the last five, when added in somewhat large proportion to the microcosmic salt, give enamel-white beads; the bead of oxide of lead is yellowish if saturated;

bb. It becomes enamel-white on cooling, even when a small portion only of the substance has been added to the bead: baryta, strontia.

b. The substance dissolves slowly and only in small quantity: 20

a. The bead is colourless, and remains so even after cooling; the undissolved portion looks semi-transparent; on adding a little ferric oxide, it acquires the characteristic colour of an iron bead: silicic acid.

β. The bead is colourless, and remains so after addition of a little ferric oxide: tin.

21 *c*. The substance does not dissolve, but floats (in the metallic state) in the bead: gold, platinum.

5. Minerals are examined for fluorine as directed in § 146, 8.

As the substance may be a mixture of the most varied kind, it is not always possible to come to a satisfactory conclusion as to its nature when examined in this way. If the phenomena indicate a mixture of two or more substances, this must be borne in mind in the subsequent examination.

When the preliminary examination has been made, the substance is dissolved as directed in § 180 (**32**).

§ 177.

II.—THE SUBSTANCE IS A METAL OR AN ALLOY.

22 1. A small portion of the substance is heated with water acidified with acetic acid. If hydrogen is evolved, this indicates a light metal (possibly also metallic manganese).

23 2. A sample of the substance is heated on charcoal in the reducing flame of the blowpipe, and note taken as to whether the substance melts, whether an incrustation is formed, or an odour emitted, &c.

In this way the following metals may be detected with more or less certainty: arsenic by the odour of garlic; mercury by its volatility; antimony, zinc, lead, bismuth, cadmium, tin, and silver by their fusibility and the incrustation on the charcoal (comp. **16**); copper by the green colour of the outer flame. It is only when there is a single metal in a pure or nearly pure state, that further inferences can be drawn; for instance, gold fuses without incrustation; platinum, iron, manganese, nickel, and cobalt, when pure, do not fuse in the blowpipe flame.

24 3. A sample of the substance is heated either in a glass tube sealed at one end, before the blowpipe, or in a gas-burner furnished with a chimney.

a. No sublimate is formed in the colder part of the tube: absence of mercury.

b. A sublimate is formed: presence of mercury, cadmium, or arsenic. The sublimate of mercury, which consists of small globules, cannot easily be confounded with that of cadmium or arsenic.

When the preliminary examination is finished, the substance is dissolved as directed in § 181 (**42**).

B. THE SUBSTANCE UNDER EXAMINATION IS A LIQUID.

§ 178.

1. A small portion of the liquid is evaporated in a platinum capsule, or in a small porcelain crucible, in order to ascertain whether it contains anything in solution; if there is a residue, this must be examined as directed in § 176. 25

2. Test with litmus-paper (blue and red). 26

a. The liquid reddens blue litmus-paper. This reaction may be caused by a free acid or an acid salt, as well as by a metallic salt soluble in water. To distinguish between these two cases, a small quantity of the liquid is poured into a watch-glass, and a small glass rod, the extreme point of which has been previously moistened with dilute solution of carbonate of soda is dipped into the liquid; if the liquid remains clear, or if the precipitate which may form at first, redissolves on stirring, a free acid or of an acid salt is present; but if the liquid becomes turbid and remains so, this generally denotes the presence of a soluble metallic salt.

b. Reddened litmus-paper becomes blue: this indicates the presence of a free alkali or an alkaline carbonate, free alkaline earths, alkaline sulphides; many other salts containing an alkali or, it may be, an alkaline earth, in combination with a weak acid, produce a similar effect. The only compounds of the heavy metals which have an alkaline reaction are some of the basic salts, such as basic acetate of lead, and solutions of thallious oxide and carbonate of thallium. 27

3. The odour of the liquid is noted, or, should this fail to give any definite result, it is distilled to ascertain whether the simple solvent present is water, alcohol, ether, &c. If it is not water, the solution is evaporated to dryness, and the residue treated as directed in § 176. 28

4. If the solution is aqueous, and has an acid reaction, a portion of it is diluted largely with water. Should this impart a milky appearance to it, the presence of antimony or bismuth (or possibly also of tin) may be inferred. Comp. § 121, 9, and § 131, 4. 29

When the preliminary examination is finished, the special examination must be proceeded with. If the solution is aqueous, and neutral, it can only contain substances soluble in water; but if it has an acid reaction, arising from the presence of free acid, the special examination must be conducted with due regard to the possible presence of compounds which are soluble in acids, although insoluble in water. If only one acid and one base are present, the neutral aqueous solution is examined as directed in § 182, the acid solution as directed in § 185; where there is reason to suppose the presence of several bases and acids, the method adopted must be that given in § 189. With solutions of alkaline reaction, the method given in § 182 should be employed, unless there be reason to suppose the presence of more than one acid and one base, when § 189 must be followed. 30

II. DISSOLUTION OF SUBSTANCES,

or Classification of Substances, according to their Behaviour with Certain Solvents.*

§ 179.

Water and acids (hydrochloric acid, nitric acid, aqua regia) are the solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. The various substances are divided into three classes, according to their behaviour with these solvents. 31

First class.—Substances soluble in water.

Second class.—Substances insoluble or sparingly soluble in water, but soluble in hydrochloric acid, nitric acid, or aqua regia.

Third class.—Substances insoluble or sparingly soluble in water, hydrochloric acid, nitric acid, and aqua regia.

As the dissolution of alloys is more conveniently effected in a somewhat different manner, the special method pursued in that case will be given in § 181.

The following method is employed to dissolve the substance.

A. THE SUBSTANCE IS NEITHER A METAL NOR AN ALLOY.

§ 180.

Simple Substances.†

In examining a simple substance, its behaviour towards the more usual solvents is first ascertained. For this purpose, a small quantity is treated successively with water, dilute hydrochloric acid, concentrated hydrochloric acid, nitric acid, and aqua regia, in the order given, first at the ordinary temperature, and then on warming. 32

If the small sample dissolves in one of the solvents, a larger amount, about 1 gram, is treated in a similar manner, and the solution, if aqueous, is examined according to § 182; if in acid, according to § 185; whilst insoluble or very sparingly soluble compounds are treated according to § 188.

The reactions which may take place on treating a simple sub- 33

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* Consult the remarks in the Third Section of the Second Part.

† This name has been adopted for the sake of brevity, and will frequently be employed to indicate compounds which contain only *one* base and *one* acid, or *one* metal and *one* non-metal.

stance with hydrochloric acid must be carefully noticed, and are as follows:—

α. Effervescence, indicating carbonic acid or sulphuretted hydrogen.

β. Evolution of chlorine, indicating peroxides, chromates, &c.

γ. There is an odour of hydrocyanic acid, indicating the presence of insoluble cyanides (as, however, the latter are decomposed in an anomalous manner, a separate section has been devoted to them, *vide* § 204).

In treating with nitric acid, the evolution of nitric oxide or nitrous acid indicates that an oxidizing action is taking place. If the substance dissolves in acids, with simultaneous separation of sulphur (which may be recognized by its colour and sp. gr., and may be filtered off after boiling for some time), or if a gelatinous precipitate of hydrated silicic acid is formed, the presence of a sulphide, or a silicate, decomposable by acids is indicated. The solution after dilution,* and filtration if necessary, is examined according to § 185, and any insoluble residue is treated according to § 188.

Mixed Substances.†

34 If the substance to be examined is a mixture, it is usually advisable to separate the various ingredients from one another by means of their different solubilities. This is best performed as follows:—

1. From 1 to 3 grams of the finely pulverized substance is put into a small flask or a test-tube, about ten times the amount of distilled water added, and the mixture heated to boiling over a spirit lamp or gas lamp.

35 *a.* The substance dissolves completely. In that case it belongs to the first class; regard must be had to what has been stated in the preliminary examination (**30**) with respect to reaction. The solution is examined for the bases according to § 189, and for the acids as described in § 199 and § 200 respectively.

36 *b.* There is an insoluble residue even after prolonged boiling. The residue is allowed to subside, and the liquid filtered, if practicable in such a manner that the residue remains in the test-tube. A few drops of the clear filtrate are then evaporated on platinum foil; if nothing remains, the substance is completely insoluble in water; in which case proceed as directed in **37**. If a residue remains, the substance is partly soluble; in this case, it is repeatedly boiled with water so as to dissolve out all the soluble ingredients as far as

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* If the solution becomes turbid on dilution, the presence of bismuth or antimony is indicated; the solution becomes clear again on adding more hydrochloric acid.

† By mixed substances are understood compounds or mixtures in which the more frequently occurring bases, acids, metals, or non-metals are present together.

possible,* and the filtrate examined according to 35; the insoluble residue is treated as in 37.

37 2. A small portion of the residue which has been boiled out with water is treated with dilute hydrochloric acid. If it does not dissolve, it is heated to boiling, and if this also fails to effect complete solution, the clear supernatant liquid is poured off into another test-tube, and the residue boiled with concentrated hydrochloric acid; if it dissolves, the solution is added to that already poured off.

For the phenomena produced by the action of hydrochloric acid compare 33.

38 *a.* The residue is completely dissolved by the hydrochloric acid (except perhaps that sulphur or hydrate of silicic acid separates; see 33). The substance insoluble in water, or the particular component parts of it, belong, therefore, to the second class; pass on to § 190; the sulphur or hydrated silicic acid, separated by filtration, is examined as directed in § 203.

b. There is a residue left. In that case the test-tube containing the specimen which has been boiled with the hydrochloric acid is put aside, and the examination proceeded with as in 39.

39 3. If the hydrochloric has not completely dissolved the substance insoluble in water, or which has been already exhausted with water, a fresh specimen is treated with boiling nitric acid, and water subsequently added. The phenomena which may take place are described in 33.

a. The sample is completely dissolved, or leaves no residue except sulphur or gelatinous silicic acid (see 33); in this case also the substance belongs to the second class. The solution in nitric acid is treated as directed in § 189, III. (109), and for the rest as in 38.

b. There is still a residue left. Pass on to 40.

40 4. If the residue insoluble in water is not completely soluble in hydrochloric acid or in nitric acid, it should be treated with nitrohydrochloric acid. For this purpose, the contents of the tube treated with nitric acid is mixed with the contents of the tube treated with concentrated hydrochloric acid; the mixture is then heated to boiling, and, should this fail to effect complete solution, the clear liquid is decanted from the undissolved residue, and the latter boiled for some time with concentrated nitro-hydrochloric acid; the decanted solution in dilute aqua regia as well as the solution in dilute hydrochloric acid, which was decanted in 37, are then added to this. The entire mixture is once more heated to boiling, noting whether complete solution has been effected, or whether the action of the concentrated nitro-hydrochloric acid has still left a residue. In the *latter* case, the solution is filtered—if necessary, after addition of

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* If the substance is only sparingly soluble in water, like sulphate of lime, for example, boiling with water four times will be sufficient, as it would be very difficult to completely exhaust it with boiling water.

some water*—the residue washed with boiling water, and the filtrate, mixed with the washings, is treated as directed in § 190. In the *former* case, the clear solution is treated in the same way.†

4. If boiling nitro-hydrochloric acid leaves a residue, it must be washed thoroughly with boiling water, and then treated as directed in § 203. 41

B. THE SUBSTANCE IS A METAL OR AN ALLOY.

§ 181.

The metals are best classed according to their behaviour with nitric acid, as follows: 42

I. Metals which are not attacked by nitric acid: gold, platinum.

II. Metals which are oxidized by nitric acid, but whose oxides do not dissolve in an excess of the acid or in water (to any extent): antimony, tin.

III. Metals which are oxidized by nitric acid and converted into nitrates which dissolve in an excess of the acid or in water: all the other metals.

Chemically pure metals are but seldom the subject of qualitative analysis, for almost all metals as met with in commerce are admixed with smaller or larger quantities of other metals. This being the case, no special description of the manner of dissolving pure metals will be given, but all will be considered as alloys, the method of proceeding being equally applicable to alloys, impure metals, or pure metals. In testing pure metals, it is only necessary to treat a very small portion with nitric acid; whilst for the analysis of alloys, when the small quantities of metals present as impurities are not taken into account, 1 to 3 grams will suffice. If, on the other hand, the object is to detect the traces of metallic impurities in metals obtained in metallurgical operations—for example, in testing lead for bismuth, copper, antimony, iron, zinc, silver, &c.—it is necessary to employ from 100 to 200 grams.

The sample is treated with nitric acid of sp. gr. 1·2, and, if nitrate of lead separates, an equal volume of water is added.

1. Complete solution takes place, either at once or on adding water; this proves the absence of platinum,‡ gold, 43

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[*] If the liquid becomes turbid when water is added, this indicates the presence of bismuth or antimony; the turbidity will disappear again on adding more hydrochloric acid.

[†] If the acid solution deposits acicular crystals on cooling, the latter generally consist of chloride of lead; in that case, it is often advisable to decant the liquid from the crystals, and to examine the solution and the crystals separately. If metastannic chloride has been formed on boiling with aqua regia, the washing water, dissolving this, becomes turbid on dropping into the strongly acid liquid which has run off first. In that case, the washings should be received in a separate vessel, and the two solutions treated separately with sulphuretted hydrogen as directed in § 190, but filtered afterwards through the same filter.

[‡] Alloys of silver and platinum, if the latter metal is present in small proportion only, dissolve in nitric acid.

antimony,* and tin. The solution is examined as directed in § 182, or § 189, III. (109), according as there is reason to suppose the presence of only one or of several metals.

2. A residue is left.

a. It is metallic. The solution is filtered and the filtrate treated as directed in § 189, III. (109), after it has been ascertained, in the first place, whether anything is dissolved. The residue is washed thoroughly, dissolved in nitro-hydrochloric acid, and the solution tested for gold and platinum, according to § 128. 44

b. A white pulverulent residue indicates as a rule either antimony or tin. If it may be fairly considered that only one or other of these metals is present, it is sufficient to fuse the washed and dried residue with sodium carbonate and a little potassium cyanide, on a charcoal support, in the reducing blowpipe flame, and then to ascertain whether the bead of reduced metal consists of ductile tin or brittle antimony. If, however, several metals may be present, the examination becomes more complicated, as bismuth arsenate is but very little soluble in nitric acid, and lead, copper, and other metallic oxides may remain with the antimonic and metastannic acids. In this case, it is best to fuse the washed and dried residue with about four parts of a mixture of equal weights of sodium carbonate and sulphur in a well-covered porcelain crucible, allow the melt to cool, and extract it with water. If there is any residue, it is collected, washed, dissolved in nitric acid, and the solution tested as in § 189, III. (109), for the metals of the fourth and fifth groups. The yellow alkaline solution, on the other hand, is acidified with hydrochloric acid to throw down the metals of the sixth group; the precipitate is washed and examined according to § 192. 45

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* Very minute traces of antimony, however, are often completely dissolved by nitric acid.

III. ACTUAL EXAMINATION.

SIMPLE COMPOUNDS.*

A. SUBSTANCES SOLUBLE IN WATER.

Detection of the Base.†

§ 182.

1. Some hydrochloric acid is added to a portion of the aqueous solution, which must not be too concentrated. If the solution is alkaline, the acid must be added until it has a decidedly acid reaction. 46

a. No precipitate is formed; this indicates the absence of silver and mercurous oxide, and likewise the absence of lead in large quantity. Pass on to **50**.

b. A precipitate is formed.‡ The liquid in which the precipitate is suspended must be divided into two portions, and ammonia in excess is added to one of them. 47

α. The precipitate redissolves, and the liquid becomes clear: this shows that the precipitate is chloride of silver, and consequently that silver is present; as confirmatory tests, chromate of potassa is added to the original solution, and it should also be tested with sulphuretted hydrogen (see § 115, 4, and § 138, 7).

β. The precipitate turns black: the precipitate is mercurous chloride, which has now been converted by the ammonia into black amidochloride of mercury; this proves the presence of mercurous oxide. In order to confirm this, the original solution is tested with stannous chloride and with metallic copper (see § 116, 7 and 8). 48

γ. The precipitate remains unchanged: it consists of chloride of lead, which is not dissolved by ammonia, and 49

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* This term is used to designate compounds supposed to contain only *one* base and *one* acid, or *one* metal and *one* non-metallic element. The principal object of this chapter is to facilitate instruction in analysis, as it is advantageous that the examination of complex compounds should be preceded by the analysis of simple compounds. In actual practical analysis, use can be made of this chapter only exceptionally, as there exists no outward sign by which to judge whether a substance contains only one base or acid, or several.

† Arsenious and arsenic acids, and silicic acid are included here.

‡ If the solution is concentrated and strongly alkaline, other substances may be precipitated besides chloride of silver, mercurous chloride, and chloride of lead; thus hydrated silicic acid may be thrown down, possibly also chloride of barium and metastannic chloride; and if the preliminary examination has indicated the presence of an organic substance, the precipitate may consist of benzoic or salicylic acid. Hydrate of silicic acid is gelatinous; chloride of barium, benzoic acid, and salicylic acid are crystalline. None of the compounds mentioned above will be precipitated if the solution be diluted sufficiently, and only a moderate quantity of hydrochloric acid added.

accordingly indicates the presence of lead. This is confirmed, in the first place, by diluting largely with water the second portion of the liquid in which the precipitate produced by hydrochloric acid is suspended, and then heating it; if the precipitate is chloride of lead, it will dissolve; finally, portions of the original solution are tested with sulphuretted hydrogen, and with sulphuric acid (§ 117, 4 and 8).

2. To the solution which has been acidified with hydrochloric acid, sulphuretted hydrogen water is added until it smells distinctly of the gas after it has been shaken; the mixture is then heated, some more sulphuretted hydrogen water added, and the whole allowed to remain for a short time.* 50

a. The liquid remains clear. Pass on to **56**, since this is a proof that lead, bismuth, copper, cadmium, mercuric oxide, gold, platinum, tin, antimony, arsenic, and ferric oxide are absent.

b. A precipitate is formed.

α. The precipitate is white; it consists of separated sulphur, and indicates a substance which decomposes sulphuretted hydrogen.† Of the metallic oxides which possess this property, ferric oxide is the most common (§ 111, 3). The original solution is tested for this with ammonia and ferrocyanide of potassium (§ 111, 6). If ferric oxide is not found, and, moreover, if there is no change of colour indicating the presence of chromic acid or hydroferricyanic acid,† pass on to **56**. 51

β. The precipitate is yellow; it may consist of sulphide of cadmium, sulphide of arsenic, or stannic sulphide, indicating either cadmium, arsenic, or stannic oxide. To distinguish between them, ammonia in excess is added to a portion of the liquid, with the precipitate suspended in it, then some sulphide of ammonium, and the whole warmed. 52

aa. The precipitate does not dissolve: this indicates cadmium, as sulphide of cadmium is insoluble in ammonia and sulphide of ammonium. Confirm by testing the original substance, or the precipitate thrown down from

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[*] If a precipitate is formed immediately the solution of sulphuretted hydrogen is added, it is unnecessary to apply heat, &c.; but if the liquid remains clear, or is rendered only slightly turbid, the above course of proceeding must be strictly followed, so as to guard against the risk of overlooking arsenic acid and stannic oxide.

[†] If the colour of the solution from being reddish yellow changes to green, it indicates chromic acid; if it changes from brownish yellow to bright blue, it is a sign that hydroferricyanic acid is present. In the first case, two bases remain in solution after the action of the sulphuretted hydrogen, namely, oxide of chromium, and the base which was in combination with the chromic acid; the solution is examined as described in § 194. In the other case, the dry substance (or if an aqueous solution, the residue left on evaporation) is moistened with concentrated sulphuric acid, and heated in a good draught until the greater part of the sulphuric acid has evaporated. The residue is dissolved in water, and the solution—containing the original base and also oxide of iron arising from the decomposition of the hydroferrocyanic acid—is examined as in § 194.

the original solution by carbonate of ammonia, with the blowpipe (§ 122, 9).

bb. The precipitate dissolves: this indicates stannic oxide or arsenic: ammonia is added to a small portion of the original solution.

aa. A white precipitate is formed. Stannic oxide is present. Confirm by reducing the precipitate before the blowpipe, with cyanide of potassium and carbonate of soda (§ 130, 11), or by adding nitrate of ammonia to the original solution (§ 130, 8).

ββ. No precipitate is formed. This indicates arsenic. Confirm by obtaining an arsenical mirror from the original substance or from the precipitated sulphide of arsenic, either with cyanide of potassium and carbonate of soda, or in some other way; also heat some of the original substance with carbonate of soda in the inner flame of the blowpipe (§ 132, 12 and 13). If the solution contained arsenious acid, the yellow precipitate comes down immediately the sulphuretted hydrogen is added; if arsenic acid, it is not formed until the solution has been heated or has stood for some time. For further information respecting the means of distinguishing between the two acids see § 134, 11.

γ. The precipitate is orange-coloured; it consists of sulphide of antimony, and indicates antimony. To confirm this, the original solution is tested with zinc in a platinum capsule (§ 131, 9), and examined according to § 134, 10, to ascertain which oxide of antimony is present. 53

δ. The precipitate is dark-brown; it consists of stannous sulphide, and indicates stannous oxide. As a confirmatory test, add some mercuric chloride to a portion of the original solution (§ 129, 8). 54

ε. The precipitate is brownish-black or black. It may consist of sulphide of lead, sulphide of copper, sulphide of bismuth, sulphide of gold, sulphide of platinum, or sulphide of mercury. To distinguish between these different sulphides, the following experiments are made with the original solution. 55

aa. Dilute sulphuric acid is added to a portion; a white precipitate indicates lead. Use chromate of potassa as a confirmatory test (§ 117, 9).

bb. Solution of soda or potash is added to a portion; a yellow precipitate indicates mercuric oxide. Confirm by protochloride of tin, and copper (§ 119, 6 and 9).

The presence of mercuric oxide can usually be detected, inasmuch as the precipitate produced on adding the sulphuretted hydrogen water is not black until excess of the reagent has been added; the precipitate is white at first, but changes successively to yellow, orange, and finally to black as the precipitant is gradually added (§ 119, 3). With *very* *acid* solutions, the reaction with potassa or soda is not effective (§ 119, 4).

cc. Ammonia in excess is added to a portion; if a bluish precipitate is formed which re-dissolves in excess of the precipitant to an azure-blue colour, or even if the ammonia simply colours the solution azure-blue, this indicates copper. Confirm with ferrocyanide of potassium (§ 120, 9).

dd. If the precipitate produced by ammonia is white, and excess of ammonia fails to re-dissolve it, the precipitate is collected on a filter, washed, and a portion of it dissolved on a watch-glass in 1 or 2 drops of hydrochloric acid, with addition of 2 drops of water, and more water added. If the solution turns milky, this is caused by basic chloride of bismuth, indicating bismuth. Confirm by testing some of the original solution with a solution of stannous chloride in soda (§ 121, 10).

ee. Solution of ferrous sulphate is added to a portion. A fine black precipitate indicates gold. Confirm by heating the precipitate before the blowpipe, or test the original solution with stannous chloride (§ 126, 7).

ff. Chloride of potassium and alcohol are added to a portion; a yellow crystalline precipitate indicates platinum. Confirm by igniting the precipitate (§ 127, 6).

3. Chloride of ammonium[*] is added to a small portion of the original solution, then ammonia to alkaline reaction, and, lastly, no matter whether the ammonia has produced a precipitate or not, a little sulphide of ammonium; if no precipitate separates in the cold, the solution is warmed gently. **56**

a. No precipitate is formed; pass on to **62**; for iron, cobalt, nickel, manganese, zinc, chromium, alumina, and silicic acid are not present.[†]

b. A precipitate is formed.

α. The precipitate is black; ferrous oxide,[‡] nickel, or cobalt. A portion of the original solution is mixed with some potassa or soda. **57**

aa. A dirty greenish-white precipitate is formed, which soon changes to a reddish-brown on exposure to the air; ferrous oxide. Confirm with ferricyanide of potassium (§ 110, 8).

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[*] The chloride of ammonium is used for the purpose of preventing the precipitation by ammonia of any magnesia which may be present.

[†] With regard to alumina and many of these metals, the above does not hold good in the presence of organic matter, especially of non-volatile organic acids, as these may interfere with or prevent the precipitation, not only of alumina and oxide of chromium, but also of manganese (§ 107, 5). If, therefore, the original substance contains organic matter, and if the preliminary examination pointed to one of the metals of the third or fourth group, a portion of the original substance must be fused with carbonate and nitrate of soda, the melt soaked in water, warmed with hydrochloric acid, filtered, and the filtrate tested according to **56**.

[‡] Ferric oxide would have been found already in **51**.

bb. A precipitate of a light greenish tint is produced, which does not change colour, either on exposure to the air or on boiling: nickel. Confirm with ammonia, and addition of potassa or soda (§ 108, 7).

cc. A sky-blue precipitate is formed, which turns to light red on boiling, or is discoloured and becomes brownish: cobalt. Confirm by the blowpipe (§ 109, 15).

β. The precipitate is not black. 58

aa. If the precipitate is distinctly flesh-coloured it consists of sulphide of manganese, and indicates the presence of protoxide of manganese. To confirm, add soda to the original solution, or test before the blowpipe (§ 107, 6 and 13).

bb. If the precipitate is bluish-green, it consists of hydrated sesquioxide of chromium, and indicates sesquioxide of chromium. Confirm by testing the original solution with soda, and by the blowpipe (§ 102, 3 and 9).

cc. If the precipitate is white, and does not dissolve on warming with more sulphide of ammonium,* it may consist of hydrate of alumina, hydrate of silicic acid, or sulphide of zinc, and may accordingly point to alumina, oxide of zinc, or silicic acid; if the latter, it is generally contained in the original solution as an alkaline silicate. To distinguish between these three compounds, soda is cautiously added to a portion of the original solution, to see whether it produces a precipitate; more soda is then added until the precipitate first formed is re-dissolved. 59

αα. If solution of soda produces no precipitate, silicic acid must be tested for. For this purpose, a portion of the original solution is evaporated to dryness with excess of hydrochloric acid, and the residue treated with hydrochloric acid and water (§ 150, 2); this leaves the silicic acid undissolved. Determine the nature of the alkali which remains in solution according to 66. 60

ββ. If soda produces a precipitate which re-dissolves in excess, *a little* sulphuretted hydrogen water is added to a portion of this alkaline liquid (that is, so that a considerable excess of the soda remains unchanged). A white precipitate indicates zinc. Confirm by testing a portion of the original solution with ferricyanide of potassium (§ 106, 12). If sulphuretted hydrogen produces no precipitate, chloride of ammonium is added to the rest of the alkaline liquid and the mixture heated; a white precipitate insoluble in excess of chloride of ammonium indicates alumina. As a confirmatory test collect and wash this precipitate and ignite with cobalt solution before the blowpipe (§ 101, 11).

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* A white precipitate thrown down by sulphide of ammonium and soluble in excess of the latter on warming would consist of sulphur; this might be produced by the action of some compound which destroys sulphide of ammonium in alkaline solution; such as a ferricyanide.

Note to 58 and 59.

As very minute quantities of impurities may impair the distinctness of the tints exhibited by the precipitates described in 58 and 59, it is advisable, in all cases where their presence is suspected, to adopt the following method for the detection of manganese, chromium, zinc, alumina, and silicic acid.

Solution of soda is added to a portion of the original solution, first in small quantity, then in excess.

aa. No precipitate is formed: this indicates silicic acid; proceed as directed in 60. 61

bb. A whitish precipitate is formed, which does not re-dissolve in an excess of the precipitant, and speedily turns blackish-brown on exposure to the air: manganese. Confirm by the blowpipe (§ 107, 13).

cc. A precipitate is formed, which re-dissolves in excess of the precipitant: sesquioxide of chromium, alumina, oxide of zinc.

αα. To a portion of the alkaline solution add *a little* sulphuretted hydrogen water (that is, so that a considerable excess of the soda may remain unchanged); a white precipitate indicates zinc. As a confirmatory test, precipitate a portion of the original solution with carbonate of soda, collect and wash the precipitate, and heat it before the blowpipe with nitrate of cobalt (§ 106, 8 and 14).

ββ. If the original solution is green or violet, or the alkaline solution is green, and if the precipitate produced by soda and re-dissolved by excess is of a bluish colour, sesquioxide of chromium is present. As confirmatory tests, boil the alkaline solution, or try the reaction before the blowpipe (§ 102, 3 and 9).

γγ. Chloride of ammonium is added to the alkaline solution and the mixture heated. A white precipitate insoluble in excess of chloride of ammonium indicates alumina. Confirm by collecting and washing the precipitate and heating it with cobalt solution before the blowpipe (§ 101, 11).

4. Chloride of ammonium, and carbonate of ammonia mixed with some ammonia, is added to a portion of the original solution, and the whole gently heated. 62

a. No precipitate is formed: absence of baryta, strontia, and lime. Pass on to 64.

b. A precipitate is formed: presence of baryta strontia, or lime. The precipitate is collected, washed, dissolved in dilute hydrochloric acid, the solution evaporated to dryness, and the residue warmed with water and filtered; to a portion of this solution, an equal volume of solution of sulphate of lime is added. 63

a. The solution does not become turbid, even after the lapse of five to fifteen minutes: lime. As a confirmatory test, a portion of the original solution is boiled with a concentrated solution of sulphate of ammonia, the solution filtered, and oxalate of ammonia added (§ 97, 3 and 5).

β. The solution becomes turbid, but only after the lapse of some time: strontia. A portion of the original solution is evaporated to dryness after the addition of hydrochloric acid, and the residue tested by the flame coloration (§ 96, 7 or 8).

γ. A precipitate is immediately formed: baryta. As confirmatory tests use hydrofluosilicic acid or dichromate of potassa (§ 95, 6 and 9).

5. Phosphate of soda is added to that portion of the solution in which chloride of ammonium and carbonate of ammonia failed to produce a precipitate (**62**), some more ammonia is then added, and the sides of the vessel are rubbed gently with a glass rod. **64**

a. No precipitate is formed: absence of magnesia. Pass on to **65**.

b. A crystalline precipitate is formed: magnesia.

6. A drop of the original solution is evaporated on perfectly clean platinum-foil as slowly as possible, and the residue gently ignited. **65**

a. There is no fixed residue: ammonia. The original solution is tested by adding to it hydrate of lime, and observing the odour and reaction of the escaping gas, and the fumes which it forms with acetic acid (§ 91, 3).

b. There is a fixed residue left: potassa or soda. Chloride of platinum is added to a portion of the original solution (which if alkaline must first be neutralized with hydrochloric acid, and if dilute must be concentrated by evaporation to a small bulk), and the mixture shaken or rubbed with a glass rod. **66**

a. No precipitate is formed even after ten or fifteen minutes: soda. Confirm with the flame coloration or with antimonate of potassa (§ 90, 2 and 3).

β. A yellow crystalline precipitate is formed: potassa. Confirm with tartaric acid or the flame coloration (§ 89, 4 and 5).

SIMPLE COMPOUNDS.

A. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF THE ACID.

I. Detection of Inorganic Acids.

§ 183.

In the first place, it is necessary to consider which of the inorganic acids form soluble compounds with the detected base (comp. Appendix IV.), and this must be borne in mind in the subsequent operations, due regard being given also to the results of the preliminary examination.

1. Arsenious acid and arsenic acid have already been found in the detection of the base. They are distinguished from each other by their reactions with nitrate of silver, or with potassa and sulphate of copper (see § 134, 11). **67**

2. The presence of carbonic acid in combination with bases, sulphur in combination with metals, and chromic acid and hydroferricyanic acid, have also been indicated already in the detection of the base. The first two are detected by their effervescing on the addition of hydrochloric acid; the escaping gases may be distinguished from one another by their odour. The presence of carbonic acid may be confirmed by lime water (see § 149, 5) and that of sulphuretted hydrogen by acetate of lead (§ 156, 4). Free carbonic acid and free sulphuretted hydrogen in aqueous solution may also be detected by the same reagents. The presence of chromic acid or hydroferricyanic acid is invariably indicated by the yellow or red tint of the original solution, as well as by the change of the red or yellow to a green, and the separation of sulphur, on adding sulphuretted hydrogen water. As confirmatory tests for chromic acid, use acetate of lead and nitrate of silver (§ 138, 7 and 8), and for hydroferricyanic acid use ferrous sulphate (§ 155, Appendix). **68**

3. A portion of the solution, diluted if necessary, is acidified with hydrochloric acid, or—if oxide of silver or mercurous oxide has been found—with nitric acid, and chloride of barium or nitrate of baryta added as the case may be.* **69**

a. The liquid remains clear: absence of sulphuric acid. Pass on to **70**.

b. A precipitate is produced as a fine white powder: sulphuric acid. The precipitate should not dissolve even when more dilute hydrochloric or nitric acid is added.

4. Chloride of calcium solution diluted with 4 to 5 volumes of **70**

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* Should a gelatinous precipitate of silicic acid form on adding the hydrochloric acid, the experiment is repeated after having diluted the solution considerably. In this case, it is also best to add the acid all at once and not gradually; compare § 150, 2.

water is added to another portion of the solution (which, if it has an acid reaction, must first be neutralized or made slightly alkaline by ammonia, and, if necessary, filtered).

a. There is no precipitate: absence of phosphoric acid, silicic acid, oxalic acid, fluorine, and boric acid (in large quantity). Pass on to **73**.

b. A precipitate is formed. Acetic acid is added in excess. 71

α. *The precipitate dissolves readily:* phosphoric acid or boric acid. To a portion of the original solution, chloride of ammonium, sulphate of magnesia, and ammonia are added; a crystalline precipitate shows the presence of phosphoric acid (§ 142, 7). Boric acid should be tested for as in **76**.

β. *The precipitate remains undissolved,* and after adding the acetic acid the liquid appears milk-white; the precipitate is pulverulent: oxalic acid. As a confirmatory test, treat the original substance with binoxide of manganese and sulphuric acid (§ 145, 7). 72

γ. *It dissolves with difficulty, and often incompletely; the undissolved flocculent matter is transparent:* silicic acid or fluorine. A portion of the original solution is acidified with hydrochloric acid, evaporated to dryness, and the residue treated with water and a little hydrochloric acid; an insoluble residue indicates silicic acid. Fluorine is detected by applying the etching test (§ 146, 5).

5. A fresh portion of the solution is acidified with nitric acid, and solution of nitrate of silver added. 73

a. The solution remains clear. This is a proof of the absence of chlorine, bromine, iodine, ferrocyanogen, and ferricyanogen; probably also cyanogen (in simple cyanides). (Of the soluble cyanides, cyanide of mercury is not precipitated by nitrate of silver; if, therefore, mercury has been found as the base, cyanide of mercury may be present. For the manner of detecting the cyanogen in the latter see § 155, 11.) Pass on to **76**.

b. A precipitate is formed.

α. *The precipitate is orange:* ferricyanogen. Confirm with ferrous sulphate (§ 155, Appendix). 74

β. *It is white or yellowish-white.* The precipitate is treated with ammonia in excess—immediately, if the base is an alkali or an alkaline earth, after filtering and washing, if the base is an earth or the oxide of a heavy metal.

aa. The precipitate is not dissolved: iodine or ferrocyanogen. In the former case, the precipitate is pale yellow, in the latter white and gelatinous. Confirm, for iodine, with starch and nitrous acid (§ 154, 8), for ferrocyanogen, with ferric chloride (§ 155, Appendix).

75 ββ. The precipitate is dissolved: chlorine, bromine, or cyanogen. If the original substance smells of hydrocyanic acid, and the silver precipitate dissolves with some difficulty in ammonia, cyanogen is indicated. As a confirmatory test add to the original solution ferrous sulphate, ferric chloride, soda, and finally hydrochloric acid (§ 155, 6). If bromine is present the yellowish-white precipitate dissolves in ammonia with some difficulty. As a confirmatory test add chlorine water; this gives a yellow tint to the original solution: if the bromine is present only in small proportion, chloroform or bisulphide of carbon must be used in conjunction with the chlorine water (§ 153, 6). If neither bromine nor cyanogen is present the precipitate indicates chlorine. In this case, it dissolves readily in ammonia; a portion of the original substance gives off chlorine when heated with binoxide of manganese and sulphuric acid (§ 152, 6).

76 6. To a small portion of the aqueous solution, hydrochloric acid is added drop by drop, until the solution has a distinctly acid reaction; a slip of turmeric paper is then dipped into it, taken out, and dried at 100°. If the part which has been moistened by the acid solution becomes brownish-red, boric acid is present. Confirm by the flame test (§ 144, 5, 7, 8, or 9).

77 7. With regard to nitric acid and chloric acid, these are usually discovered in the preliminary examination (5). As a confirmatory test for the former, use ferrous sulphate and sulphuric acid (§ 159, 6); for the latter, treat the solid salt with concentrated sulphuric acid (§ 160, 7).

SIMPLE COMPOUNDS.

A. Substances soluble in Water.

Detection of the Acid.

II. Detection of Organic Acids.

§ 184.

In the first place, it is necessary to consider which of the organic acids form soluble compounds with the detected base (compare Appendix IV.), and this must be borne in mind in the subsequent operations, due weight being given also to the results of the preliminary examination.

78 The following course presupposes that the organic acid is present in the free state, or in combination with an alkali or an alkaline earth. If, therefore, the base found belongs to another group, it must first be removed. If the base belongs to Group II. carbonate of soda is added to the aqueous solution until the reaction is strongly alkaline, the mixture heated to boiling, and the precipitated carbonate of the alkaline earth separated by filtration; if the base belongs to Group V. or Group VI. its removal is effected by

sulphuretted hydrogen; if it belongs to Group IV. by sulphide of ammonium. After filtering off the sulphides, and removing the excess of sulphide of ammonium by acidifying with hydrochloric acid, heating, and filtrating off the sulphur, proceed to 79. If the base is alumina or sesquioxide of chromium, an attempt should be made to precipitate these substances by boiling with carbonate of soda; should this fail, as it will when the acid is non-volatile, the latter is precipitated in a fresh portion of the solution with neutral acetate of lead, the precipitate washed, diffused through water, and decomposed by sulphuretted hydrogen; the sulphide of lead is removed by filtration, and the filtrate treated as directed below. Alumina may also be precipitated from its compounds with non-volatile organic acids by solution of soluble glass, as silicate of alumina. To separate acetic or formic acid from bases which interfere with their detection, the salt may also be distilled with dilute sulphuric acid.

1. If the aqueous solution is alkaline, hydrochloric acid must be **79** added until it has an acid reaction. (If carbonic acid is evolved in this reaction, it must be driven off by heating the solution.) Ammonia is now added to the acid or neutral solution until it has a slightly alkaline reaction, then chloride of ammonium and chloride of calcium in sufficient quantity.

a. There is no precipitate, even after shaking the liquid and after the lapse of some time:* absence of oxalic acid and tartaric acid. Pass on to **80**.

b. A precipitate is formed.

α. The precipitate takes some time to form and is crystalline: tartaric acid. Confirm by testing the behaviour of the washed precipitate with soda or with ammonia and nitrate of silver, or by testing the aqueous solution with acetate of potassa and acetic acid (§ 163, 5, 8, and 4).

β. The precipitate forms immediately and is finely pulverulent: oxalic acid. As a confirmatory test acidify a fresh portion of the aqueous solution with acetic acid and add solution of sulphate of lime (§ 145, 5).

2. The solution 1, *a*, is heated to boiling, kept at that tempera- **80** ture for some time, and some more ammonia added to the boiling liquid.

a. It remains clear: absence of citric acid. Pass on to **81**.

b. It becomes turbid, and deposits a precipitate: citric acid.† Confirm by preparing the lead salt, washing it, and testing its behaviour with ammonia, in which it readily

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* It is advisable to gently rub the sides of the vessel with a glass rod, as otherwise the crystalline precipitate of tartrate of lime may not separate for a long time. -[Editor.]

† If the ammonia contains carbonic acid, a precipitate of carbonate of lime may form here. Such a precipitate may be readily distinguished from citrate of lime by means of hydrochloric acid.

dissolves; or preferably by preparing the characteristic baryta salt and examining it with the microscope (§ 164, 6 and 5).

3. The solution 2, *a*, is mixed with 2 volumes of alcohol. **81**

a. It remains clear even after long standing: absence of malic and succinic acids. Pass on to **82**.

b. A precipitate is formed: malic or succinic acid. A portion of the solution prepared according to **78** is rendered *quite neutral* (if not already so) by ammonia or hydrochloric acid, and ferric chloride added. If a pale brownish-red precipitate is produced, it indicates the presence of succinic acid; if the solution remains clear, malic acid is present. As a confirmatory test the lead salt of the acid is prepared, and its properties examined. (Compare § 165, 5, and § 168, 5.)

4. A portion of the original solution is carefully neutralized (if not already so) with ammonia or hydrochloric acid, and ferric chloride is added. **82**

a. A reddish-yellow bulky precipitate is formed: benzoic acid. Confirm by treating the original dry substance with hydrochloric acid (§ 169, 2).

b. A deep violet colour is produced: salicylic acid.

c. The liquid acquires a tolerably intense dark red tint, and, on boiling, a light reddish-brown precipitate separates: acetic acid or formic acid. A portion of the original solid substance is warmed with sulphuric acid and alcohol (§ 172, 7). If the substance is in solution, it must be evaporated to dryness, after it has been neutralized with soda in case it is acid, and the residue tested. The odour of acetic ether indicates acetic acid.

If acetic acid is not present, the acid will be formic acid: confirm with nitrate of silver and chloride of mercury (§ 173, 4 and 6).

SIMPLE COMPOUNDS.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

Detection of the Base.[*]

§ 185.

A portion of the solution in hydrochloric acid, nitric acid, or nitro-hydrochloric acid is diluted with water,[†] and if the solvent was nitric acid, examined for oxide of silver, mercurous oxide, and large quantities of lead, by adding hydrochloric acid to the liquid: comp. **46** to **49**. **83**

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[*] Certain *salts* of the alkaline earths are included in this section, as the course of examination leads directly to their detection.

[†] If the solution becomes white and turbid on the addition of water, or deposits a white precipitate, this indicates antimony or bismuth (possibly also tin); compare § 121, 9, and § 131, 4. The solution is heated with hydrochloric acid until it has become clear again, then pass to **50**.

If the original substance was dissolved in hydrochloric acid or nitro-hydrochloric acid, or if hydrochloric acid produces no precipitate, a portion of the solution is tested for the metals of the *second division of the fifth group*, the metals of the *sixth group* and *ferric oxide* by adding to it some sulphuretted hydrogen water: see 50 to 55. If the bases of the fifth and sixth groups and ferric oxide are absent, pass on to 84.

It is to be noted here that hydrochloric acid when used as a solvent does not usually alter the state of oxidation of the base present, whilst nitric acid and nitro-hydrochloric acid generally have the effect of raising it to a higher state of oxidation either partly or completely. Hence when mercuric oxide, stannic oxide, or ferric oxide is found, and nitric or nitro-hydrochloric acid has been used as the solvent, the original substance must be examined specially to ascertain in what state the metal was present in it, if this is not already known from its behaviour towards the solvents employed. Very often, in the case of mercury salts for instance, treatment with potassa or soda would decide which of the oxides was present, as this reagent throws down yellow mercuric oxide from the salts of the oxide, and the black mercurous oxide from the mercurous salts, whilst the acid unites with the alkali and can be easily detected by examining the filtrate.

2. A small portion of the solution is rendered slightly alkaline with ammonia, and then, whether a precipitate is formed or not, ammonium sulphide is added, and the whole gently warmed. 84

a. No precipitate is formed either by the ammonia or by the ammonium sulphide.

Absence of metallic oxides of the third* and fourth groups, as also of large quantities of the salts of the alkaline earths mentioned in 85.† A small quantity of the acid solution is neutralized with ammonia and examined for the alkaline earths according to 62 to 65.

b. A precipitate is formed.

α. A *black* precipitate indicates ferrous oxide, nickel, or cobalt, detected as in 57.

β. A *flesh-coloured* precipitate: oxide of manganese. Confirm according to 58, *aa.*

γ. A *bluish-green* precipitate indicates oxide of chromium, and perhaps also phosphate of chromium. Confirm with regard to the chromium by 58, *bb.* In order to ascertain whether the chromium is combined with phosphoric acid, the original hydrochloric acid solution must be evaporated almost to dryness with nitric acid and tested with ammonium molybdate (§ 142, 10).

δ. A *white* precipitate. This may be sulphide of zinc. 85
If this precipitate is produced by ammonia alone, it may also

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[*] The note † on page 275 indicates that as far as aluminium and chromium oxides are concerned, this conclusion is true only under certain conditions.

[†] If small quantities of one of these salts, as for instance calcium borate, is dissolved in a large excess of hydrochloric acid, and excess of ammonia then added, it will be retained in solution by the ammonium chloride which is formed.

be alumina, hydrate of silicic acid, or if the substance is insoluble in water but dissolves in hydrochloric acid; for in that case a white precipitate produced by ammonia, in presence of chloride of ammonium, may consist also of a phosphate, borate, oxalate, or silicate of an alkaline earth or a fluoride of their metals, since all these are insoluble in water, but dissolve in hydrochloric acid, and (being only sparingly soluble in chloride of ammonium) are precipitated again on neutralizing the acid. If organic substances are present, the precipitate may also be a compound of tartaric acid or citric acid with certain of the alkaline earths.

The following is the method of discriminating between these different compounds:—

aa. If the preliminary examination gave indications of the presence of silicic acid (**20**), a portion of the hydrochloric acid solution is evaporated to dryness, the residue moistened with hydrochloric acid, and water added. If silicic acid be present, it will remain undissolved. The base is determined in the solution as directed in **56** or **62**, as the case may be. **86**

bb. To a portion of the original hydrochloric acid solution, potassa or soda is added until it has an alkaline reaction, then more of the alkali to see whether the precipitate produced is soluble in excess of the reagent.

αα. No permanent precipitate is formed. The clear alkaline liquid is divided into two parts; to the one half chloride of ammonium is added, and to the other half some sulphuretted hydrogen water. The formation of a precipitate with chloride of ammonium insoluble in excess indicates alumina; a precipitate with sulphuretted hydrogen indicates zinc. To ascertain whether the aluminia is present as phosphate it must be examined as directed in **84**, *b*, *γ*. **87**

ββ. A permanent precipitate is formed; presence of a salt of an alkaline earth.

1. In order to test for phosphoric acid and the alkaline earth combined with it, ammonia is added to a portion of the hydrochloric acid solution until a precipitate forms; then acetic acid drop by drop until this is re-dissolved; and lastly, acetate of soda and a drop of ferric chloride; the formation of a white flocculent precipitate indicates phosphoric acid. More ferric chloride is now added until the mixture is distinctly red, when it is boiled, filtered boiling hot, and (after the iron which may have been dissolved has been removed by ammonia) the filtrate, now free from phosphoric acid, is tested as directed in **63** for the alkaline earth with which the phosphoric acid was combined. **88**

2. To test for *oxalic acid*, ammonia must be added

to a portion of the original hydrochloric acid solution until the greater part of the free acid is neutralized, then to the clear solution chloride of calcium and acetate of soda; a white precipitate indicates oxalic acid. Some of the original substance, also, is put on a watch-glass, with a few drops of water and some binoxide of manganese free from carbonates; some concentrated sulphuric acid is then added (§ 145, 7); evolution of carbonic acid indicates oxalic acid. To find the base, a fresh sample is ignited, the residue dissolved in dilute hydrochloric acid, and the solution examined as directed in 63.

89 3. Boric acid is detected in the weak hydrochloric acid solution by turmeric-paper (§ 144, 6), and the base combined with it, by boiling a portion of the original substance with water and carbonate of soda, filtering, washing, dissolving the carbonate formed in the least possible amount of dilute hydrochloric acid and treating the solution according to 63.

4. Fluorine is tested for by heating a portion of the original substance, or of the precipitate produced in the hydrochloric acid solution by ammonia, with sulphuric acid (§ 146, 5). After the fluorine has been removed, the nature of the alkaline earth (which is in the residue, in combination with sulphuric acid) may be ascertained by treating it with hydrochloric acid, and testing it as described in 62 for lime, and in 64 for magnesia. If neither of these is present, the residue insoluble in hydrochloric acid is tested for baryta and strontia as in § 188.

5. Tartaric acid or citric acid could only be present if the substance carbonized when ignited in the glass tube. In that case, the base combined with it is tested for by boiling some of the original substance with a solution of carbonate of soda and filtering. The alkaline earth is then left on the filter as carbonate, whilst the acid passes into solution as soda salt. The precipitate is examined as directed in 63, and the solution according to 79 and 80.

SIMPLE COMPOUNDS.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

DETECTION OF THE ACID.

I. Detection of Inorganic Acids.

§ 186.

90 1. Chloric acid cannot be present, as all chlorates are soluble in water; nitric acid, which may be present in the form of a basic salt, would have been already detected during the ignition of

the substance in a glass tube, and cyanogen also (8). For the analysis of the cyanides insoluble in water see § 204. The test with microcosmic salt will have directed attention to the presence of silicic acid; this may be confirmed by evaporating the hydrochloric acid solution to dryness, and treating the residue with hydrochloric acid and water.

91 2. Arsenious and arsenic acid,* carbonic acid, chromic acid and sulphur in the form of metallic sulphides, would have been already detected in the preliminary examination, in the process of solution, or in the examination for the base. Chromic acid would have been indicated by the yellow or red colour of the substance, by the evolution of chlorine on boiling it with hydrochloric acid and by the subsequent detection of sesquioxide of chromium in the solution. This is confirmed by fusing with carbonate of soda (§ 138, 10).

92 3. A portion of the substance is boiled with nitric acid.

a. If nitric oxide is evolved, and sulphur separates, this establishes the presence of a metallic sulphide.

b. If violet vapours escape, the compound is a metallic iodide.†

c. If reddish-brown fumes of a chlorinous odour are evolved, the compound is a metallic bromide; † in this case the fumes will colour starch yellow (§ 153, 8).

93 4. A small portion of the nitric acid solution—or of the filtrate of this solution, should the nitric acid have left a residue—is diluted, and nitrate of silver added. A white precipitate, which, after washing, is soluble in ammonia, and fuses without decomposition when heated, indicates chlorine.†

94 5. A portion of the substance is boiled with hydrochloric acid, filtered if necessary, diluted with water, and chloride of barium added. A white precipitate, which does not re-dissolve even on adding a large quantity of water, indicates sulphuric acid.

95 6. Boric acid is tested for as directed in § 144, 6 or 8.

7. If none of the acids above enumerated (1 to 6) are present, there is reason to suspect the presence of phosphoric acid, oxalic acid, or fluorine, or the total absence of acids. In most cases, the presence of oxalic acid will have been already noted in the course of the preliminary examination (8). Phosphoric acid will have been found already if combined with an alkaline earth, alumina, or chromium; fluorine if in combination with an alkaline earth, and also oxalic acid, if combined with baryta, strontia, or lime, 84 to 90. It is unnecessary, therefore, to test for them here unless some other base has been found. For that purpose, the base, if belonging to Group V. or VI., is precipitated with sulphuretted

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* Their behaviour with sulphuretted hydrogen is the best means of distinguishing between arsenious and arsenic acids in compounds insoluble in water but soluble in hydrochloric acid, § 134, 11.

† Sometimes it is more convenient, as for instance in the case of mercurous iodide, bromide, and chloride, to test for the halogen by boiling the substance with soda, filtering, and testing the filtrate according to 73.

hydrogen, or if belonging to Group IV., with sulphide of ammonium, and the solution filtered. If sulphide of ammonium has been used as the precipitant, hydrochloric acid is added to the filtrate to acid reaction, the sulphuretted hydrogen is expelled by boiling in either case, and the solution filtered if necessary. A portion of this solution is tested for phosphoric acid, oxalic acid, and fluorine, as directed in 70 to 73. If the base is alumina, sesquioxide of chromium, or magnesia, oxalic acid is tested for with binoxide of manganese and sulphuric acid (§ 145, 7); fluorine with sulphuric acid (§ 146, 5).

SIMPLE COMPOUNDS.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN ACIDS.

DETECTION OF THE ACID.

II. Detection of Organic Acids.

§ 187.

1. Formic acid cannot be present, as all the formates are soluble in water. 96

2. Acetic acid has been detected already in the preliminary examination, by the evolution of acetone. Confirm with sulphuric acid and alcohol (§ 171, 7).

3. Benzoic acid or salicylic acid are usually detected by their separating when the substance is dissolved in hydrochloric acid, or when the hydrochloric solution cools. As a confirmatory test, collect the precipitate, wash it with a small quantity of water, dissolve it in a little dilute ammonia, and test the neutral solution with ferric chloride as directed in § 169, 3, and § 170, 3.

4. A portion of the substance is boiled for some time with solution of carbonate of soda in excess, and filtered hot; in most cases, the organic acid passes into solution as a soda salt. The solution is slightly acidified with hydrochloric acid, the carbonic acid expelled by heat, and then tested as directed § 184. With bases of the fourth group, and also in presence of oxide of lead, the separation is incomplete. In exceptional cases of the kind, after boiling with carbonate of soda, sulphide of ammonium should be added to the filtrate until the whole of the metallic oxide is thrown down; it is then filtered and examined as above. 97

SIMPLE COMPOUNDS.

C. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, AND NITRO-HYDROCHLORIC ACID.

DETECTION OF THE BASE AND THE ACID.

§ 188.

Under this head we have to consider the following substances as the only ones likely to be met with—viz., sulphate of baryta, sulphate of strontia, sulphate of lime, fluoride of 98 calcium, silica, strongly ignited or native alumina, sulphate of lead, compounds of lead with chlorine and bromine; compounds of silver with chlorine, bromine, iodine, and cyanogen; ignited or native binoxide of tin, ignited sesquioxide of chromium, and lastly sulphur and carbon. For the simple silicates, the student is referred to § 205, for the ferrocyanides and ferricyanides to § 204. The preliminary examination will have shown whether the presence of these compounds is to be suspected.

Sulphate of lime and chloride of lead are not altogether insoluble in water, and sulphate of lead may be dissolved in hydrochloric acid. However, as these compounds are so sparingly soluble that they are but seldom completely dissolved, they are included here to ensure their detection, should they have been overlooked in the examination of the aqueous or acid solution.

1. Free sulphur will have been detected already in the preliminary examination.

2. Carbon is generally black; it is insoluble in aqua regia; heated on platinum foil, before the blowpipe, it is consumed;* on deflagration with nitrate of potassa, it yields carbonate of potassa.

3. Sesquioxide of chromium is green or blackish-green, and will have been already detected in the microcosmic bead (18).

4. Sulphide of ammonium is poured on to a very small quantity of the substance. 99

a. It turns black; this indicates the presence of a salt of lead or silver.

α. *The compound fuses in the glass tube without decomposition* (3): chloride or bromide of lead; chloride, bromide, or iodide of silver. One part of the compound is fused with 4 parts of carbonate of soda and potassa in a small porcelain crucible, allowed to cool, the residue boiled with water, and the filtrate tested for chlorine, bromine, and iodine, as directed in 73. The residue, which consists either of metallic silver or oxide of lead, is dissolved in nitric acid, and the solution tested as directed in 46.

β. *It evolves cyanogen when ignited in the glass tube, and leaves a residue of metallic silver:* cyanide of silver.

γ. *The substance remains unaltered on ignition in the glass tube:* sulphate of lead. A sample of it is boiled with solution of carbonate of soda, filtered, the filtrate acidified with hydrochloric acid, and the filtrate tested with chloride of barium for sulphuric acid; the washed residue is dissolved in nitric acid, and the solution tested for lead with sulphuretted hydrogen and with sulphuric acid.

b. It remains white: absence of a salt of lead or silver. 100

α. A portion is tested for stannic oxide with a borax

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* Graphite is not completely burned unless strongly heated in a current of oxygen.

bead coloured slightly blue with oxide of copper (§ 129, 12). If a reddish-brown to ruby-red colour is produced, a confirmatory test for the presence of tin is made by reducing a portion with carbonate of soda and cyanide of potassium (§ 129, 11).

β. A small portion is ground up with finely powdered quartz, the mixture placed in a small crucible moistened with a few drops of strong sulphuric acid and warmed gently on an iron plate or a small sand bath (if heated directly by the lamp an incorrect inference may be drawn).

aa. White fumes are evolved, which redden litmus, and render turbid a drop of dilute ammonia: this indicates fluoride of calcium. A portion of the substance in fine powder is decomposed in a platinum crucible with sulphuric acid, and the action of the vapour on glass tried (§ 146, 5) to confirm the presence of fluorine: the residue is boiled with hydrochloric acid, filtered, the filtrate neutralized with ammonia, and tested for lime with oxalate of ammonia.

bb. There are no fumes evolved which redden litmus, or render aqueous ammonia turbid. A portion of the very finely pulverized substance is mixed with 4 times the quantity of pure carbonate of soda and potassa, and fused in a platinum crucible (or on platinum foil). The fused mass is boiled with water, filtered if it does not dissolve entirely, and the residue washed. A portion of the filtrate is acidified with hydrochloric acid, and tested with chloride of barium for sulphuric acid; if this acid is not formed, another portion of the filtrate is tested for silicic acid, by evaporating the solution acidified with hydrochloric acid (§ 150, 2). If silicic acid is absent, the residue left on evaporating the solution is dissolved in hydrochloric acid and tested with ammonia for alumina.

If silicic acid alone were present, the mass resulting from the fusion with carbonate of soda and potassa would have dissolved in water without residue; but if silicates also happen to be present, the bases with which the silicic acid is combined will remain undissolved, and may be further examined. If alumina is present, the melt will not dissolve completely in water unless a large quantity of the flux and a high temperature have been employed.

If sulphuric acid has been found, the alkaline earth which was combined with it remains on the filter as carbonate. This is washed, dissolved in dilute hydrochloric acid, evaporated to dryness, taken up with water, and the solution tested for baryta, strontia, and lime, as directed in **63**.

COMPLEX COMPOUNDS.*

A. SUBSTANCES SOLUBLE IN WATER, AND ALSO SUCH AS ARE INSOLUBLE IN WATER, BUT DISSOLVE IN HYDROCHLORIC ACID, NITRIC ACID, OR NITRO-HYDROCHLORIC ACID.

Detection of the Bases.†

§ 189.‡

Treatment with Hydrochloric Acid: *Detection of Silver, Mercurous Oxide* [*Lead*].

The systematic course for the detection of the bases is essentially the same for compounds soluble in water, as for those which are soluble only in acids. Where the different nature of the original solution occasions a variation in the course of analysis, such variation will be distinctly stated. **101**

I. THE SUBSTANCE IS IN AQUEOUS SOLUTION.

Some hydrochloric acid is added to the portion set aside for the detection of the bases. **102**

1. The solution had an acid or neutral reaction before the hydrochloric acid was added.

a. No precipitate is formed: this indicates the absence of silver and mercurous oxide. Pass on to § 190.

b. A precipitate is formed. Some more hydrochloric acid is added, drop by drop, until the precipitate no longer increases; then 6 or 8 drops more of hydrochloric acid are added, the mixture shaken and filtered.

The precipitate produced by hydrochloric acid may consist of chloride of silver, mercurous chloride, chloride of lead, a basic salt of antimony, basic chloride of bismuth, metastannic chloride, possibly also benzoic and salicylic acid. The basic salt of antimony and the basic chloride of bismuth, however, are re-dissolved by the excess of hydrochloric acid; consequently, if the instructions given have been strictly followed, the precipitate collected upon the filter can consist only of the three first, that is, chloride of silver, mercurous chloride, and chloride of lead (possibly also of the rarely occurring metastannic chloride and benzoic and salicylic acids, which, however, are disregarded *here*).

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* This term is used to designate compounds in which all the more frequently occurring bases, acids, metals, and metalloïds are supposed to be present.

† Compare the explanations in the Third Section, with the contents of which the student should become thoroughly acquainted *before proceeding further*. Regard is here had also to the presence of the acids of arsenic, and of those salts of the alkaline earths which dissolve in hydrochloric acid, and separate again from that solution unaltered on neutralization of the acid by ammonia.

‡ Consult the remarks in the Third Section.

The precipitate is washed twice on the filter with cold water and the filtrate and washings examined according to § 190. 103

If a turbidity is produced by the washings as they mix with the acid filtrate (indicating antimony or bismuth compounds, or possibly also chloride of lead or metastannic chloride), this is disregarded, and the examination carried out according to § 190.

The precipitate collected on the filter is treated in the following manner:

a. Hot water is poured on to the precipitate upon the filter, and the filtrate is tested with sulphuretted hydrogen and with sulphuric acid for lead. (If there is no precipitate, this simply proves that the precipitate produced by hydrochloric acid contains no lead, and does not by any means establish the total absence of this metal, as hydrochloric acid does not throw down lead from dilute solutions.) If the hydrochloric acid precipitate contains chloride of lead, wash it several times with hot water to dissolve out the lead as far as possible.

β. If there is a residue on the filter, it is treated with ammonia. If this changes its colour to black or gray, mercurous oxide is present.

γ. Nitric acid is added to the ammoniacal fluid running off in *β* until it has a strongly acid reaction. The formation of a white, curdy precipitate indicates the presence of silver; if, however, the quantity of silver is but very small, the solution becomes opalescent merely. (If the precipitate still contained lead, the ammoniacal solution generally appears turbid, owing to the separation of a basic lead salt. This, however, does not interfere with the testing for silver, since the basic salt of lead re-dissolves on the addition of nitric acid.)

2. The original aqueous solution has an alkaline reaction. 104

a. The addition of hydrochloric acid to strongly acid reaction does not cause any evolution of gas or produce a precipitate, or the precipitate which forms at first re-dissolves on adding more hydrochloric acid: pass on to § 190.

b. The addition of hydrochloric acid produces a precipitate which does not re-dissolve in excess of the precipitant, even on boiling.

a. The formation of the precipitate is attended neither with evolution of sulphuretted hydrogen nor of hydrocyanic acid. The precipitate is collected and the filtrate treated as directed in § 190. 105

aa. The precipitate is white. It may, in that case, consist of a salt of lead or silver, insoluble or sparingly soluble in water and hydrochloric acid (chloride of lead, sulphate of lead, chloride of silver, &c.), or it may be hydrate of silicic acid. It is tested for the bases and acids of these compounds as directed in § 203, bearing in mind that the chloride of lead or chloride of silver thrown down may possibly have been formed in the process.

bb. The precipitate is yellow or orange. In that case, it may consist of sulphide of arsenic, if it was not boiled for long, or only with very dilute hydrochloric acid, also of sulphide of antimony, or stannic sulphide, which were originally dissolved in ammonia, potassa, soda, phosphate of soda, or some other alkaline liquid (with the exception of alkaline sulphides and cyanides). The precipitate, which may also contain hydrate of silicic acid, is examined as directed in **40**.

*β. The formation of the precipitate is attended with evolution of sulphuretted hydrogen, but not of hydrocyanic acid.** **106**

aa. The precipitate is pure white, and consists of separated sulphur. In that case a sulphuretted alkaline sulphide is generally present; its presence may be detected also by the yellow or brownish-yellow colour of the alkaline solution, and the odour of persulphide of hydrogen, which accompanies that of the sulphuretted hydrogen on the addition of an acid. The filtrate is boiled, filtered, and treated as directed in § 194, the precipitate according to § 203.

bb. The precipitate is coloured. In that case it may be concluded that a metallic sulphur salt is present, that is, a combination of an alkaline sulphur base with a metallic sulphur acid. The precipitate may consist of tersulphide of gold, bisulphide of platinum, stannic sulphide, sulphide of arsenic, or sulphide of antimony. It may, however, also be sulphide of mercury or sulphide of copper or sulphide of nickel, or contain these substances, as the former dissolves readily in sulphide of potassium, and in small quantities in sulphide of ammonium, and the last two are slightly soluble in sulphide of ammonium. The solution is filtered, and the filtrate treated as directed in § 194, the precipitate according to **40**.

γ. The formation of the precipitate is attended with evolution of hydrocyanic acid, with or without sulphuretted hydrogen. This indicates the presence of an alkaline cyanide, and, if sulphuretted hydrogen is simultaneously **107**

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* Should the odour of the evolved gas leave any doubt as to whether hydrocyanic acid is actually present or not, some chromate of potassa should be added to a fresh portion of the solution before adding the hydrochloric acid.

evolved, also of an alkaline sulphide; in that case, the precipitate may contain many other substances (such as cyanide of nickel, cyanide of silver, &c.), besides the compounds enumerated in *a* and *β*. More hydrochloric acid, or nitric acid is added, and the liquid boiled until the whole of the hydrocyanic acid is expelled; the solution, or, if an undissolved residue has been left, the filtrate, is treated as directed in § 190; and the residue (if any) according to § 203 or § 204.

c. No permanent precipitate is produced on adding hydrochloric acid, but there is an evolution of gas. **108**

a. The gas smells of sulphuretted hydrogen: this indicates a simple alkaline sulphide, or sulphur salt with alkaline or alkaline earthy base. Proceed as directed in § 194.

β. The gas is inodorous: in that case it is carbonic acid which was in combination with an alkali. Pass on to § 190.

γ. The gas smells of hydrocyanic acid (no matter whether sulphuretted hydrogen or carbonic acid is evolved at the same time or not). This indicates an alkaline cyanide. Boil until the whole of the hydrocyanic acid is expelled, then pass on to § 190.

II. Solution in Hydrochloric Acid or in Nitro-hydrochloric Acid.

Proceed as directed in § 190.

III. Solution in Nitric Acid.

A small portion is diluted; if this produces turbidity or a precipitate (indicative of bismuth), nitric acid is added until the solution is clear again, then hydrochloric acid. **109**

1. No precipitate is formed. Absence of silver and mercurous oxide. The principal solution is treated according to § 190.

2. A precipitate is formed. A larger portion of the nitric acid solution is treated in the same way, filtered, and the precipitate examined as directed in **103**, the filtrate according to § 190.

§ 190.*

Treatment with Sulphuretted Hydrogen.† *Precipitation of the Metallic Oxides of Group V., Division 2, and Group VI.*

Sulphuretted hydrogen water is added to a *small portion* of the clear acid solution, until the odour of the gas is distinctly perceptible after shaking the mixture; it is then warmed gently.

1. No precipitate is formed, even after the lapse of some time. Pass on to § 194, as lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, and arsenic,‡ are not present;‖ the absence of ferric oxide and of chromic acid, and of hydroferricyanic acid is also indicated by this negative reaction. **110**

2. A precipitate is formed.

a. The precipitate is pure white, light, and finely pulverulent, and does not re-dissolve on addition of hydrochloric acid. It consists of separated sulphur, and indicates the presence of ferric oxide.¶ None of the other metals enumerated in **110** can be present. The principal solution is treated as directed in § 194. **111**

If the separation of sulphur, the colour of the original solution, and the change of colour produced by sulphuretted hydrogen give reason to suspect the presence of chromic acid, the latter should be reduced to oxide of chromium by adding an aqueous solution of sulphurous acid, or—if this is likely to produce a precipitate—by heating it with hydrochloric acid and alcohol (see § 138, 5).

b. The precipitate is coloured.

To the greater portion of the acid or acidified solution, best in a small flask, sulphuretted hydrogen water is added in excess, that is to say, until the solution smells distinctly of it after shaking, and the precipitate does not increase on add- **112**

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[*] Consult the remarks in the Third Section.

[†] For details of other analytical methods in which hyposulphite of ammonia or soda is employed instead of sulphuretted hydrogen, see C. Himly, Ann. Chem. Pharm., **43**, 150, H. Vohl, *ibid.*, **96**, 237, and A. Orlowski, Zeit. anal. Chem., **22**, 357.

[‡] To be certain of the absence of arsenic acid, the solution must be allowed to stand for some time at a gentle heat (about 70°), or it may be heated with sulphurous acid previous to the addition of the sulphuretted hydrogen. (Compare § 133, 3.) The preliminary examination affords the best means of knowing whether this treatment is necessary.

[‖] In solutions containing much free acid, the precipitates very often do not form until a relatively large quantity of sulphuretted hydrogen water has been added.

[¶] Sulphur will also be precipitated if sulphurous acid, iodic acid, bromic acid, or nitrous acid be present (these are not included in this analytical course), and also if chromic acid, or chloric acid, or free chlorine is present; the same effect is produced by hydroferricyanic acid; if the mixture is warmed for some time with chromic acid, the reddish-yellow colour of the solution changes to green, whilst with hydroferricyanic acid the solution acquires a blue tint, so that the separated sulphur suspended in it appears as if it were a bluish precipitate.

ing more of the reagent; the mixture is gently heated, shaken vigorously for some time, filtered, and the filtrate (which contains the oxides present belonging to Groups I.—IV.) kept for further examination according to § 194; the precipitate, which contains the sulphides of the metals present belonging to Groups V. and VI.* is *carefully washed* (see p. 9).

In many cases, and more particularly where there is any reason to suspect the presence of arsenic, it is more convenient to pass a current of sulphuretted hydrogen through the solution *diluted with water*, instead of adding sulphuretted hydrogen water. When arsenic is suspected, it is also well to keep the liquid at about 70°, while the gas is being passed into it.

If the precipitate is yellow, it consists principally of **113** sulphide of arsenic, bisulphide of tin, or sulphide of cadmium; if orange-coloured, this indicates sulphide of antimony; if brown or black, one at least of the following oxides is present; oxide of lead, oxide of bismuth, oxide of copper, mercuric oxide, oxide of gold, oxide of platinum, stannous oxide. However, as a yellow precipitate may contain small particles of an orange coloured, a brown, or even a black precipitate, without its colour being very perceptibly altered, it is the safest way to assume the presence of all the metals named in **110** in any precipitate produced by sulphuretted hydrogen, and to proceed accordingly as the next paragraph (§ 191) directs.

§ 191.†

The Precipitate produced by Sulphuretted Hydrogen is treated with Sulphide of Ammonium; *Separation of Division 2 of Group V. from Group VI.*

114 A small portion of the thoroughly washed precipitate produced by sulphuretted hydrogen from the acidified solution is introduced into a test-tube,‡ a little water, and from ten to twenty drops of yellow sulphide of ammonium or sulphide of sodium added, and the mixture warmed gently for a short time.||

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* As an exception, the precipitate thrown down from the acid solution by sulphuretted hydrogen may contain zinc and iron—for instance, zinc if the acetate of an alkali is present, iron when the solution contains stannic chloride and but little free hydrochloric acid (L. Storch).

† Consult the notes in the Third Section.

‡ If there is a somewhat large precipitate, this may be readily effected by means of a small spatula of platinum, glass, or horn; but if the amount of precipitate is only very trifling, a hole should be made in the bottom of the filter, and the precipitate rinsed into the test-tube by means of the wash-bottle; the precipitate is then allowed to subside, and the water decanted.

|| If the solution contains copper, which may generally be known by the colour of the liquid, and may be ascertained with certainty by testing with a clean iron rod (see § 120, 11), sulphide of sodium should be used instead of sulphide of ammonium (in which sulphide of copper is not absolutely insoluble, see § 120, 5), and the mixture boiled. But if the solution contains mercuric oxide as well as copper (the presence of the former is generally sufficiently indicated by the several changes of colour exhibited by the precipitate formed on adding the sulphuretted hydrogen water [§ 119, 3], and which, in doubtful cases, may be detected with positive cer-

115 1. The precipitate dissolves completely in sulphide of ammonium (or sulphide of sodium, as the case may be): absence of the metals of Group V.—cadmium, lead, bismuth, copper, and mercury. The remainder of the precipitate (a portion of which has been digested with sulphide of ammonium) is treated according to § 192. If the precipitate produced by sulphuretted hydrogen was so trifling that the whole of it has been used in the treatment with sulphide of ammonium, the solution obtained in that process is precipitated by hydrochloric acid, and the precipitate filtered, washed, and treated as directed § 192.

116 2. The precipitate is not dissolved, or at least not completely, even on heating with more sulphide of ammonium (or sulphide of sodium, as the case may be): presence of metals of Group V. The liquid is diluted with 4 or 5 parts of water, filtered, and the filtrate mixed with hydrochloric acid in slight excess.

a. A pure white turbidity is produced from the separation of sulphur: absence of the metals of Group VI.—gold, platinum, tin, antimony, and arsenic.* The rest of the precipitate (of which a portion has been digested with sulphide of ammonium) is treated according to § 193.

117 *b. A coloured precipitate is formed:* presence of metals of Group VI. and of Group V. The entire precipitate produced by sulphuretted hydrogen is treated like the small portion (**114**), that is, it is digested with yellow sulphide of ammonium or sulphide of sodium, as the case may be, allowed to subside, and the supernatant liquid, which should be yellow, is poured on to a filter; the residue in the tube is digested once more with yellow sulphide of ammonium (or sulphide of sodium), and filtered. The residue† (containing the sulphides of Group

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tainty by testing a portion of the original solution with stannous chloride after it has been acidified with hydrochloric acid), sulphide of ammonium must be used, although the separation of the sulphides of the sixth group from the sulphide of copper is not fully effected in such cases. Were sulphide of sodium used, the sulphide of mercury would dissolve in this reagent, and this would render the ulterior examination of the sulphides of the sixth group more difficult. But even when this precaution is taken the dissolution of the copper cannot be always guarded against, as sulphide of copper is soluble in certain sulphur salts, such as those which sulphide of arsenic and sulphide of tin form with sulphide of sodium.

* It is self-evident that this inference becomes uncertain if the precipitate produced by sulphuretted hydrogen, instead of being digested with a small quantity of yellow sulphide of ammonium, has been treated with a large quantity of that reagent; for in that case such a large quantity of sulphur separates that any traces of sulphide of arsenic or stannic sulphide which may have been thrown down cannot be detected. Compare also notes to § 190 and § 191 in the Third Section.

If the residue suspended in the liquid containing sulphide of ammonium, and insoluble therein, subsides readily, it should not be transferred to the filter, but washed in the tube by decantation. If the subsidence proceeds slowly and with difficulty, however, the precipitate is transferred to the filter, and washed there; a hole is then made in the bottom of the filter, and the residue rinsed into a small porcelain basin by means of a wash-bottle: the application of a gentle heat will now materially aid the subsidence of the residue, and the supernatant water may then be decanted. The sulphides are occasionally suspended in the liquid in a state of such minute division that a clear filtrate cannot be obtained; in cases of the kind, some nitrate of ammonia should be added to the liquid, and it should be allowed to settle at a gentle heat for some time before filtering.

V.), is washed, and then treated as directed in § 193. The filtrate (which contains the metals of Group VI. in the form of sulphur salts) is diluted with water, hydrochloric acid added to distinctly acid reaction, and the whole gently heated; the precipitate, which contains the sulphides of the metals of Group VI. mixed with sulphur, is collected, washed thoroughly, and treated as directed in the next paragraph (§ 192).

§ 192.*

Detection of the Metals of Group VI.: *Arsenic, Antimony, Tin, Gold, Platinum.*

If the precipitate consisting of the sulphides of Group VI. is of a pure yellow colour, this indicates principally arsenic and stannic oxide; if it is distinctly orange-yellow, antimony is sure to be present; if it is brown or black, this denotes the presence of stannous oxide, platinum, or gold. **118**

Beyond these general indications the colour of the precipitate is not a safe guide. It is therefore always advisable to test a yellow precipitate also for antimony, gold, and platinum, since minute quantities of the sulphides of these metals are completely masked by a large quantity of stannic sulphide or sulphide of arsenic.

In many cases, it will be possible to determine from the general examination whether gold and platinum are present, and, as the presence of these metals renders the analysis more complicated, the method employed when gold and platinum are present will differ from that used when they are not.

1. There is no reason to believe that gold and platinum are present.

A little of the precipitate is heated on the lid of a porcelain crucible, or on a piece of porcelain or glass.†

a. There is no fixed residue: probable presence of arsenic, absence of the other metals of Group VI. As a confirmatory test, a portion of the precipitate is reduced with cyanide of potassium and carbonate of soda (§ 132, 12).‡ Whether the arsenic was present in the form of arsenious acid or of arsenic acid may be ascertained by the methods described in § 134, 11. **119**

b. There is a fixed residue. In that case tin, antimony, and arsenic must be sought for.|| The remainder of the pre- **120**

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* Consult the notes in the Third Section.

† It is self-evident that this preliminary examination may be omitted if the precipitate has any other colour than yellow; moreover, it will not give a decisive result unless the precipitate has been thoroughly washed.

‡ If the precipitate contains much free sulphur, the sulphide of arsenic which may be present is dissolved by digestion in carbonate of ammonia, the solution filtered, evaporated to dryness with addition of a small quantity of carbonate of soda, and the residue heated with cyanide of potassium and carbonate of soda.

|| The method given in *b* for the detection of tin, antimony, and arsenic is especially applicable when the tin and arsenic are present in somewhat large quantity. If the precipitate contains only a very small proportion of these, the process described in § 134, 2, is preferable.

cipitate is thoroughly dried on the filter, ground up with about 1 part of anhydrous carbonate of soda and 1 part of nitrate of soda, and the mixture transferred in small portions at a time to a porcelain crucible, in which 2 parts of nitrate of soda have been previously heated to fusion at as low a temperature as possible.* As soon as the oxidation is complete, the melt is poured on to a piece of porcelain. After cooling, the fused mass† (the portion still sticking to the inside of the crucible as well as the portion poured out on the porcelain) is treated with cold water, the insoluble residue—which will remain if the mass contained antimony or tin—collected on a wetted filter, and washed thoroughly with a mixture of about equal parts of water and alcohol. (The alcohol is added to prevent the dissolution of the antimonate of soda. The washings are not added to the filtrate.) The filtrate and the residue are examined in the following way:—

a. Examination of the filtrate for arsenic (which will be present in it in the form of arsenate of soda). The solution is acidified with nitric acid until it has a distinctly acid reaction;‡ it is then heated to expel carbonic acid and nitrous acid, and a small portion of the solution added to 2 or 3 c.c. of a solution of molybdate of ammonia in nitric acid (§ 52), the mixture being heated until it boils. If there is a yellow or yellowish precipitate (a pure white precipitate is to be disregarded), arsenic is present (§ 133, 9). **121**

To confirm this, the remainder of the liquid is divided into two portions; to the one some nitrate of silver (not too little) is added and the solution filtered if chloride of silver‖ separates; a layer of dilute solution of ammonia (1 part of ammonia solution to 2 of water) is now poured on to the surface of the filtrate down the side of the tube, which must be held in a slanting position, and the tube put on one side with-

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* Special care should be taken not to heat the mixture too strongly. If the amount of the precipitate is so minute that the operation described above cannot be conveniently performed, the filter and precipitate adhering to it, after being dried, is cut into small pieces, ground up with some carbonate and nitrate of soda, and the mixture projected into the fusing nitrate of soda. It is *preferable*, however, in such cases, to procure, if practicable, a larger amount of the precipitate, as otherwise there will be but little hope of effecting the detection of all the metals of Group VI. with certainty.

† Supposing all the metallic sulphides of the sixth group above mentioned to have been present, the fused mass would consist of antimonate and arsenate of soda, stannic oxide, metallic gold and platinum, sulphate, carbonate, nitrate, and some nitrite of soda. If the heat has been too strong, stannate of soda will have been formed. See § 134, 1. When gold and tin are present together, the fused mass often has a peculiar light red colour.

‡ In some cases where a somewhat large proportion of carbonate of soda has been used, or a very strong heat applied, a trifling precipitate (hydrated stannic oxide) may separate on acidifying the filtrate with nitric acid. This may be collected on a filter, and then treated in the same manner as the undissolved residue. It should be noted, however, that it may contain arsenic; so that arsenic present in small quantity may be overlooked if the fusion has been made at too high a temperature and tin is also present.

‖ Chloride of silver will separate if the reagents were not perfectly pure, or the precipitate has not been thoroughly washed.

out shaking. The formation of a reddish-brown precipitate, which appears hovering cloud-like between the two layers (and may be seen far more readily and distinctly by reflected than by transmitted light), denotes the presence of arsenic. If the arsenic is present in some quantity, and the free nitric acid of the solution is exactly saturated with ammonia, stirring in the meantime, the precipitate of arsenate of silver colours the whole of the liquid brownish-red.

To the other portion of the acidified solution, ammonia is 122 added, and then a mixture of sulphate of magnesia and chloride of ammonium, the sides of the vessel being rubbed with a glass rod. A crystalline precipitate of arsenate of magnesia and ammonia, which frequently does not form until after long standing, and is deposited more particularly on the sides of the vessel, shows the presence of arsenic. As a confirmatory test, the precipitate, after being washed with water containing ammonia, may be dissolved in dilute hydrochloric acid and the solution precipitated by sulphuretted hydrogen with the aid of a gentle heat, or the arsenic may be reduced to the metallic state (compare § 132 and § 133). In order to ascertain whether the arsenic was originally present in the form of arsenious acid or of arsenic acid the methods described in § 134, 11, should be employed.

β. Examination of the residue for antimony, tin, 123 gold, platinum.

As the antimony, if present, exists in the residue as white pulverulent antimonate of soda, the tin as white flocculent stannic oxide, the appearance alone of the residue sometimes indicates its nature; it must be noted, however, that a little oxide of copper may also be present in this residue, as sulphide of copper is slightly soluble in sulphide of ammonium and also in the double salts which sulphide of arsenic and sulphide of tin form with sulphide of sodium. The precipitate is transferred to the lid of a platinum crucible, or to a small platinum capsule, heated with hydrochloric acid, a little water added, and a small compact lump of pure zinc (free from lead) thrown in, no matter whether the precipitate has completely dissolved in the hydrochloric acid or not. The tin and antimony are reduced to the metallic state by the action of the zinc. The presence of antimony is detected at once, or after a short time, by the blackening of the platinum. As soon as the disengagement of hydrogen has nearly ceased, the lump of zinc is taken out, the solution of chloride of zinc removed by cautious decantation, the metals warmed with hydrochloric acid, and the solution—which, if tin is present, will contain stannous chloride—tested with mercuric chloride (§ 129, 8). The antimony which has been deposited (and also any copper present) is scarcely acted on by the warm hydrochloric acid, and may be examined before the blowpipe (§ 131, 13), or dissolved in hot nitric acid containing a little tartaric acid, and tested with sulphuretted hydrogen. If the solution contains copper, this is precipitated as sulphocyanate (§ 120, 10) before adding the sulphuretted hydrogen. In order to ascertain in what state of oxidation the tin or antimony were originally present, the methods given in § 134, 9 and 10, should be employed.

2. There is reason to suspect the presence of gold or platinum. **124**

In this case, advantage is taken of the fact that tin, antimony, and arsenic sulphides may be volatilized as chlorides by heating them with an intimate and well-dried mixture of 3 to 5 parts of ammonium chloride and 1 part of nitrate of ammonia, the gold and platinum sulphides yielding a residue of the respective metals. The operation is carefully conducted in the apparatus shown in fig. 43, which does not require explanation.

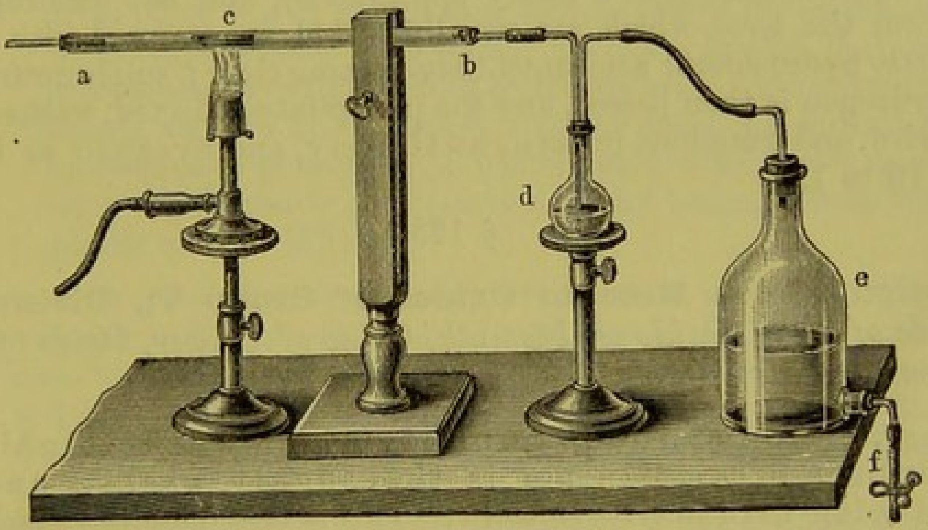

Fig. 43.

The tube *ab* is from 30 to 40 c.m. long, and about 16 m.m. in diameter. The porcelain boat *c*, into which the mixture to be examined is introduced, is similar to that shown in fig. 40 (p. 175), but should usually be somewhat longer (7 c.m. long). The boiling flask *d* holds about 150 to 180 c.c., and is half filled with water. The bottle *e*, which serves as a respirator, has a capacity of about 2 litres.

When the apparatus has been arranged, the sulphides of Group VI., or the dried precipitate containing them, is carefully ground up with about 6 parts of the mixture of chloride of ammonium and nitrate of ammonia; the whole is placed in the porcelain boat and pushed into the tube *ab*, until it occupies the position shown in the figure. A cork, through which a short, open, glass tube passes, is then inserted at *a*, the tap *f* is opened (either a glass tap or a screw pinchcock), and a moderate stream of air allowed to pass from *a* to *b*. The porcelain boat and its contents are then heated, at first gently, but afterwards gradually, up to a high temperature. A white sublimate soon begins to form close to *c* (between *c* and *b*), and gradually increases in quantity.

As soon as all the volatile compounds have been driven off from the boat, it is allowed to cool, and then removed from the tube by means of a hooked wire. If there is no residue in the boat, gold and platinum are absent; if there is a residue having a metallic appearance, the first part of the operation may be considered as completed; but if the appearance of the residue renders it probable that all the antimony, tin, or arsenic have not been completely volatilized, the operation must be repeated as before, with the addition of a further quantity of the mixture of chloride of ammonium and nitrate of ammonia. The residue and the sublimate are then tested as follows :—

> *α*. The residue. This is dissolved in aqua regia, the solution evaporated to a small bulk, and then tested for gold and platinum according to § 128.
>
> *β*. The sublimate. The tube *ab* is rinsed out with the water contained in the flask *d* (which, when antimony is present, sometimes has a milky appearance), and the washings from the tube, which are usually turbid, are warmed with a little hydrochloric acid until they become clear; sulphuretted hydrogen is then passed, and the precipitate collected, washed, dried, and examined for tin, antimony, and arsenic as in **119** to **124**.

§ 193.*

Detection of the Metallic Oxides of Group V., Division 2; *Oxide of Lead, Oxide of Bismuth, Oxide of Copper, Oxide of Cadmium, Mercuric Oxide.*

The portion of the precipitate which was insoluble in sulphide of ammonium is thoroughly washed and boiled with dilute nitric acid. This is best done in a small porcelain dish, heating the precipitate with some water, and then gradually adding nitric acid with constant stirring. Any great excess of acid must be avoided. **125**

1. The precipitate dissolves, and there remains floating in the liquid nothing but the separated, light, flocculent, yellow sulphur: this indicates the absence of mercury. Cadmium, copper, lead, and bismuth may be present. The separated sulphur is filtered off, and the filtrate treated as follows after the greater part of the nitric acid has been removed by evaporation. **126**

Dilute sulphuric acid in moderate quantity is added to a portion of the filtrate, the mixture heated gently, and allowed to stand for some time.

> *α*. No precipitate is formed: absence of lead. The remainder of the filtrate is mixed with ammonia in excess, and gently heated. **127**
>
> *a*. *There is no precipitate:* absence of bismuth. If the liquid is blue, copper is present; very minute traces of copper, however, might be overlooked if the colour of the ammoniacal liquid alone were regarded. To be quite certain, and also to test for cadmium, the ammoniacal solution **128**

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* Consult the notes in the Third Section.

is evaporated nearly to dryness, some water added, and sufficient hydrochloric acid to render the solution *very slightly* acid.

aa. A small portion of the solution is tested for copper with ferrocyanide of potassium. A reddish-brown precipitate indicates copper; if the amount is very small, there is only a light brownish-red turbidity. **129**

bb. If copper is absent, some more hydrochloric acid is added to the remainder and then sulphuretted hydrogen; a yellow precipitate indicates cadmium. If copper is present, it is most conveniently removed as cuprous sulphocyanate by means of sulphurous acid and sulphocyanate of potassium, warming the mixture, and allowing it to stand; the filtrate, after being evaporated to drive off excess of sulphurous acid, is tested for cadmium with sulphuretted hydrogen. Or both metals may be precipitated by sulphuretted hydrogen after adding hydrochloric acid to the solution and the sulphides separated by cyanide of potassium (in which case the sulphides must have been recently precipitated), or by boiling dilute sulphuric acid (§ 123).* **130**

β. A precipitate is formed: bismuth is present.† The solution is filtered and the filtrate tested for copper and cadmium (zinc may also be possibly present) as directed in **128**. The washed precipitate is tested especially for bismuth by slightly drying the filter containing it between blotting-paper, removing the still moist precipitate with a platinum spatula or a knife, dissolving it on a watch-glass in the *least possible quantity* of hydrochloric acid, and adding plenty of water. The appearance of a milky turbidity confirms the presence of bismuth. **131**

b. Sulphuric acid produces a precipitate: presence of lead. The whole of the nitric acid solution is mixed with a sufficient quantity of dilute sulphuric acid in a porcelain dish, and evaporated on the water-bath until the nitric acid is expelled; the residue is added to some water containing sulphuric acid, the sulphate of lead left undissolved is filtered off at once, and the filtrate tested for bismuth, copper, and cadmium (zinc and iron may possibly be present also) as directed in **127**;‡ the precipitate, after being washed, is tested by one of the methods given in § 123. **132**

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* If the precipitate thrown down from the acid solution by sulphuretted hydrogen contains sulphide of zinc (see note *, p. 296), the zinc will be found in the filtrate from the sulphide of cadmium and sulphide of copper, and is precipitated as white sulphide of zinc on adding ammonia to the solution, and, if necessary, a little sulphide of ammonium.

† If the precipitate thrown down from the acid solution by sulphuretted hydrogen contains sulphide of iron (see note *, p. 296), this is found in the precipitate β produced by ammonia, and may generally be detected by its reddish-brown colour. As a confirmatory test, sulphocyanate of potassium is added to a portion of the hydrochloric acid solution.

‡ For another method of separating cadmium, copper, lead, and bismuth, see the Third Section, Second Part, Appendix and notes to § 193.

2. The precipitate of the sulphides does not dissolve entirely in the boiling nitric acid, but leaves a residue, besides the sulphur that floats in the fluid. Mercuric oxide is probably present; if the precipitate is heavy and black, this is almost certain.[*] The precipitate is allowed to subside, and the solution, which is still to be tested for cadmium, copper, lead, and bismuth, is filtered off (zinc and iron may possibly be present); a small portion of the filtrate is mixed with a large quantity of sulphuretted hydrogen water, and if no precipitate is produced some ammonia and sulphide of ammonium is added; if any precipitate is formed or a coloration becomes visible, the remainder of the filtrate is treated according to **126**. **133**

The residue, besides sulphide of mercury, may also contain sulphate of lead formed by the action of the nitric acid on sulphide of lead, stannic oxide, and possibly sulphide of gold and sulphide of platinum, as the separation of the sulphides of tin, gold, and platinum from the sulphides of the metals of the fifth group is often incomplete. This residue is washed, and one half of it is dissolved in some hydrochloric acid, with addition of a very little chlorate of potassa, and the solution tested for mercury[†] with copper or stannous chloride (§ 119). The other half is fused with cyanide of potassium and carbonate of soda, and the fused mass treated with water; if metallic grains, or a metallic powder, is left undissolved, this residue is washed, heated with nitric acid, and the solution obtained is tested for lead with sulphuric acid. If the nitric acid leaves a residue, this is washed, and any hydrate of metastannic acid which it may contain is extracted as metastannic chloride, according to § 130, 1. Should a heavy metallic powder be left undissolved in the process, it is heated with aqua regia, and the solution tested for gold and platinum as directed in § 128.

§ 194.[‡]

Precipitation with Sulphide of Ammonium, Separation and Detection of the Oxides of Groups III. and IV.: *Alumina, Sesquioxide of Chromium; Oxide of Zinc, Protoxide of Manganese, Protoxide of Nickel, Protoxide of Cobalt, Oxides of Iron; also of those Salts of the Alkaline Earths which are precipitated by Ammonia from their Solution in Hydrochloric Acid: Phosphates, Borates, Oxalates, Silicates, and Fluorides.*

The precipitation of the above-named bases and salts by ammonia and sulphide of ammonium is satisfactory only when organic substances (especially non-volatile ones) are absent, since many of them, such as citric acid, interfere with the precipitation of alumina,

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[*] If the metallic sulphides (125) have been boiled with concentrated instead of dilute nitric acid, the white compound, $2HgS + HgO,NO_5$ [$2HgS + Hg(NO_3)_2$], will be obtained instead of the black sulphide. Compare § 119, 3.

[†] If it is an aqueous solution, or a solution in very dilute hydrochloric acid, the mercuric oxide was present in the original substance in that form; but if the solution has been prepared by boiling with concentrated hydrochloric acid, or by heating with nitric acid or aqua regia, the mercury may have been originally present as mercurous oxide or chloride.

[‡] Compare the notes in the Third Section.

oxide of chromium, phosphate of lime, &c. It is necessary, therefore, if organic matter has been found in the preliminary examination (**10**), to destroy it before precipitating with ammonia and sulphide of ammonium. There are therefore two sets of conditions.

A. Organic Substances are Absent.

A *small portion* of the solution in which sulphuretted hydrogen has failed to produce a precipitate (**110**), or the filtrate from the precipitate if formed (**112**), is put into a test-tube, and it is noted whether it is coloured or not;[*] it is now boiled to expel any sulphuretted hydrogen which may be present, a few drops of nitric acid added, the whole boiled, and the colour of the liquid again noted; ammonia is then cautiously added just to alkaline reaction, the solution is heated (observe whether this produces a precipitate), and some sulphide of ammonium added, no matter whether ammonia has produced a precipitate or not. **134**

a. Neither ammonia nor sulphide of ammonium produces a precipitate. Pass on to § 195, as neither iron, nickel, cobalt, zinc, manganese, sesquioxide of chromium, nor alumina is present, neither are phosphates, borates,[†] silicates, nor oxalates[‡] of the alkaline earths; nor fluorides of the metals of the alkaline earths, nor silicic acid—originally in combination with other bases. **135**

b. Sulphide of ammonium produces a precipitate, but ammonia alone does not: absence of phosphates, borates,[†] silicates, and oxalates[‡] of the alkaline earths; of the fluorides of the metals of the alkaline earths; of silicic acid, originally in combination with other bases; and also of iron, sesquioxide of chromium, and alumina. Pass on to **138**. **136**

c. Ammonia produces a precipitate before the addition of sulphide of ammonium. The course of proceeding to be pursued now depends on whether (*α*) the original solution was simply an aqueous solution, and has a neutral reaction, or (*β*) whether it is acid or alkaline. **137**

α. In the former case pass on to **138**, since phosphates, borates, oxalates, and silicates of the alkaline earths,

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[*] If the solution is colourless, it contains no chromium, or only traces of it. If coloured, the nature of the substance present may, to some extent, be inferred from the tint; thus a green tint, or a violet tint turning green on boiling, points to chromium; a bright green tint, to nickel; a reddish colour, to cobalt; if the solution turns yellow on boiling with nitric acid, it indicates iron. It must, however, be always borne in mind that these tints are perceptible only when the metallic oxides are present in large quantity; moreover, complementary colours, such, for instance, as the green of the nickel solution and the red of the cobalt solution, will destroy each other, so that a solution may contain both metals and yet appear almost colourless.

[†] If much chloride of ammonium is present, it has a great tendency to prevent the precipitation of the borates of the alkaline earths.

[‡] Oxalate of magnesia is thrown down from hydrochloric acid solution by ammonia after some time only, and never completely; dilute solutions are not precipitated by ammonia.

fluorides of the metals of the alkaline earths, and silicic acid in combination with other bases cannot be present.

β. In the latter case pass on to **150**, for, if the solution was acid, regard must be had to the possible presence of all the substances enumerated in **135**. If the original solution was alkaline, it is also examined according to **150**; as a rule, however, it is only necessary to test for the bases of the third and fourth groups and for silicic acid, phosphate of alumina, and phosphate of oxide of chromium, as it is quite an exception to find the salts of the alkaline earths mentioned in **135** in an alkaline solution.

138 1. Detection of the bases of Groups III. and IV. when phosphates, &c., of the alkaline earths are not present.*

The solution mentioned at the beginning of **134**, a portion of which has been submitted to a preliminary examination, is mixed with some chloride of ammonium; ammonia is then added, just to alkaline reaction, and lastly sulphide of ammonium until the liquid, after being shaken, smells distinctly of that reagent; the mixture is now shaken until the precipitate begins to separate in flakes, heated gently for some time, and filtered.

The filtrate,† which may contain the bases of Groups II. and I., is kept for subsequent examination according to § 195. The precipitate is washed with water to which a very little sulphide of ammonium has been added, and treated as follows:—

139 *α.* It is pure white: absence of iron, cobalt, and nickel. It must be tested for all the other bases of Groups III. and IV., as the faint tints of hydrated oxide of chromium and sulphide of manganese are imperceptible in a large quantity of a white precipitate. The precipitate is dissolved by heating it in a small dish with the least possible amount of hydrochloric acid, and then boiled until the sulphuretted hydrogen (if any is evolved) is completely expelled; to the solution, filtered if necessary, and concentrated by evaporation to a *small bulk*,‡ a tolerably concentrated solution of soda or potassa is added in excess, the whole heated to boiling, and kept for some time in a state of ebullition.

140 *a. The precipitate formed at first dissolves completely in the excess of soda:* absence of manganese and chromium, presence of alumina or oxide of zinc. A portion of the alkaline solution is tested with sulphuretted hydrogen water (a little, not excess) for zinc; the remainder is

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* This simpler method fully answers the purpose in most cases; for very accurate analysis, the method beginning at **150** is preferable, as this allows of the detection of any minute quantities of the alkaline earths which may have been thrown down with alumina or sesquioxide of chromium. Solutions which are distinctly coloured by chromium, and therefore contain relatively much oxide of chromium, should always be examined by **150**.

† If the filtrate is brownish, this points to nickel; sulphide of nickel, as is well known, being slightly soluble in sulphide of ammonium under certain conditions. In this case, the solution is acidified with acetic acid, heated for some time, the sulphide of nickel separated by filtration, and the filtrate treated as in § 195.

‡ Compare § 106, 6.

acidified with hydrochloric acid, ammonia added in *slight* excess, and the solution warmed. A white flocculent precipitate insoluble in more chloride of ammonium indicates alumina.*

β. *The precipitate formed does not dissolve, or dissolves only partially in the excess of soda.* The solution is diluted, filtered, and the filtrate tested for zinc and alumina according to **140**. The undissolved precipitate, which looks brown or brownish if it contains manganese, is washed and treated as follows:— **141**

aa. If the colour of the solution gives you no reason to suspect the presence of chromium, test the precipitate for manganese, with carbonate of soda in the outer blowpipe flame.

bb. When, however, the colour of the solution indicates chromium, the examination of the residue insoluble in solution of soda becomes more complicated, since in that case it may contain oxide of zinc also, possibly even the whole of the latter which is present (§ 112). The precipitate, therefore, is dissolved in hydrochloric acid, the solution evaporated to a small residue, washed into a small flask with some water, and the free acid nearly neutralized with carbonate of soda; carbonate of baryta is now added to the clear liquid in slight excess, the mixture allowed to digest in the cold with frequent shaking until the liquid has become colourless (this sometimes takes a tolerably long time), filtered, and the precipitate tested for chromium, by fusion with carbonate of soda and chlorate of potassa (§ 102, 8). The baryta is removed from the filtrate by sulphuric acid, it is then filtered, evaporated to a small residue, and concentrated solution of potassa or soda added in excess; the filtrate is tested for zinc with sulphuretted hydrogen, the precipitate, if any, for manganese as in *aa.* **142**

b. It is not white: this indicates chromium, manganese, iron, cobalt, or nickel. If it is black, or inclines to black, one of the three metals last mentioned is present. Under any circumstances, all the oxides of Groups III. and IV. must be looked for. **143**

The washed precipitate is removed from the filter by means of a spatula, or by rinsing it with the aid of a washing-bottle through a hole made in the bottom of the filter, and rather dilute cold hydrochloric acid (1 part of hydrochloric acid sp. gr. 1·12 : 5 parts of water) is poured on to it in moderate excess.

a. It dissolves completely (except perhaps a little sulphur): **144**

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* It is of course assumed that the soda or potassa used is free from alumina and silicic acid. As this is often not the case, it is convenient to make a comparative experiment with a similar quantity of the alkali alone; if a very small precipitate is obtained whilst that obtained in the analysis (**140**) is far larger, the presence of alumina in the substance may be safely inferred.

absence of cobalt and nickel, or at least of notable quantities of these two metals.

The solution is boiled until the sulphuretted hydrogen is *completely* expelled, nitric acid added, the mixture boiled, filtered if particles of sulphur are suspended in the liquid, and concentrated by evaporation to a *small bulk;* concentrated solution of potassa or soda in excess is then added, the mixture boiled for some time with constant stirring, diluted, and filtered from the insoluble precipitate which is sure to remain; the latter is washed. The examination of the filtrate is first proceeded with, then that of the precipitate.

aa. A small portion of the *filtrate* is tested for zinc by sulphuretted hydrogen; the remainder is acidified with hydrochloric acid, and then tested with ammonia for alumina. Compare **140**. **145**

bb. A small portion of the *precipitate* is dissolved in hydrochloric acid and tested for iron* by ferrocyanide of potassium added drop by drop, or by sulphocyanate of potassium. Another portion is tested for chromium by fusion with carbonate of soda and chlorate of potassa, and boiling out the melt with water. If the melt or its aqueous solution is yellow, chromium is present; if it is green or red from the presence of manganate or permanganate of soda, it must be heated with a few drops of alcohol. If no chromium has been found, and it cannot be inferred, from the green or red colour of the melt or its solution, that manganese is present, the remainder of the precipitate is examined for manganese, by carbonate of soda in the oxidizing flame. If chromium is present, on the other hand, the remainder of the precipitate is dissolved in hydrochloric acid and tested for manganese and zinc (the whole of which may possibly be in this precipitate (§ 112)) as directed in **142**. **146**

β. The precipitate is not completely dissolved, a black residue being left. This indicates cobalt and nickel. This indication is not certain, especially in the presence of much sulphide of iron, particles of which may become enveloped in the separated sulphur, and thus be protected from the action of the hydrochloric acid. The mixture is filtered, the precipitate washed, and the filtrate examined according to **144**. The precipitate together with the filter is ignited in a porcelain crucible until the filter is incinerated. **147**

The residue is warmed with hydrochloric acid and a drop or two of nitric acid, water added, then ammonia in moderate excess, and the solution filtered. **148**

The ammoniacal filtrate will be blue if much nickel is

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* As prussian-blue dissolves in ferrocyanide of potassium to a colourless solution, small quantities of iron may easily be overlooked if the ferrocyanide is added rapidly in large quantity. The original solution must be tested with ferricyanide of potassium and sulphocyanate of potassium to see whether the iron was present as ferrous or ferric oxide.

present, brownish if there is much cobalt, and will have a less distinct mixed colour if both metals are present. A portion of it is tested with sulphide of ammonium; if a black precipitate is formed, which does not re-dissolve on acidifying with hydrochloric acid, the presence of cobalt or nickel is proved.

In that case, the rest of the ammoniacal solution is evaporated to dryness, the ammonia salts driven off by gentle ignition, and the residue treated as follows:—

aa. A small portion of it is tested with borax, first in the outer and then in the inner blowpipe flame. If the bead in the oxidizing flame is violet whilst hot, and of a pale reddish-brown when cold, and becomes gray and turbid in the reducing flame, nickel is present; but if the colour of the bead is blue, whether it is hot or cold, or whether heated in the outer or the inner flame, cobalt is present. As in the latter case the presence of nickel cannot be distinctly recognized, and also if much nickel is present traces of cobalt may be overlooked, the examination is conducted as follows:—

bb. The remainder of the residue is dissolved in hydrochloric acid and a few drops of nitric acid, evaporated nearly to dryness, carbonate of soda added to alkaline reaction, then acetic acid until the precipitate produced is re-dissolved, and lastly nitrite of potassa (§ 109, 14). If a yellow precipitate is formed in the solution acidified with acetic acid after it has stood for some time at a gentle heat, this confirms the presence of cobalt. After about twelve hours, the solution is filtered, and the filtrate tested with solution of soda for nickel. **149**

2. Detection of the bases of Groups III. and IV. in cases where phosphates, borates, oxalates, and silicates of the alkaline earths, fluorides of the metals of the alkaline earths, or hydrate of silicic acid may possibly have been thrown down with these bases, that is, in cases where the original solution was acid (or alkaline, compare **137**) and a precipitate was produced by ammonia in the preliminary examination of **134**. **150**

The solution mentioned in **134** is mixed with some chloride of ammonium, then with ammonia until the reaction is just alkaline, lastly with sulphide of ammonium until the liquid, after being shaken, smells distinctly of the reagent; the mixture is shaken until the precipitate begins to separate in flakes, heated gently for some time, and filtered.

The filtrate, which may contain bases of Groups II. and I., is kept for subsequent examination according to § 195.* The precipitate is washed with water to which a very little sulphide of ammonium has been added, and then examined in the following way. To gain a clear notion of the difficulties to be overcome in

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[*] If this is brown from the presence of nickel, it must be treated as described in the note †, p. 306.

this analytical process, it should be remembered that it is necessary to examine the precipitate for the following substances: Iron, nickel, cobalt (these show their presence to a certain extent by the black or blackish colour of the precipitate), manganese, zinc, oxide of chromium, and phosphate of oxide of chromium (the last two are usually indicated by the colour of the solution), alumina and phosphate of alumina; also baryta, strontia, lime, and magnesia, these may have been thrown down in combination with phosphoric acid, boric acid, oxalic acid, silicic acid, in the form of fluorides, or in combination with sesquioxide of chromium. Besides all these substances, hydrate of silicic acid and free sulphur may be present in the precipitate.

As the original substance must be afterwards examined for all acids that might possibly be present, it is not *indispensable* to test for the above enumerated acids at this stage; yet, as it is often of interest to detect these acids at once, especially in cases where a somewhat large proportion of some alkaline earth has been found in the sulphide of ammonium precipitate, the method of detecting the acids in question will be appended to the method for the detection of the bases. 151

As soon as the washing is finished, the precipitate is removed from the filter by means of a small spatula or with the washing-bottle, and cold dilute hydrochloric acid (1 part of hydrochloric acid sp. gr. 1·12 with about 5 parts of water) in moderate excess is poured over it. 152

a. A residue remains. The solution is filtered, and the filtrate treated as directed in **154**. The residue, if it is black, may contain sulphide of nickel and sulphide of cobalt, and, besides these, sulphur and silicic acid, possibly also fluoride of calcium (which is somewhat sparingly soluble in hydrochloric acid); it is washed, and a part of it warmed with hydrochloric and a little nitric acid, evaporated to dryness, and the residue treated with hydrochloric acid and water. If silicic acid is present it remains undissolved; the solution or filtrate is tested for cobalt or nickel, according to **148**. The rest of the precipitate is incinerated and tested first for fluorine—according to § 146, 5, if silicic acid is absent; according to § 146, 6, if silicic acid is present. If fluorine has been found, the residue left, after testing for fluorine with sulphuric acid, is examined for lime by treating it with a little water, filtering, and adding three times its volume of alcohol (compare **155**, *aa*). 153

b. There is no residue (except a little sulphur, whose purity is to be proved by washing, drying, and burning): absence of nickel and cobalt, at least in any notable proportion. 154

The solution is boiled until the sulphuretted hydrogen is expelled, filtered if necessary, and then tested as follows:—

a. A small portion of the solution is mixed with dilute sulphuric acid. 155

aa. There is no precipitate. The solution is mixed with thrice its volume of spirit of wine. If a white precipitate is formed, this consists of sulphate of lime; it is collected, dissolved in water, and oxalate of ammonia added to the filtered solution.*

bb. Dilute sulphuric acid produces a precipitate. This may consist of the sulphates of baryta and strontia, possibly also of sulphate of lime. The solution is filtered and examined for lime according to *aa.* The precipitate is washed, or decomposed by fusing it with carbonate of potassa and soda mixture, the carbonates produced are washed, dissolved in hydrochloric acid, evaporated to dryness, taken up with water, and the solution tested as directed in **164**.

β. A somewhat larger sample is heated with some nitric acid, and a small portion of the solution tested for iron † with ferrocyanide of potassium added drop by drop, or with sulphocyanate of potassa; the remainder is mixed with so much ferric chloride ‡ that a drop of the solution will give a yellowish precipitate when mixed with a drop of ammonia on a watch-glass; the solution is then evaporated on a water-bath to a small bulk, washed into a flask with a little water, a few drops of carbonate of soda added just sufficient to *nearly* neutralize the free acid, and lastly to the still clear solution carbonate of baryta in excess; it is now shaken and allowed to remain in the cold until the liquid above the precipitate has become colourless. The precipitate *aa* is separated from the solution *bb* by filtration, and washed. **156**

aa. The *precipitate* is boiled for some time with solution of soda or potassa, filtered, and the filtrate tested for alumina,‖ by acidifying it with hydrochloric acid, adding ammonia to alkaline reaction, and boiling. The part of the precipitate insoluble in solution of soda is examined for chromium, by fusion with chlorate of potassa and carbonate of soda (§ 102, 8), and heating the fused mass with water. **157**

bb. The *solution* is first mixed with a few drops of hydrochloric acid, boiled to expel the whole of the

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* As the precipitated sulphate of lime may also contain traces of sulphate of strontia, it is advisable, in accurate analyses, to take the precaution to extract with water and test the residue spectroscopically for strontia (§ 96, 8).

† The original solution in hydrochloric acid must be tested with ferricyanide of potassium and sulphocyanate of potassium to ascertain whether the iron was present as ferrous or ferric oxide.

‡ The addition of ferric chloride is necessary to effect the separation of any phosphoric acid and silicic acid which may be present. These, as well as oxalic acid, boric acid, and fluorine, may be in the precipitate produced by carbonate of baryta.

‖ If the solution or the soda contains silicic acid, the precipitate taken for alumina may also contain silicic acid. If this is to be suspected, the remainder of the supposed alumina precipitate is ignited on the lid of a platinum crucible, some acid sulphate of potassa added, the mixture fused, and treated with hydrochloric acid, which will dissolve the alumina, leaving the silicic acid undissolved; the alumina is thrown down from the solution by ammonia.

carbonic acid, some ammonia added, and then sulphide of ammonium.

aa. There is no precipitate: absence of manganese and zinc. The solution containing chloride of barium is mixed with dilute sulphuric acid in slight excess, boiled, filtered, supersaturated with ammonia, and oxalate of ammonia added. If a precipitate of oxalate of lime is formed, it is filtered off, and the filtrate tested for magnesia with phosphate of soda. 158

ββ. A precipitate is formed. This is filtered off and the filtrate treated according to **158**. The precipitate, which may contain sulphide of manganese, sulphide of zinc, with traces of sulphide of cobalt and sulphide of nickel, is washed and tested for manganese, zinc, cobalt, and nickel, according to **143–150** (if the last two metals have not been found in **153**). 159

γ. If alkaline earths have been found in *a* and *β*, and it is wished to know what acids were in combination with them in the precipitate produced by sulphide of ammonium, the following experiments may be made with the remainder of the hydrochloric acid solution of the sulphide of ammonium precipitate. It is to be noted that phosphoric acid in combination with alumina or oxide of chromium may be present in the sulphide of ammonium precipitate. 160

aa. A small portion of the solution is evaporated on the water-bath to dryness, in a dish or watch-glass, the residue dried thoroughly in the water-bath, and then treated with hydrochloric acid. If there is any silicic acid in the solution, it will be left undissolved. The solution is evaporated with nitric acid and tested for phosphoric acid, by means of molybdic acid (§ 142, 10).

bb. Another portion is concentrated by evaporation, mixed with carbonate of soda *in excess*, boiled for some time, and filtered; one portion of the filtrate is examined for oxalic acid, by acidifying with acetic acid and adding solution of sulphate of lime; another portion for boric acid, by slightly acidifying with hydrochloric acid, and testing with turmeric-paper (§ 144, 6, and § 145, 5).

cc. The remainder of the solution is precipitated with ammonia, the precipitate collected, washed, dried, and examined for fluorine according to § 146, 5 and 6, respectively.

B. Organic Substances are Present.

In this case, the liquid in which sulphuretted hydrogen has caused no precipitate (**110**), or which has been filtered off from any precipitated sulphides (**112**), is divided into two portions of about one-third and two-thirds respectively. The smaller portion is examined for alkalies according to § 197, and the larger, after the organic matter has been destroyed, is examined for the alkaline earths and the bases and salts treated of in § 194. For this 161 purpose, it is evaporated nearly to dryness, a slight excess of carbonate of soda added and some nitrate of potassa, the mixture heated in a platinum vessel until all the organic matter is destroyed, the melt soaked in water, hydrochloric acid added to it in a glass or porcelain vessel, the mixture heated, if the solution is yellow from the presence of chromic acid, a little alcohol must be added; see § 138, 5), and the solution examined according to **134**.

§ 195.*

Separation and Detection of the Oxides of Group II. *which are precipitated by Carbonate of Ammonia in Presence of Chloride of Ammonium, viz., Baryta, Strontia, Lime.*

Before commencing the examination, it must be decided whether it is to be an ordinary analysis, or a strictly accurate one in which minute traces of the alkaline earths are to be detected if present. For ordinary analyses, the method A suffices, but for strictly accurate analyses the method B must be followed.

A. METHOD FOR AN ORDINARY ANALYSIS.

To a small portion of the solution in which ammonia and sulphide of ammonium have failed to produce a precipitate (**135**), or of the filtrate from the precipitate, if formed, chloride of ammonium is added, if there is no ammoniacal salt in the solution, then carbonate of ammonia and some caustic ammonia; and the mixture is heated for some time very gently (not to boiling). **162**

1. There is no precipitate: absence of any notable quantity of baryta, strontia, or lime. Traces of these alkaline earths may, however, be present; in order to detect them, proceed as follows. Some sulphate of ammonia (prepared by supersaturating dilute sulphuric acid with ammonia) is added to another portion of the solution; if it becomes turbid, it contains traces of baryta. To a third portion some oxalate of ammonia is added, and it is allowed to stand; if the liquid becomes turbid, traces of lime are present. The remainder of the solution is treated as directed in § 196, after the traces of lime and baryta which may be present have been removed by means of the reagents that have served to detect them.

2. A precipitate is formed: presence of lime, baryta, or strontia. The whole of the solution, of which a portion has been tested with ammonia and carbonate of ammonia, is treated in the same way as the sample, the precipitate which is formed is filtered off, after gently heating, and portions of the filtrate are tested with sulphate and oxalate of ammonia for traces of lime and baryta, which it may possibly still contain; should these be found, they are removed by means of the said reagents, and the solution, thus perfectly freed from baryta, strontia, and lime, is examined for magnesia, according to § 196. The precipitate produced by **163**

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* Compare the notes in the Third Section.

carbonate of ammonia is washed, dissolved in the smallest possible quantity of dilute hydrochloric acid, and evaporated to dryness on the water-bath; a small portion of the residue is treated with *a little* water, and an equal volume of solution of sulphate of lime added to this concentrated solution containing little or no free acid.

a. No precipitate is formed, even after the lapse of some time: absence of baryta and strontia,* presence of lime. As a confirmatory test the remainder of the residue is boiled with a concentrated solution of sulphate of ammonia, filtered, and tested with oxalate of ammonia.

b. A precipitate is produced by solution of sulphate of lime.

a. It is formed immediately; this indicates baryta. 164 Besides this, strontia and lime may also be present.

The remainder of the residue obtained by evaporating the hydrochloric acid solution of the precipitate produced by carbonate of ammonia is digested with strong alcohol, the solution decanted from the undissolved chloride of barium, diluted with an equal volume of water, mixed with a few drops of hydrofluosilicic acid (which will throw down the small portion of baryta that had dissolved in the form of chloride of barium), and allowed to stand for some time; it is then filtered, and dilute sulphuric acid and alcohol added to the filtrate. The formation of a precipitate indicates the presence of strontia or lime, or of both. After some time the precipitate is filtered off and tested according to pp. 101–102 for strontia and lime. It should be noted that, although the separation by boiling the sulphates with sulphate of ammonia suffices for ordinary cases, in very delicate analyses the nitrates must be separated by means of ether-alcohol, and the residue examined spectroscopically.

β. The precipitate is formed only after some time: absence 165 of baryta, presence of strontia. Concentrated solution of sulphate of ammonia, in not too small a quantity, is added to the remainder of the residue from 2, p. 313–14, and the whole boiled for some time, renewing the water as it evaporates, and adding ammonia to keep the liquid alkaline. The undissolved sulphate of strontia is then separated by filtration, and the filtrate tested for lime with oxalate of ammonia.

B. Method for Very Accurate Analyses.

As the precipitation of baryta, strontia, and lime, by means of 166 carbonate of ammonia, is affected by the presence of large quantities of ammonia salts, they must be removed before testing for the alkaline earths, whether originally present or introduced in the preceding operation. For this purpose, the solution, to which

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* Very minute traces of strontia cannot be detected in this way, as the sulphate of strontia, although very sparingly soluble, is not absolutely insoluble. For the method of detecting minute traces of strontia see § 99.

ammonia and sulphide of ammonium have been added with negative results (135), is evaporated at once to dryness, or the filtrate from the precipitate, obtained by means of ammonia and sulphide of ammonium, is boiled for some time with hydrochloric acid, the sulphur filtered off, and the filtrate evaporated to dryness. In either case the ammonia salts are got rid of by heating; the residue is then moistened with hydrochloric acid, water and ammonia added, the solution filtered, and the filtrate treated according to 162.

§ 196.

Examination for Magnesia.

To a portion of the solution in which carbonate, sulphate, and oxalate of ammonia have failed to produce a precipitate (162), or of the filtrate from such precipitate if formed (163), chloride of ammonium is added if ammonia salts are not already present, then some ammonia and phosphate of soda; should a precipitate not form at once, the inner sides of the test-tube should be rubbed with a glass rod, and the mixture allowed to remain for some time.

1. No precipitate is formed: absence of magnesia. Pass **167**
on to § 197.

2. A crystalline precipitate is formed: presence of magnesia. To test for the alkalies, pass on to § 197. Phosphate of magnesia and ammonia is invariably crystalline; if phosphate of soda produces a slight flocculent precipitate, it does not necessarily follow that magnesia is present. The slight flocculent precipitate, which is sometimes obtained here, may consist of phosphate of alumina. It is produced when alumina is present in the original substance, and too large an excess of ammonia has been used in precipitating the oxides of the third and fourth groups. Its formation depends on the fact that phosphate of alumina is less soluble in ammonia than the hydrate. Phosphate of alumina differs also from phosphate of ammonia and magnesia in that it is insoluble in acetic acid. In order to ascertain with certainty whether magnesia is present or not in the flocculent precipitate thrown down by phosphate of soda, this is collected, treated with a little acetic acid, and the solution filtered; the filtrate, which should give no turbidity with sulphate or oxalate of ammonia, is then tested with ammonia and a few drops of phosphate of soda. If magnesia is present, a crystalline precipitate will be obtained.

§ 197.

Examination for Potassa and Soda.

Any of the following solutions will do to test for potassa and soda.

1. If organic substances are absent.

a. The remainder of the solution tested for magnesia with negative results (§ 196, 1).

b. The remainder of the solution in which magnesia has been detected (§ 196, 2).

2. If organic substances are present.

The third of the solution in which sulphuretted hydrogen formed no precipitate (110), or the filtrate from the solution in which it produced a precipitate (112).

A different process will have to be adopted accordingly as one or the other of these solutions is employed.

α. *In the case of* 1, *a*.

A portion of the solution which was found to contain no magnesia (§ 196, 1) is gradually evaporated to dryness on the lid of a platinum crucible and gently ignited: if there is no residue, potassa and soda are absent; pass on to § 198. If a residue remains, the whole of the solution is treated in a similar manner, and the residue free from ammonia salts is examined according to 169. 168

β. *In the case of* 1, *b*.

The remainder of the solution in which magnesia had been detected (§ 196, 2) is evaporated to dryness, ignited until all the ammonia salts are removed, and the residue heated with water and a few drops of chloride of barium added. If a precipitate is formed, a few more drops of chloride of barium are added until no further precipitate is produced, and then baryta water, prepared from crystals of baryta, or a thin milk of lime perfectly freed from all alkalies by repeated extraction with water, is added until the solution strongly browns turmeric-paper. After boiling for some time, the solution is filtered, ammonia and a slight excess of carbonate of ammonia added to the filtrate, the whole gently warmed for some time, and filtered; the filtrate is then evaporated to dryness and gently ignited until all the ammonia salts are driven off. If there is no residue, potassa and soda are absent; pass on to § 198. If a residue remains, it is examined according to 169.

γ. *In the case of* 2.

This solution, which may contain organic compounds, and in which all the bases and salts treated of in § 194, as also all the alkaline earthy metals, may be present, is first of all evaporated to dryness in a porcelain basin, the residue moistened with concentrated sulphuric acid, and heated in a draft cupboard or in the open air until the greater part of the acid is driven off; cold water is then added, the solution filtered, and chloride of barium added to the hot filtrate as long as a precipitate is formed, baryta water or milk of lime is then added, and the analysis conducted as in β (case 1, *b*).

The fixed residue free from ammonia salts, obtained according to α, β, or γ, cannot be examined directly for potassa and soda, for, as a rule, it still contains small portions of the alkaline earths. It is therefore dissolved in a little water, ammonia and carbonate of ammonia added, and 169 the whole gently warmed for some time. If a precipitate is formed, it is filtered off and the clear filtrate again evaporated to dryness, and ignited very gently in order to drive off the small amount of ammonia salts present. If after this a residue remains, either potassa or soda is present. The residue is dissolved in a small quantity of water, with which it should form a clear solution,* half is transferred to a watch-glass, whilst the other half is retained in the porcelain dish.

aa. To the one-half in the porcelain dish, a few drops of *chloride of platinum* are added. If a yellow crystalline precipitate is formed immediately, or after some time, potassa is present. Should no precipitate form, the mixture is evaporated to dryness at a gentle heat, and the residue treated with a very small quantity of water, or, if chlorides alone are present, with a mixture of water and alcohol; the presence of the most minute traces of potassa will be shown by a small quantity of a heavy yellow powder being left undissolved (§ 89, 3). In the presence of an iodide, the deep brown colour of the liquid interferes with the detection of potassa by chloride of platinum (§ 92); under these circumstances, it is better to test for potassa with acid tartrate of soda. **170**

bb. Some *antimonate of potassa* is added to the other half of the liquid (in the watch-glass) after its action on test-paper has been tried, and any free acid present neutralized with carbonate of potassa. If a crystalline precipitate is produced at once, or after some time, soda is present. If, after standing twelve hours, no crystals have separated, it may safely be concluded that soda is absent. With regard to the crystalline form of the precipitate, and the precautions to be taken, see § 90, 2. **171**

§ 198.

Examination for Ammonia.

There now remains the examination for ammonia. Some of the substance or solution is ground up with an excess of hydrate of lime, and, if necessary, a little water. If the escaping gas smells of ammonia, if it blues moist red litmus-paper, and forms white fumes when a glass rod moistened with hydrochloric acid is brought in contact with the gas, ammonia is present. The reaction is most sensitive when the trituration is performed in a small beaker, and the latter covered with a glass plate with a slip of moistened turmeric- or red litmus-paper adhering to the under-side. **172**

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* If the solution thus obtained is not clear, the purification of the residue from the alkaline earths, as described above, must be again repeated.

COMPLEX COMPOUNDS.

A, 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF THE ACIDS.*

I. In the Absence of Organic Acids.

§ 199.

173 In the first place, it is necessary to consider which acids form salts soluble in water when in combination with the bases found; this will serve as a guide in the examination; students will find the table given in Appendix IV. of considerable assistance. The following plan of examination works best when the acids are combined exclusively with alkalies; it is therefore advisable before testing for the acids to precipitate the metals present by heating the solution with carbonate of soda, filter, and examine the filtrate.

1. The acids of arsenic, carbonic acid, sulphur combined with metals or hydrogen, chromic acid, hydroferrocyanic acid, and silicic acid will usually have been detected in the examination for bases (see **20**, **67**, and **68**). Chromic acid is also usually recognized by the yellow or reddish-yellow colour of the solution. If there is any doubt, the solution is tested with acetate of lead and acetic acid (§ 138, 8) or—for very minute quantities—with decoction of logwood (§ 138, 12).

174 2. If the solution is not neutral, a considerable portion of it is *exactly neutralized* with nitric acid or ammonia, as the case may be. If a precipitate—consisting of silicic acid, hydrate of magnesia, &c.—is produced, it is removed by filtration, whilst, if carbonic acid is evolved on neutralizing, the solution is boiled until it is entirely expelled. The clear neutralized solution is divided into four parts and examined as described in 3, 4, 7, and 8.

175 3. To a portion of the neutral solution (2), chloride of barium is added, or, if lead, silver, or mercurous oxide is present, nitrate of baryta.

> *a.* There is no precipitate: absence of sulphuric acid, phosphoric acid, chromic acid, silicic acid, oxalic acid, arsenious and arsenic acids; also boric acid and hydrofluoric acid in any considerable quantity.† Pass on to **176**.
>
> *b.* A precipitate is formed. The solution is diluted, and hydrochloric acid or nitric acid added, as the case may be; if the precipitate does not dissolve, or only incompletely, sulphuric acid is present.

176 4. Nitrate of silver is added to another portion of the clear neutral solution (see 2).

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* Consult also the explanations in the Third Section.

† If the solution contains considerable quantities of an ammoniacal salt, the experiment is not conclusive, since the baryta salts of most of these acids (not the sulphate) are more or less soluble in presence of ammoniacal salts.

a. There is no precipitate. Pass on to **181**, as neither chlorine, bromine, iodine, cyanogen,* ferrocyanogen, ferricyanogen, nor sulphur is present; nor phosphoric acid, arsenic acid, arsenious acid, chromic acid, oxalic acid, silicic acid; nor boric acid, if the solution was not too dilute.

b. A precipitate is produced. Observe the colour † of it, then add nitric acid, and shake the mixture. **177**

a. The precipitate dissolves completely: absence of chlorine, bromine, iodine, cyanogen, ferrocyanogen, and ferricyanogen, and also of sulphuretted hydrogen. Pass on to **181**.

β. A residue is left: chlorine, bromine, iodine, cyanogen, **178** ferrocyanogen, or ferricyanogen may be present; and if the residue is black or blackish, sulphuretted hydrogen or a soluble metallic sulphide. The presence of sulphur may, if necessary, be readily confirmed by adding a solution of oxide of lead in soda to another portion of the solution.

aa. A portion of the original solution, or the solution precipitated with carbonate of soda, is tested, first for iodine, and subsequently for bromine, by the methods described in § 157 (p. 226); comp. also *cc.*

bb. A small portion of the same solution as *aa* is **179** tested for ferrocyanogen with ferric chloride; and, if the colour of the silver precipitate leads you to suspect the presence of ferricyanogen, another portion is tested for the latter with a solution of sulphate of iron (freshly prepared, by warming wire with dilute sulphuric acid). If the original solution has an alkaline reaction, some hydrochloric acid must be added before testing with ferric chloride or ferrous sulphate, as the case may be.

cc. Cyanogen, if present as a simple cyanide of an alkali metal soluble in water, may usually be recognized by the odour of hydrocyanic acid; this becomes stronger on adding a little dilute sulphuric acid. If ferrocyanogen and ferricyanogen are not present, the cyanogen may be detected in the solution mentioned in *aa* by the method described in § 155, 6. For the detection of cyanogen when these are present, comp. § 157 and § 226.

As hydrocyanic acid interferes most seriously with the detection of iodine and bromine by nitrous acid, or chlorine water and bisulphide of carbon, negative results obtained in *aa* cannot by any means be taken as a proof

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* It has been already mentioned (**73**) that the cyanogen in cyanide of mercury is not indicated by nitrate of silver.

† Chloride, bromide, cyanide, ferrocyanide, oxalate, silicate, and borate of silver are white; iodide, tribasic phosphate, and arsenite of silver are yellow; arsenate and ferricyanide of silver are brownish-red; chromate of silver is deep purple-red; sulphide of silver black.

of the absence of iodine and bromine if cyanogen is present in the solution. In that case, it becomes necessary to destroy the cyanogen before testing for iodine and bromine as described in § 157.

180 *dd.* If bromine, iodine, cyanogen, ferrocyanogen, ferricyanogen, and sulphur are not present, the precipitate insoluble in nitric acid consists of chloride of silver.

But where one or other of the above-mentioned substances is present, a special examination for chlorine may become necessary, particularly when the quantity of the precipitate is so small that the presence of chlorine cannot be inferred with certainty.* In such cases the method described on p. 226 is applicable.

181 5. Chloric acid is known by the yellow colour produced when a little of the solid substance is added to some concentrated sulphuric acid in a watch-glass (§ 160, 7).

6. Nitric acid is tested for in the original solution with ferrous sulphate and sulphuric acid (§ 159, 6). The presence of certain other acids, especially chloric, chromic, hydriodic, and hydrobromic, interferes with or prevents this reaction. If any of these acids are present they must be destroyed or removed. Chloric acid is destroyed by ignition (§ 161, at the end); chromic acid is reduced by sulphurous acid, the sesquioxide of chromium being precipitated afterwards with ammonia; hydriodic acid and hydrobromic acid may be removed by sulphate of silver.

There still remain to be tested for, phosphoric acid, boric acid, silicic acid, oxalic acid, and hydrofluoric acid.

It is not necessary to test for the first four acids unless both chloride of barium and nitrate of silver have produced precipitates in neutral solutions. Compare also foot-note to **175**.

182 7. Phosphoric acid is tested for by adding ammonia in excess to a portion of the neutral solution (**174**), then chloride of ammonium and sulphate of magnesia (§ 142, 7). Very minute quantities of phosphoric acid are detected most readily by means of molybdic acid (§ 142, 10). If arsenic acid is present, it must be first separated by sulphuretted hydrogen, the solution being acidified and kept at 70° during the passage of the gas.

8. To detect oxalic acid and hydrofluoric acid, chloride of calcium is added to a fresh portion of the neutral solution prepared as in 2, and then, if a precipitate is produced, acetic acid. If the precipitate is soluble in acetic acid, or if there is no precipitate, neither oxalic acid nor hydrofluoric acid is present. In the opposite case, however, it must not be assumed that these acids are necessarily present, but they must be separately tested for. A portion of the original substance therefore is examined for fluorine according to § 146, 5, and another portion for oxalic acid according to § 145, 7.

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* For instance, if a copious precipitate insoluble in nitric acid has been obtained with solution of nitrate of silver, and the subsequent examination shows mere traces of iodine and bromine, chlorine is most certainly present.

9. Boric acid must be tested for in the original solution (or the solution precipitated with carbonate of soda) slightly acidified with hydrochloric acid, by means of turmeric-paper (§ 144, 6). As chloric, chromic, and hydriodic acids interfere with or prevent this reaction, they must, if present, be removed or destroyed before the test for boric acid is applied. Comp. § 199, 6. 183

10. If silicic acid has not been found already in the course of testing for the bases, a portion of the solution is acidified with hydrochloric acid, evaporated to dryness, and the residue treated with hydrochloric acid (§ 150, 2).

COMPLEX COMPOUNDS.

A, 1. Substances Soluble in Water.

Detection of the Acids.

II. In Presence of Organic Acids.

§ 200.

1. The examination for the inorganic acids, including oxalic acid, is made in the manner described § 199. As the tartrates and citrates of baryta and silver are insoluble, or at least only sparingly soluble in water, tartaric acid and citric acid cannot be present unless both chloride of barium and nitrate of silver produce precipitates in the neutral solution; still, in drawing a conclusion, it must be borne in mind that these salts are slightly soluble in solutions containing salts of ammonia. 184

In testing for organic acids, a neutral solution free from carbonic acid is employed, which has been freed from the bases of Groups II., III., IV., V., and VI. by the method described in 173 and 174. If these bases are not completely precipitated by carbonate of soda, as is often the case when non-volatile organic acids are present, their separation must be effected by the method given in § 184. If the *original solution* is to be employed instead of that prepared in this way, a special note to that effect will be inserted.

2. A portion of the solution, sufficiently concentrated, is made feebly alkaline with ammonia, some chloride of ammonium added, then a sufficient quantity of chloride of calcium, the mixture shaken vigorously, and allowed to remain for a couple of hours. 185

a. No precipitate is formed, either immediately or after the lapse of some time: absence of tartaric acid; pass on to 186.

b. A precipitate is formed, immediately, or after some time. The solution is filtered, the filtrate kept for further examination according to 186, and the precipitate washed. As the latter may contain phosphate or oxalate of lime as well as tartrate of lime, it is necessary to digest it, and shake it with solution of soda, without applying heat, dilute with a little water, filter, and boil the filtrate some time. If a precipitate separates, tartaric acid is present. Filter hot, and test the precipitate with ammonia and nitrate of silver as in § 163, 8).

3. The solution in which chloride of calcium has produced no precipitate, or that which has been filtered from the precipitate formed (in which latter case some more chloride of calcium is to be added), is mixed with thrice its volume of spirit, and allowed to stand for some hours at as low a temperature as possible. 186

a. No precipitate is formed: absence of citric, malic, and succinic acids. Pass on to 190. 187

b. A precipitate is formed. This is collected and the filtrate treated as directed in 190. The precipitate after being washed with alcohol is treated as follows:— 188

It is dissolved on the filter in *a little* dilute hydrochloric acid, ammonia added to the filtrate to alkaline reaction, and the mixture boiled for some time.

a. It remains clear: absence of citric acid. More alcohol is added to the solution, which must still be alkaline, the mixture put aside for some hours at a low temperature, the precipitate, which may contain malate and succinate of lime, is collected on a filter, washed with a little alcohol, dried until all the alcohol is removed,* removed from the filter, dissolved in a porcelain dish in about 2 c.c. of strong nitric acid (sp. gr. 1·35), and evaporated to dryness on the water-bath; 2 c.c. more of nitric acid are added to the residue, the mixture again evaporated to dryness, and the same treatment repeated a third time. Some succinic acid will remain unchanged, whilst the malic acid if present is converted into oxalic acid with evolution of carbonic acid. The residue is boiled with a slight excess of carbonate of soda solution, filtered, a portion acidified with acetic acid, and a few drops of chloride of calcium added. If a white precipitate of oxalate of lime is formed, malic acid is indicated. To test for succinic acid the remainder of the alkaline solution is nearly neutralized with hydrochloric acid, the feebly alkaline solution mixed with excess of chloride of calcium, filtered, and alcohol added to the filtrate; a precipitate indicates that succinic acid may be present. To confirm this, the precipitate is washed with spirit, suspended in a little water, and dilute sulphuric acid is added; the mixture is then shaken repeatedly with ether, the ethereal solution separated, and the ether distilled off, when the succinic acid will be obtained as hydrate (§ 171, p. 246). If malic acid has not been found, the remainder of the alkaline solution is exactly neutralized with hydrochloric acid, and tested for succinic acid with ferric chloride (§ 168, 5).†

β. A heavy white precipitate is formed: presence of citric acid. The solution is filtered boiling, and the 189

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* Oxalic acid would be produced by the action of the nitric acid on the alcohol if the latter were not entirely driven off.

† For other methods of separating malic acid from succinic acid, see Barfoed (Zeit. anal. Chem., 7, 409).

filtrate tested for malic and succinic acids as in *a*. In order to be certain that the precipitate is citrate of lime, it is redissolved in hydrochloric acid, heated, supersaturated again with ammonia, and boiled; the precipitate will now be thrown down again. (Compare § 164, 3.)

190 4. The filtrate of **188**, or the solution which yielded no precipitate on addition of alcohol (**187**), is heated to expel the alcohol, neutralized *exactly* with hydrochloric acid, and ferric chloride added. If there is a violet coloration, this indicates salicylic acid; if a precipitate is produced, benzoic acid is present. To confirm this the precipitate is collected, washed, and heated and digested with ammonia in excess; it is then filtered, the filtrate evaporated nearly to dryness, and tested for benzoic acid with hydrochloric acid (§ 169, 2). If salicylic acid is absent, benzoic acid may generally be readily detected in the original substance, by treating a small portion of it with dilute hydrochloric acid; this will leave the benzoic acid undissolved, and it may be collected and heated on platinum foil (§ 169, 1).

191 5. A portion of the original solution is evaporated to dryness—if acid, after previous saturation with soda—the residue or a portion of the original dry substance is introduced into a test-tube, some alcohol poured over it, about an equal volume of concentrated sulphuric acid added, and the mixture heated to boiling. If there is an odour of acetic ether, this indicates the presence of acetic acid.* This odour is more distinctly perceptible on shaking the cooling or cold mixture.

192 6. Formic acid is tested for by just acidifying a portion of the prepared solution (**184**) with hydrochloric acid, adding mercuric chloride, and heating. A white turbidity from the separation of mercurous chloride indicates formic acid (§ 173, 6). This is confirmed by nitrate of silver and by nitrate of mercurous oxide (§ 173, 4 and 5).*

COMPLEX COMPOUNDS.

A, 2. Substances Insoluble in Water, but Soluble in Hydrochloric Acid, Nitric Acid, or Nitro-hydrochloric Acid.

Detection of the Acids.

I. In Absence of Organic Acids.

§ 201.

In the examination of these compounds attention must be directed to all acids, with the exception of chloric acid. Cyanogen

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* In the presence of chromic or chloric acid, acetic acid or formic acid cannot be detected by the methods given. If chromic acid is present, the original solution should be mixed with sulphuric acid, excess of oxide of lead added, the mixture shaken and filtered; the filtrate is then mixed with excess of dilute sulphuric acid and distilled. The distillate is saturated with soda, evaporated almost to dryness, and the residue tested according to **191** and **192**. If organic acids of the first and second groups are present in large quantities, it is advisable to add sulphuric acid to the solution, and distil. If chloric acid is present, it is reduced as described in § 160, 9.

compounds and silicates are not examined by this method. (Compare § 204 and § 205.)

1. Carbonic acid, sulphur (in the form of metallic sulphides), arsenious acid, arsenic acid, and chromic acid, if present, have been found already in the examination for bases; nitric acid, if present, has been detected in the preliminary examination, by the ignition in a glass tube (**8**). 193

2. A portion of the substance is mixed with 4 parts of pure carbonate of soda and potassa, and, if a metallic sulphide is present, some nitrate of soda must be added; the mixture is then fused in a platinum crucible if there are no reducible metallic oxides present, in a porcelain crucible if such oxides are present; the fused mass is boiled with water, filtered, and the filtrate examined for the acids according to § 199.* 194

3. As the phosphates of the alkaline earths are not completely decomposed by fusion with carbonate of soda and potassa, it is always advisable in cases where alkaline earths are present, and phosphoric acid has not yet been detected (comp. **160**), to dissolve a fresh sample of the substance in nitric acid, and test for phosphoric acid with solution of molybdic acid (§ 142, 10). If silicic or arsenic acid is present, a solution in hydrochloric acid is prepared, and these acids separated; nitric acid is then added, the mixture evaporated nearly to dryness, diluted with water containing nitric acid, and tested with molybdate of ammonia. 195

4. If in the examination for bases, alkaline earths have been found, and fluorine has not already been detected (comp. **160**), it is also advisable to test a separate portion for fluorine, by § 146, 5.

5. That portion of the substance which has been treated as directed in **194** can be tested for silicic acid only in cases where the fusion has been effected in a platinum crucible; if a porcelain crucible has been used, a separate portion is examined by evaporating the hydrochloric or nitric acid solution (§ 150, 3). 196

6. A separate portion of the substance must be examined for oxalic acid by boiling with carbonate of soda; see **198**. The alkaline filtrate is acidified with acetic acid, and tested with solution of sulphate of lime; if a white pulverulent precipitate is formed, this indicates oxalic acid. As a confirmatory test, a fresh portion of the substance is examined according to § 145, 7, first removing the carbonic acid, if necessary by dilute sulphuric acid.

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* In the presence of a metallic sulphide, a separate portion of the substance must be examined for sulphuric acid, by heating it with hydrochloric acid, filtering, diluting the filtrate, and adding chloride of barium.

COMPLEX COMPOUNDS.

A, 2. Substances Insoluble in Water, but Soluble in Hydrochloric Acid, Nitric Acid, or Nitro-hydrochloric Acid.

Detection of the Acids.

II. In Presence of Organic Acids.

§ 202.

1. The examination for inorganic acids is made according to § 201. **197**

2. Acetic acid is tested for in a portion of the original substance or in the distillate obtained with sulphuric acid, as described in § 172, 7. Compare the foot-note on p. 323.

3. A little dilute hydrochloric acid is added to a small portion of the substance in a watch-glass. If it does not dissolve entirely, the residue should be tested for benzoic acid and salicylic acid according to § 171. Any considerable quantity of these acids is most readily detected in this way, but, as very small quantities may dissolve completely, it is necessary to examine the substance as described in the next paragraph (**198**).

4. A portion of the substance is boiled for a few minutes with a large excess of solution of carbonate of soda, adding some of the solid if the solution is not strong, and the precipitate is separated by filtration. All the organic acids will be in the filtrate as soda salts. The filtrate is concentrated by evaporation, acidified with hydrochloric acid, heated to drive off carbonic acid, and treated according to **185**. If any of the heavy metals or alumina have passed into solution through the agency of organic acids, these must first be removed by the method given in § 184 before the organic acids are tested for. **198**

COMPLEX COMPOUNDS.

B. Substances Insoluble or Sparingly Soluble in Water, Hydrochloric Acid, Nitric Acid, and Nitro-hydrochloric Acid.

Detection of the Bases, Acids, and Non-metallic Elements.

§ 203.*

The following substances belong to this class:— **199**

Sulphate of baryta, sulphate of strontia, and sulphate of lime.†

Sulphate of lead‡ and chloride of lead.||

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[*] Compare the notes in the Third Section, on the cyanogen compounds insoluble in acids, § 204.

[†] Sulphate of lime passes partially into the aqueous solution, and often completely into that effected by acids.

[‡] Sulphate of lead may pass completely into the solution effected by acids.

[||] Chloride of lead will only be found here if the precipitate insoluble in acids has not been thoroughly washed with hot water.

Chloride of silver, bromide of silver, iodide of silver, and cyanide of silver.*

Silicic acid and many silicates.

Native and ignited alumina, and many aluminates.

Ignited sesquioxide of chromium and chrome-iron ore (a compound of sesquioxide of chromium and ferrous oxide).

Ignited and native bioxide of tin (tin-stone).

Some metaphosphates and some arsenates.

Fluoride of calcium and a few other compounds of fluorine.

Sulphur.

Carbonaceous matter.

Of these compounds those spaced (like sulphate of baryta) are more frequently met with. As the silicates are so very important in mineral analysis, they have been specially treated in §§ 205–209.

The substance insoluble in water or acids is, in the first place, submitted to the preliminary examination described in *a–e*, unless the quantity at disposal is too small, in which case pass on to **205**, bearing in mind, however, that the substance may contain all the aforesaid substances.

a. The physical condition of the residue is attentively examined **200** to ascertain whether it is homogeneous or not, whether it is sandy or pulverulent, whether it has the same colour throughout or is made up of variously coloured particles, &c. A microscope, or even a lens, will be found very useful for this purpose.

b. A small portion is heated in a glass tube sealed at one end; **201** if brown fumes arise, and sulphur sublimes, this element is present.

c. If the substance is black, this indicates, in most cases, the **202** presence of carbonaceous matter (charcoal, coal, bone-black, lamp-black, graphite, &c.). A small portion is heated on platinum-foil over the blowpipe flame; if the black substance is consumed, it consisted of carbon in some shape or other. Graphite (which may be readily recognized by its property of communicating its colour to the fingers, to paper, &c.) is not completely consumed unless it is heated to bright redness in oxygen.

d. A small portion is heated for some time with a small lump **203** of cyanide of potassium and some water, and filtered; one half the filtrate is acidified with nitric acid, the other half tested with sulphide of ammonium. If the former gives a white precipitate and the latter (provided always that the quantity of cyanide of potassium is not too large) a brownish-black precipitate, this indicates silver.

e. If a residue has been left undissolved in *d*, it is washed **204** thoroughly with water, and, if white, moistened with sulphide of ammonium; if it turns black, salts of lead are present. If, however, the residue left in *d* is black, it is heated with a concentrated

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* Bromide, iodide, and cyanide of silver are decomposed by boiling with nitro-hydrochloric acid, and converted into chloride of silver; they can accordingly be found here only in cases where the operator has to deal with a substance which—as nitro-hydrochloric acid has failed to effect its solution—is examined directly by the method described in § 203.

slightly acid solution of acetate of ammonia,[*] filtered, and the filtrate tested for lead, by means of sulphuric acid and sulphuretted hydrogen.[†]

The results obtained by these preliminary experiments serve as a guide in the following course.

1, *a.* Salts of lead are not present. Pass on to **206**. 205

b. Salts of lead are present. Heat the substance repeatedly with a concentrated slightly acid solution of acetate of ammonia[*] until the salt of lead is completely dissolved out. A portion of the filtrate is tested for sulphuric acid with chloride of barium, another portion for lead by adding sulphuric acid in excess, and by sulphuretted hydrogen, whilst the remainder is diluted with about 20 parts of water acidified with nitric acid and tested for chlorine by nitrate of silver. If the acetate of ammonia has left a residue, this is washed, and treated as directed in **206**.

2, *a.* Silver salts are not present. Pass on to **207**. 206

b. Silver salts are present. The substance, which is free from lead, or from which the lead has been extracted by treatment with acetate of ammonia, is digested repeatedly with cyanide of potassium and water, at a gentle heat (in the cold if sulphur is present), until all the salt of silver is dissolved and removed. If a *residue* is left, this is washed and treated according to **207**. A small portion of the filtrate is tested for sulphuric acid.[‡] The remainder, after it has been sufficiently diluted, is acidified with nitric acid either in the open air or in a good draught. The precipitate, after being collected, washed, and fused with carbonate of soda on charcoal, will yield metallic silver (§ 115, 8). To ascertain whether the silver was originally in combination with a halogen, and with which halogen it was united, it must be tested according to **214**.

3, *a.* Sulphur is not present. Pass on to **208**. 207

b. Sulphur is present. The substance free from silver and lead is heated in a covered porcelain crucible until all the sulphur is expelled, and if a residue is left, this is treated according to **208**.

4. A considerable portion of the substance free from silver, lead, and sulphur is mixed with 2 parts of carbonate of soda, 2 parts of carbonate of potassa, and 1 part of nitrate of potassa,[||] 208

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[*] To prepare this, acetic acid is added to strong ammonia solution until it has a slightly acid reaction.

[†] The presence of lead in silicates, such as in glass, cannot be detected by this method.

[‡] As the carbonate of potassa contained in the cyanide of potassium may have produced a total or partial decomposition of sulphates of the alkaline earths.

[||] Addition of nitrate of potassa is useful even in the case of white powders, as it counteracts the injurious action of silicate of lead, should any be present, on the platinum crucible. In the case of black powders, the proportion of nitrate of potassa must be correspondingly increased, in order that the carbon, if present, may be consumed as completely as possible, and that any chrome-iron ore present may be more thoroughly decomposed.

heated in a platinum crucible until the mass is in a state of calm fusion, the red-hot crucible placed on a thick, cold iron plate, and allowed to cool. By this means, the fused mass may generally be removed entire from the crucible in a cake. If this does not happen, it is heated again until the edge of the cake in the crucible begins to melt. When quite cold, sufficient water is poured into the crucible to well cover the cake, and it is heated carefully; the cake then becomes loosened (if the crucible has no bruises) (Stöckmann). The melted mass, together with the crucible, is placed in a beaker, the cake soaked in water, boiled, filtered, and the residue washed until chloride of barium no longer produces a precipitate in the washings. (Only the first washings should be added to the filtrate.)

a. The solution thus obtained contains the acids which were present in the substance decomposed by fusing. But it may, besides these acids, contain also such bases as are soluble in caustic alkalies. It is treated as follows:— 209

α. A small portion is acidified with hydrochloric acid and tested for sulphuric acid by chloride of barium.

β. Another portion (after being acidified with nitric acid) is tested with molybdic acid for phosphoric acid and arsenic acid (§ 142, 10, and § 133, 9). If a yellow precipitate is formed, arsenic acid must be tested for in another portion of the solution, and, if present, removed by acidifying it with sulphuric acid, concentrating on the water-bath to a small bulk, and precipitating with sulphuretted hydrogen. The filtrate must then be tested again for phosphoric acid.

γ. Another portion is tested for fluorine (§ 146, 7).

δ. If the solution is yellow, chromic acid is present. As a confirmatory test acidify a portion of the solution with acetic acid, and add acetate of lead.

ε. The remainder is acidified with hydrochloric acid, evaporated to dryness, and the residue treated with hydrochloric acid and water. If there is a residue which will not dissolve even in boiling water, it consists of silicic acid. The hydrochloric acid solution is now tested in the usual way for those bases which, being soluble in caustic alkalies, may be present, and especially for alumina. 210

b. The residue left in 208 is dissolved in hydrochloric acid (effervescence indicates the presence of alkaline earths—a residue insoluble in hydrochloric acid would have to be examined according to 213), and the solution tested for the bases as directed in § 190. If much silicic acid has been found in 210, it is advisable to evaporate the solution of the residue to dryness, and treat it with hydrochloric acid and water, in order that the silicic acid remaining may also be removed as completely as possible. With regard to the alkalies present in silicates see 212. 211

5. If it was found in 4 that the residue insoluble in acids 212

contained a silicate, a separate portion of it is treated according to **228**, to ascertain whether this silicate contains alkalies.

6. If anything is still left undissolved on treating the residue left in **208** with hydrochloric acid (**211**), it may consist either of silicic acid which has separated, or of a portion of the sulphate of baryta which has not been decomposed, or possibly of stannic oxide; it may also be fluoride of calcium, and, if it is dark coloured, chrome-iron ore, as the two compounds last named are only decomposed with difficulty by the method given in **208**. It should be noted that stannic oxide may be detected in the manner described in § 130, 11, and that fluoride of calcium may be easily decomposed by sulphuric acid (§ 146, 5). The disintegration of chrome-iron ore, however, may be readily effected by igniting 1 part of the ore with about 8 parts by weight of a mixture of 1 part of chlorate of potassa and 3 parts of soda lime at a bright red heat for an hour and a half in a covered platinum crucible. The melt then contains all the chromium as an alkaline chromate, which may be extracted by means of water. If the chrome-iron ore contains tin oxide, it is partly converted into an alkaline stannate, which is extracted by the water, and partly remains in the residue insoluble in water, from which it may be extracted by hydrochloric acid as stannic chloride. **213**

7. If the residue insoluble in acids contains silver, it must be determined whether it was present in the original substance as a compound insoluble in acids, or whether the subsequent treatment of the substance with solvents has converted it into chloride, bromide, iodide, or cyanide of silver. This has to be determined, but under certain circumstances it can hardly be done by a simple qualitative examination; this can be easily understood. If, for instance, a mixture of iodide of potassium and chloride of silver is treated with water, iodide of silver and chloride of potassium will be obtained. Again, a mixture of mercuric iodide with nitrate of silver when treated with water will yield mercuric nitrate and iodide of silver, and so forth. **214**

In order to find this out as far as possible, a portion of the original substance is exhausted with boiling water, and then with dilute nitric acid; the residue is washed with water, and a small portion of it tested for silver according to **203**. If silver is present, proceed to ascertain the salt-radicle with which the metal is combined; this is effected by treating the remainder of the residue with finely granulated zinc and water, adding some dilute sulphuric acid, shaking repeatedly, and filtering after the lapse of some hours. The filtrate may be tested at once for chlorine, bromine, iodine, and cyanogen, as in § 157; or the zinc may be thrown down by carbonate of soda, so as to obtain the salt-radicles in combination with sodium.

SECTION II.

PRACTICAL COURSE IN PARTICULAR CASES.

I. ANALYSIS OF CYANIDES, FERROCYANIDES, ETC., INSOLUBLE IN WATER, AND ALSO OF INSOLUBLE MIXED SUBSTANCES CONTAINING SUCH COMPOUNDS.*

§ 204.

215 THE analysis of cyanogen compounds insoluble in water, as also of ferrocyanides, ferricyanides, &c., in the ordinary way, is often attended by the manifestation of such anomalous reactions as easily to mislead the analyst. Moreover, acids often fail to effect the complete solution of these compounds.† For these reasons, it is advisable to analyse them, and mixtures containing them, by the following special method :—

1. The residue left after all the soluble substances have been extracted with water is boiled with strong solution of potassa or soda; after a few minutes' ebullition, some carbonate of soda is added and the mixture boiled again for some time; it is filtered from the residue, should there be any, and the residue is washed.

a. The residue, which is now free from cyanogen (unless the substance contains cyanide of silver), is examined in the ordinary way, beginning at **37**.

216 *b. The solution*, which, if combinations of compound cyanogen radicles (ferrocyanogen, cobalticyanogen, &c.) are present, contains these combined with alkali metals, may also contain other acids, which have been separated from their bases by boiling with carbonate of soda, and lastly, also, such oxides as are soluble in caustic alkalies.

a. A portion is carefully mixed with sulphuretted hydrogen water.‡

aa. No permanent precipitate is formed : absence of zinc and lead and also of other metals of the Groups IV. and V. (which may have passed into solution owing to

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* The explanatory notes to § 240 contained in the Third Section of the Second Part must be carefully studied before commencing the examination.

† The presence of insoluble cyanides, ferrocyanides, &c., is generally detected in the preliminary examination on igniting the substance in a glass tube, cyanogen and sometimes nitrogen being evolved, whilst, if water is present, hydrocyanic acid and ammonia are given off, and generally a metal mixed or combined with carbon remains in the residue. Most of the insoluble ferrocyanides and ferricyanides yield blue or green products of decomposition when boiled with hydrochloric acid.

‡ Adding sulphuretted hydrogen water, or passing the gas into the solution, until the mixture smells of the reagent must naturally be avoided (that is, until all the alkali present has been converted into hydrosulphide of sulphide of alkali metal), since this might lead to the precipitation of any alumina which may be present in the alkaline solution, and even of sulphides of metals of the sixth group—a precipitation which is not intended here.

the presence of organic matter), with the exception of mercury, the sulphide of which may remain dissolved in the sulphide of sodium solution. Pass on to **217**.

bb. A permanent precipitate is formed. A little yellow sulphide of sodium is added, drop by drop, to the greater part of the alkaline solution (**216**) so long as a precipitate is produced, avoiding any great excess of the precipitant. The mixture is gently heated, filtered, and the filtrate treated as directed in **217**. The washed precipitate is heated with dilute nitric acid, which may leave sulphide of mercury and sulphate of lead undissolved, and the solution examined for metals of the fourth and fifth groups in the ordinary way. If a residue is left on heating with nitric acid, this is examined for sulphide of mercury and sulphate of lead according to **133**.

β. The alkaline liquid, in which sulphuretted hydrogen **217**
water has produced no precipitate, or which has been filtered off from the precipitate produced by sulphide of sodium, is acidified with dilute sulphuric acid, and if the solution does not smell strongly of sulphuretted hydrogen, some more of it is added.

aa. There is no precipitate other than a little sulphur: absence of mercury and the oxides of the sixth group. Pass on to **218**.

bb. A precipitate is formed. The greater portion of the solution mentioned in **217** is treated like the small portion, the precipitate collected, washed, and examined for mercury and the metals of the sixth group according to § 191. The filtrate is examined according to **218**.

γ. The solution which has given no precipitate with sul- **218**
phuretted hydrogen, whether alkaline or acid, or which has been filtered off from such precipitates, must now be examined for those metals (iron, cobalt, manganese, chromium), which form compound radicles with cyanogen, also for alumina. It has also to be tested for cyanogen, ferrocyanogen, cobalticyanogen, &c., as well as for the other acids. It is treated as follows:—

aa. Samples of this are employed for the detection of the acids according to § 199 and § 200 respectively. If the solution is already acidified with sulphuric acid, the examination for the acids must be proceeded with without delay, as otherwise any hydroferrocyanic or hydroferricyanic acids present will be decomposed. For this purpose, ferric chloride and ferrous sulphate are first added to the acid solution in order to detect the presence of ferrocyanogen and ferricyanogen respectively.* If

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* It must be remembered that the ferricyanide originally present may be converted into ferrocyanide not only by sulphuretted hydrogen, but also by bases capable of being more highly oxidized, &c.; for example,

$$3K,C_{12}N_6Fe_2 + KO,HO + 2FeO = 2(2K,C_6N_3Fe) + Fe_2O_3 + HO$$

$$[K_6Fe_2(CN)_{12} + 2KOH + 2FeO = 2K_4Fe(CN)_6 + Fe_2O_3 + H_2O].$$

sulphuretted hydrogen is present, this test is naturally of no avail, as hydroferricyanic acid is converted into hydroferrocyanic acid by sulphuretted hydrogen; it is advisable in such a case to free the solution as much as possible from sulphuretted hydrogen by passing through it a rapid stream of air. Cobalticyanogen may be recognized by its giving a greenish precipitate with nickel salts and white precipitates with zinc and manganese salts; the presence of cobalt in them may be recognized by means of the borax bead.

bb. Another portion of the solution mentioned in 218 is acidified with dilute sulphuric acid and evaporated nearly to dryness; some pure concentrated sulphuric acid is then added, and the mixture heated until the greater part of the free acid is expelled. The residue is dissolved in water and the solution tested for iron, manganese, cobalt, alumina, and sesquioxide of chromium according to § 194.

δ. Another portion of the solution mentioned in 216 from which all the metallic sulphides have been precipitated, is tested for sulphuric acid by adding hydrochloric acid and chloride of barium, or nitric acid and nitrate of barium, and for ferricyanogen * by ferrous sulphate with subsequent addition of hydrochloric acid. 219

2. Another portion of the original solution is decomposed by continued heating with pure concentrated sulphuric acid, and tested for alkalies after removing all other bases.

II. ANALYSIS OF SILICATES.

§ 205.

It may be ascertained whether the substance is a silicate or contains one, by a preliminary examination with microcosmic salt before the blowpipe; during the fusion, the metallic oxides dissolve, whilst the separated silicic acid floats about in the liquid bead as a translucent swollen mass (§ 150, 8). 220

The analysis of silicates, strictly speaking, differs from the usual course only in so far as the preparatory treatment is concerned, to separate the silicic acid from the bases, and to obtain the latter in solution.

The silicates and double silicates are divided into two classes, which must be clearly distinguished, as they require different methods of analysis; viz., (1) silicates readily decomposable by acids (hydrochloric acid, nitric acid, sulphuric acid), and (2) silicates which are not decomposed by acids, or only with difficulty. Many rocks consist of mixtures of the two classes of silicates.

In order to ascertain to which class a given silicate belongs, it is reduced to a very fine powder, and a portion digested with hydrochloric acid at a temperature near the boiling-point. If this does

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* Compare note on p. 331.

not decompose it, another portion is heated for a long time with a mixture of 3 parts of concentrated sulphuric acid and 1 part of water. If this also fails, the silicate belongs to the second class. The appearance generally tells whether decomposition has been effected by the acid or not, as a coloured solution is almost invariably formed, and the separated gelatinous, flocculent, or finely pulverulent hydrate of silicic acid takes the place of the original heavy powder which grated when it was stirred with a glass rod. To ascertain whether the decomposition is complete, or extends only to one of the components of the rock, the separated hydrate of silicic acid, after being washed, is boiled in a solution of carbonate of soda. If it dissolves completely, it has been entirely decomposed; if not, the decomposition is only partial. The results of these preliminary tests will show whether the silicates should be examined according to § 206, § 207, or § 208.

Before proceeding further, a portion of the substance is examined also for water, by heating it in a glass tube thoroughly dry. If the substance contains hygroscopic moisture, it must first be dried at 100° for a long time. The sample is exposed to a gentle heat at first, but is finally intensely ignited by means of the gas lamp (p. 22) or the blowpipe; it is also convenient to make a preliminary examination for fluorine here (§ 146, 8).

A. Silicates Decomposable by Acids.

§ 206.

a. Silicates decomposable by hydrochloric or nitric acid.*

1. The finely powdered silicate is made into a homogeneous paste **221** with a little water, hydrochloric or nitric acid added, and the mixture digested at a temperature near the boiling-point until it is completely decomposed; a small portion of the solution is then filtered, and the remainder, together with the silicic acid suspended therein, is evaporated to dryness, and the residue heated at 100° (or but little above) with constant stirring, until hardly any more hydrochloric or nitric acid fumes escape; when cold, it is moistened with hydrochloric acid or nitric acid, as the case may be, a little water is subsequently added, and the mixture heated gently for some time.

This operation effects the separation of the silicic acid, whilst the bases pass into solution as chlorides or nitrates. The solution is filtered, the residue thoroughly washed, and the solution examined in the ordinary way for the bases, beginning at § 189, II. or III. The residual silicic acid must always be tested, as it cannot be considered pure. It frequently contains titanic acid, occasionally sulphate of baryta, possibly also sulphate of strontia, and often a little alumina. It is best tested by repeatedly heating it in a platinum dish with hydrofluoric and sulphuric acids, until all the silicic acid has been removed as fluoride of silicon. The residue is then ignited, fused with bisulphate of

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* Nitric acid is preferable to hydrochloric acid when compounds of silver or lead are present.

potassa, and treated with cold water; if anything insoluble remains, it is filtered off and tested according to § 99 for sulphate of baryta (and strontia). The diluted aqueous solution is tested by long boiling for titanic acid* (§ 104, 8), and the filtrate therefrom is tested by ammonia for alumina. (If there is any chance of the presence of chloride of silver in the silicic acid, a portion of it is digested with ammonia, filtered, and the filtrate tested by adding nitric acid in excess.)

2. As silicates, and more particularly those decomposed by hydrochloric acid, often contain other acids, and also metalloïds, the following observations and instructions must be attended to, in order that none of these substances may be overlooked:— 222

a. Carbonates are detected when treating the substance with hydrochloric acid. Sulphides are often detected in the same operation, otherwise they are tested for according to § 156, 8 or 9.

β. If the separated silicic acid is black, and turns white on ignition in the air, this indicates the presence of carbon or of organic substances. When the latter are present, the silicates emit an empyreumatic odour on being heated in the glass tube.

γ. The portion of the hydrochloric acid solution filtered off before evaporating is tested for sulphuric acid, phosphoric acid, and arsenic acid—for sulphuric acid by diluting and adding chloride of barium; for arsenic acid by passing sulphuretted hydrogen into the solution at 70°; for phosphoric acid by molybdate of ammonia, after the hydrochloric acid is removed by adding nitric acid, evaporating to dryness on the water-bath, warming the residue with nitric acid, and filtering. If arsenic has been found, phosphoric acid is tested for in the solution filtered from the sulphide of arsenic.

δ. Boric acid is best detected by fusing a portion of the substance in a platinum spoon with carbonate of soda and potassa, boiling the fused mass with water, and testing the solution for boric acid by § 144, 6. 223

ε. With many silicates, the chlorides present may be extracted by boiling with water and testing the filtrate by nitrate of silver; the safest way, however, is to dissolve the

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* If the silicic acid has been separated by evaporation on the water-bath, only a small portion of the titanic acid will be found along with it, the remainder will be in the hydrochloric acid solution and will be precipitated by ammonia along with the ferric oxide and alumina. To find this, the dried precipitate is fused with bisulphate of potassa, the melt dissolved in cold water, filtered if necessary, diluted considerably, and sulphuretted hydrogen passed until the ferric oxide is completely reduced to ferrous oxide; the liquid (without filtering off the sulphur) is then kept boiling for half an hour with a constant current of carbonic acid passing through it. The precipitate is collected, washed, and ignited; the sulphur will burn off, leaving the titanic acid. Should it still contain iron, it must be re-dissolved by fusion with bisulphate of potassa and treatment with cold water, and then precipitated by boiling with hyposulphite of soda.

mineral in dilute nitric acid, and test the solution with nitrate of silver.

ζ. Fluorides, more or less of which often occur in silicates, are detected by § 146, 6.

3. If the silicates contain iron, as is usually the case, it is necessary to ascertain whether it is present in the ferrous or ferric state or both. For this purpose, a portion of the finely powdered substance is heated with moderately concentrated hydrochloric acid, avoiding access of air as far as possible, the solution diluted, filtered, and then tested with ferricyanide of potassium and sulphocyanate of potassium (§ 110, 8, and § 111, 8). **224**

b. Silicates which resist the action of hydrochloric acid, but are decomposed by concentrated sulphuric acid.

The finely pulverized mineral is heated with a mixture of 3 parts of concentrated pure sulphuric acid and 1 part of water (best in a platinum dish), the greater portion of the sulphuric acid is finally driven off, the residue boiled with hydrochloric acid, diluted, filtered, and the filtrate treated as directed in § 190; the residue, which, besides the separated silicic acid, may contain also sulphates of the alkaline earths, &c., is examined as directed in § 206, 1. If it is wished to examine silicates of this class for acids and salt-radicles, a separate portion of the substance must be treated according to § 207. **225**

B. SILICATES WHICH ARE NOT DECOMPOSED BY ACIDS.*

§ 207.

As the silicates of this class are most conveniently decomposed by fusion with carbonate of soda and potassa, the portion so treated cannot, of course, be examined for alkalies. The analytical process is therefore divided into two principal parts, a portion of the mineral being examined for the silicic acid and the bases, with the exception of the alkalies, whilst another portion is specially examined for the latter. The mineral must also be examined for other acids. **226**

1. Detection of the silicic acid and the bases, with the exception of the alkalies.

The mineral in very fine powder is mixed with 4 parts of carbonate of soda and potassa mixture, and then heated in a platinum crucible over a gas lamp or Berzelius spirit lamp until the mass is in a state of calm fusion. The red-hot crucible is placed on a thick, cold iron plate, and allowed to cool there; or it is treated as in **208**, so as to remove the fused cake from the crucible. If this is successful, the mass is broken in pieces, and a portion kept for the **227**

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* It will be understood, from what has been stated in § 205, that these are not decomposed by heating with hydrochloric acid and sulphuric acid in open vessels. If, however, they are finely powdered, and heated in a sealed glass tube, with a mixture of 3 parts of concentrated sulphuric acid and 1 part of water, or with hydrochloric acid, at 200°–210°, most of them are decomposed, and may accordingly be analysed in this manner (A. Mitscherlich).

examination for acids. The portion intended for testing for the bases, whether in loose pieces or still adhering to the crucible, is placed in a porcelain dish, water poured over it, hydrochloric acid added, and the mixture heated gently until the mass is dissolved with the exception of the silicic acid, which separates in flocks. The crucible is removed from the dish if necessary, the mixture evaporated to dryness, and the residue treated as directed in **122**.

2. Detection of the alkalies.

To effect this the silicate must be decomposed by means of a substance free from alkalies. Hydrofluoric acid or a metallic fluoride answers best; but fusion with hydrate of baryta may also be employed. **228**

a. Decomposition by aqueous hydrofluoric acid.—The finely powdered substance is rubbed up with water, in a platinum dish, to the consistency of a thin paste, aqueous hydrofluoric acid and hydrochloric acid are added, and the mixture heated until the silicate is dissolved. (This operation may be conducted in the open air, but care must be taken that the vapours are neither breathed nor allowed to come into contact with the hands.) Dilute sulphuric acid is then added, and the mixture evaporated until all the hydrochloric and hydrofluoric acids and nearly all the sulphuric acid have been driven off. After cooling, water is added, the mixture heated to boiling, a slight excess of chloride of barium added and then milk of lime to alkaline reaction. After repeated boiling, the solution is filtered and ammonia and carbonate of ammonia added to the filtrate as long as any precipitate is formed; after standing an hour, the precipitate is filtered off and the filtrate tested for potassa and soda according to § 168, *β*, and for lithia, cæsia, and rubidia according to the directions given on p. 92.

b. Decomposition by means of a metallic fluoride.—One part of the very finely pulverized mineral is mixed with 5 parts of fluoride of barium, or of pure, finely pulverized fluoride of calcium, or with 3 parts of fluoride of ammonium, and the mixture stirred with concentrated sulphuric acid, in a platinum crucible, to a thickish paste; it is then gently heated for some time in the open air or in a place where the fumes will be well carried away, and finally a little more strongly, until the excess of sulphuric acid is completely expelled. The residue is boiled with water, chloride of barium cautiously added as long as a precipitate continues to form, then milk of lime, &c., and treated as in *a*.

c. Decomposition by means of baryta.—One part of the very finely pulverized substance is mixed with 3 to 4 parts of carbonate of baryta and 2 of chloride of barium, and heated as strongly as possible for half an hour in a platinum crucible; the fused mass is soaked in water, boiled with a small quantity of milk of lime, filtered, precipitated with ammonia and carbonate of ammonia, and for the rest treated as in *a*. **229**

3. Examination for fluorine, chlorine, boric acid, phosphoric acid, arsenic acid, and sulphuric acid.

For this purpose, the portion of the fused mass reserved in 227 is employed, or, if necessary, a separate portion of the finely pulverized substance is fused with 4 parts of pure carbonate of soda and potassa mixture until the mass flows calmly; the melt is boiled with water, and the solution filtered; the filtrate contains all the fluorine as fluoride of sodium, all the chlorine as chloride of sodium, all the boric acid as borate, all the sulphuric acid as sulphate, all the arsenic acid as arsenate, and at least part of the phosphoric acid as phosphate of soda; it is treated as follows:— 230

a. A small portion is acidified with nitric acid, and tested for chlorine with nitrate of silver.

b. Another portion is tested for boric acid as directed in § 144, 6.

c. To detect fluorine, a third portion is treated as directed in § 146, 7.

d. The remainder is acidified with hydrochloric acid, and a small portion tested with chloride of barium for sulphuric acid; whilst the remainder is heated to 70°, and tested for arsenic acid by sulphuretted hydrogen. If there is no precipitate, the solution is evaporated to dryness, with addition of nitric acid; if a precipitate forms, the filtrate is treated in the same way; in either case the residue is taken up with nitric acid and water, and the solution examined for phosphoric acid with a solution of molybdate of ammonia in nitric acid (§ 142, 10).

C. Silicates which are Partially Decomposed by Acids.

§ 208.

Most rocks are mixtures of several silicates, of which very often some are decomposable by acids, others not. If such substances were analysed by the same method as the silicates insoluble in acids, the analyst would indeed detect all the elements present, but the analysis would afford no satisfactory insight into the actual composition of the rock. 231

It is therefore advisable to examine separately those constituents which behave differently with acids. For this purpose, the very finely pulverized substance is digested for some time with moderately concentrated hydrochloric acid at a gentle heat, a small portion of the solution is filtered off, and the remainder with the residue evaporated to dryness; it is then heated at 100°, or a little above, with constant stirring, until no more, or only very little, hydrochloric acid fumes are evolved, allowed to cool, moistened with hydrochloric acid, heated gently with water, and filtered.

The filtrate, which contains the bases of that part of the mixed mineral which has been decomposed by hydrochloric acid, is examined as directed in 221, and the portion first filtered off according to 222, γ. Portions of the original substance must be tested for other acids as directed in 222, α and β, and 223; and according to 224 to ascertain in what stage of oxidation the iron is. The residue, which, besides the silicic acid separated from the decomposed portion of the silicate, contains that part of the mixed mineral which has resisted the action of the hydrochloric acid, is boiled with an excess of solution of carbonate of soda, filtered hot, and washed, first with hot solution of carbonate of soda, and finally with boiling water. The undecomposed portion of the mineral, thus freed from the admixed separated silicic acid, is treated according to § 207, whilst the alkaline filtrate is acidified with hydrochloric acid, evaporated to dryness, treated with hydrochloric acid and water, and the silicic acid filtered off; the filtrate is now rendered alkaline with ammonia, and warmed; if a precipitate is formed, it should be treated with the separated silicic acid according to 221, to test it for titanic acid. In cases where it is of no interest to effect the separation of the silicic acid of the part decomposed by acids, the troublesome treatment with carbonate of soda may be omitted, and the examination of the residue proceeded with directly.

III. ANALYSIS OF NATURAL WATERS.

§ 209.

In the examination of natural waters the analytical process is 232 simplified by the circumstance that we know from experience what substances are usually present. Now, although a quantitative analysis alone can properly inform us of the true character of a water—since the differences between waters are principally caused by the different proportions of the constituents—still a qualitative analysis may render very good service, especially if the analyst notes whether a reagent produces a faint or a distinctly marked turbidity, a slight or a copious precipitate; as in this way an approximate estimation of the relative proportions of the constituents may be made.

The analysis of ordinary drinking waters is here treated separately from that of mineral waters, in which sea-water may also be included; for, although no sharply defined line can be drawn between the two classes, yet the analytical examination of the former is necessarily far simpler, as the number of substances to be looked for is much more limited.

A. Analysis of Potable Waters (Spring-water, Well-water, River-water, &c.)

§ 210.

From experience we know that the substances to be looked for 233 in the analysis of such waters are the following:—

a. Bases: Potassa, soda, ammonia, lime, magnesia, ferrous oxide.

b. Acids, &c.: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, nitrous acid, chlorine.

c. *Organic matter.*

d. *Mechanically suspended substances*: Clay, &c.

It cannot indeed be said that potable waters contain no other constituents; in fact, many others are present, as may be inferred from the origin and formation of springs, &c., and this has been fully established by the results of analytical investigations.[*] The quantity of such constituents, however, is so trifling that they usually escape detection, when pounds instead of hundredweights of the water are examined; the mode of their detection is therefore omitted here, and the student is referred for the manner of their detection, as also for that of the oxygen and nitrogen always present in potable waters, to § 211, and also to § 208, 10, and § 210, of the sixth edition of the QUANTITATIVE ANALYSIS.

1. The water is clear.

234 1. 1000 to 2000 grams of the carefully collected water is evaporated in a porcelain dish to one-half (glass vessels cannot be recommended, as boiling water attacks them much more than porcelain); this generally produces a precipitate. The liquid is poured on to a perfectly clean filter free from iron and lime, so that as much of the precipitate as possible may remain in the dish; the precipitate is well washed after the filtrate has been removed, and then both are examined as follows:—

a. *Examination of the precipitate.*

235 The precipitate contains those constituents of the water which were kept in solution by the free carbonic acid present, that is, in the form of bicarbonates—namely, carbonate of lime, carbonate of magnesia, ferric oxide (which was in solution as ferrous bicarbonate, and is precipitated on boiling as ferric hydrate, silicate, and in presence of phosphoric acid, also as phosphate), phosphate of lime; also silicic acid, sometimes sulphate of lime (if that substance is present in large proportion). A small quantity of hot dilute hydrochloric acid (1 : 3) is poured over the precipitate on the filter, the point of which has been previously pierced with a platinum wire, and the liquid passing through is collected in the dish which contains the main part of the precipitate formed on boiling. As a rule, effervescence takes place, due to the evolution of *carbonic acid*. The dish is then heated, and the solution, which is often somewhat turbid, is examined as follows:—

236 *α.* A small portion of the solution is tested for *iron* with sulphocyanate of potassium.[†]

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[*] *Chatin* (Jour. Pharm. Chim. [**3**], 27, 418) found iodine in all fresh-water plants, but not in land plants, so that the water of rivers, brooks, ponds, &c., must contain traces of metallic iodides, even though extremely minute. According to *Marchand* (Compt. rend., **31**, 495), all natural waters contain iodine, bromine, and lithia. *Van Ankum* has shown that iodine is present in almost all the potable waters of Holland. And it may be affirmed with the same certainty that all, or at all events most, natural waters contain compounds of strontia, baryta, fluorine, &c.

[†] When the presence of iron has to be detected with certainty, there must be

β. The remainder of the solution is evaporated to dryness in a small porcelain dish on the water-bath, the residue is moistened with a few drops of hydrochloric acid, water added, and the undissolved silicic acid filtered off. A small portion of the filtrate is evaporated with nitric acid to a small bulk, and tested for phosphoric acid with molybdic acid solution (§ 142, 10). A second portion is tested for sulphuric acid with barium chloride. Ammonia in excess is added to the remainder, it is filtered if necessary, oxalate of ammonia added, and the mixture allowed to remain for some time in a warm place. A white precipitate indicates lime (in the form of carbonate, or of sulphate if sulphuric acid has been detected in the solution obtained by boiling the precipitate with dilute hydrochloric acid). The precipitate is filtered off, the filtrate mixed with more ammonia, some phosphate of soda added, the mixture stirred with a glass rod, and allowed to stand for twelve hours. A white crystalline precipitate, which is often visible only on the sides of the vessel when the liquid is poured out, indicates magnesia (as carbonate).

b. Examination of the filtrate.

237 α. A little hydrochloric acid and chloride of barium is added to a portion of it. A white precipitate, which makes its appearance either at once or after standing some time, indicates sulphuric acid.

β. A portion is mixed with nitric acid, and nitrate of silver added; a white precipitate or turbidity indicates chlorine.

γ. A portion is tested for phosphoric acid, by evaporating with nitric acid, taking up with the same, and adding molybdic acid solution (§ 142, 10).

238 δ. A large portion is evaporated until highly concentrated; if the solution has an alkaline reaction, if a drop of the concentrated clear solution effervesces when mixed on a watch-glass with a drop of acid, and if carbonate of lime is precipitated on cautiously adding chloride of calcium to the alkaline liquid, then a carbonate of an alkali is present. Should this be the case, the solution is evaporated completely to dryness, the residue boiled with spirit of wine, filtered, and the solution evaporated to dryness; the residue is dissolved in a little water, and the solution tested for nitric acid as directed, § 159, 7, 8, 9, or 10.*

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no possibility of its introduction by dust, &c., during the evaporation. This is best effected by evaporating a sample of the water to a small bulk in a retort or flask, with a few drops of hydrochloric and a single drop of nitric acid. The concentrated solution is then tested directly with sulphocyanate of potassium.

* This somewhat tedious but accurate process is not always necessary; the nitric acid may often be found without trouble, by evaporating the water to a small residue, and testing this at once for it. Well-water will often give the nitric acid reaction with diphenylamine (§ 159, 10) or brucine (§ 159, 8) without concentrating.

ε. Some hydrochloric acid is added to the remainder of the filtrate, and it is evaporated to dryness, finally on the water-bath; the residue is moistened with a little hydrochloric acid, and water added; the mixture is then warmed, filtered from any residue of silicic acid, made alkaline with ammonia, and oxalate of ammonia added; it is then allowed to stand for some time; if there is any precipitate, it indicates lime. This is filtered off, and **239**

aa. A small portion of the filtrate is tested for magnesia by ammonia and phosphate of soda.

bb. The rest is evaporated to dryness, ignited, the magnesia which may be present is removed (**168**, β), and the solution tested for potassa and soda, according to **169** and **172**.

2. In order to test for ammonia, about 300 c.c. of the fresh water is placed in a glass cylinder, in a place free from ammonia vapours, 2 c.c. of a solution of carbonate of soda added (1 part of carbonate of soda and 2 parts of distilled water), and 1 c.c. of a solution of soda (1 part of soda and 2 parts of distilled water); the cylinder is then stoppered, and the mixture shaken and allowed to settle. 100 c.c. of the clear liquid is decanted or filtered (through a washed filter) into another cylinder, and 1 c.c. of the solution of potassio-mercuric iodide, and potassa (Nessler reagent), described on p. 90, *b*, is added. If a yellow colour or, by the addition of another c.c. of the Nessler reagent, possibly a reddish-brown precipitate is produced, the presence of a larger or smaller amount of ammonia is indicated. **240**

3. In order to test for nitrous acid,* 1 c.c. of dilute sulphuric acid and about 1 c.c. of potassium or zinc iodide and starch solution (see note *, p. 228) are added to about 50 c.c. of the fresh water. If a blue coloration appears immediately or in a few moments, the presence of a relatively large quantity of nitrous acid is indicated; if, however, the blue colour does not appear until after some time, only a small amount is present. The action of daylight, and especially of direct sunlight, must be carefully avoided during this examination, for otherwise a blue coloration may be produced even when nitrous acid is absent. It is advisable to use the precaution of performing a duplicate blank experiment with the same reagents on a water quite free from nitrous acid. If it is desired to still further increase the delicacy of the test, or if substances are present which may influence the direct test, a larger portion of the water may be acidified with acetic acid and distilled, the portion passing over first being tested as described (comp. § 158, 1). **241**

4. In testing for organic matter qualitatively, it is usually enough to evaporate 200 c.c. to dryness and gradually heat the residue. The presence of organic matter is shown by its browning or blackening. If the heating has not been carried too far, the carbonic acid which is evolved on adding dilute hydrochloric acid to the residue generally has an empyreumatic odour. If this

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* Compare § 205, 4 and 12, of the sixth edition of the Quantitative Analysis.

method is to give conclusive results, both the evaporation and the ignition must be conducted in a glass flask or retort.*

5. Fetid substances (decaying organic matter) are detected best by filling a bottle two-thirds with the water, covering it with the hand, shaking, and smelling. If there is an odour of sulphuretted hydrogen, proceed as directed in § 212, 3. It can be readily ascertained if there are other odorous organic matters present besides sulphuretted hydrogen, by adding a little sulphate of copper to the water before smelling it. 242

6. Another portion of the water, freshly taken, is mixed with lime water. If a precipitate is produced, free carbonic acid or bicarbonates are present. If free carbonic acid is present, no permanent precipitate is obtained when a large portion of the water is mixed with a little lime water only, since in that case soluble bicarbonate of lime is formed.

7. As oxide of lead may be present, arising from leaden pipes, a large quantity of the water is treated with sulphuretted hydrogen, and allowed to remain for some time; if a black precipitate forms, it is examined as directed in § 193. In order to detect very minute traces of lead, 6 or 8 litres of the water is acidified with acetic acid, and a little acetate of ammonia added to prevent the lead from being precipitated as sulphate; it is then evaporated to a small residue, filtered, and sulphuretted hydrogen passed into the filtrate, any black precipitate which may form being examined by § 193.

II. The water to be examined is not clear.

1. A large bottle of glass is filled with the water, stoppered, and allowed to stand in a cold and dark place until clear. The clear water is then siphoned off and tested according to I. 1, 4, and 6. 243

2. In order to test for ammonia (I. 2), nitrous acid (I. 3), volatile organic substances (I. 5), and lead (I. 7), fresh portions of the turbid water are taken, the nitrous acid being generally tested for by the distillation method; lead is tested for by passing sulphuretted hydrogen through a portion of the water which has previously been evaporated with acetic acid and sodium acetate, and filtered.

3. If it is desired to ascertain the nature of the substance rendering the water turbid, the residue remaining in the large bottle (II. 1), after siphoning off the clear water, is filtered, and the solid matter remaining on the filter examined. As this may consist of the exceedingly fine dust of different minerals, it is first treated with dilute hydrochloric acid, and the insoluble residue examined for silicates according to the method given at § 205.†

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* For more exact methods of detecting organic matter, see § 205, 11, of the QUANTITATIVE ANALYSIS (sixth edition), and for microscopic methods of research for bacteria, consult Hueppe, *Die Methoden der Bakterien-Forschung* (Wiesbaden, 1885).

† With regard to more accurate examinations, compare § 205, II. 2, of the sixth edition of the QUANTITATIVE ANALYSIS.

B. ANALYSIS OF MINERAL WATERS.

§ 211.

The analysis of mineral waters includes a larger number of constituents. The following are the principal of the additional substances to be looked for:— 244

Cæsia, rubidia, oxide of thallium, lithia, baryta, strontia, alumina, oxide of manganese, boric acid, titanic acid, bromine, iodine, fluorine, sulphuretted hydrogen (hyposulphurous acid),* crenic acid, and apocrenic acid (formic acid, propionic acid, &c., nitrogen gas, oxygen gas, and marsh gas).*

The analyst has moreover to examine the muddy ochreous or hard sinter-deposits of the spring, or the residue left on evaporating very large quantities of water, for arsenious acid, arsenic acid, teroxide of antimony, oxide of copper, oxide of lead, oxide of zinc, protoxide of cobalt, protoxide of nickel, and the oxides of other heavy metals. The greatest care is required in this examination, to ascertain whether these oxides come really from the water, and do not perhaps proceed from metal pipes, stopcocks, &c.† The absolute purity of the reagents employed in these delicate investigations must also be ascertained with the greatest care.

I. EXAMINATION OF THE WATER.

a. Operations at the Spring.

§ 212.

1. If not perfectly clear, the water is filtered through washed filter-paper (p. 7) into large bottles with glass stoppers. The sediment remaining on the filter, which possibly contains, besides the flocculent matter suspended in the water, also those constituents which separate at once on coming in contact with the air (hydrated ferric oxide, and compounds of ferric oxide with phosphoric acid, silicic acid, arsenic acid), is taken to the laboratory, to be examined afterwards according to § 214. 245

2. The presence of free carbonic acid is usually sufficiently visible to the eye. For additional evidence, the water may be tested with freshly prepared solution of litmus and with lime water. If carbonic acid be present, the former will change to a wine-red colour; the latter produces turbidity, which should disappear again on adding the mineral water in excess. 246

3. Free sulphuretted hydrogen is most readily detected 247

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[*] Respecting the constituents in brackets, the student is referred to the corresponding chapter in the QUANTITATIVE ANALYSIS (sixth edition), § 206 *et seq.*, as the detection of these substances generally comprises also their quantitative estimation.

[†] In this as in other subjects connected with the analysis of mineral matters the student is referred to the author's numerous analyses of mineral waters as noted on pp. 178–179 of the QUANTITATIVE ANALYSIS (sixth edition).

by the smell. For this purpose, a bottle is half filled with the mineral water, covered with the hand, shaken, and the contents smelt. In this way, distinct traces of sulphuretted hydrogen are often found which would escape detection by reagents. To test for it, a large white bottle is filled with the water, a few drops of solution of acetate of lead in soda added, and the bottle placed on a white surface; on looking in at the top, it can be readily seen whether the water has acquired a brownish colour or whether a blackish precipitate is formed. Another method of testing, which is also very delicate, depends on the formation of methylene blue, and is conducted as follows:—Fuming hydrochloric acid equal to $\frac{1}{50}$ of the volume of the water to be examined is first added, and then a small crystal of sulphide of paramidodimethylaniline; as soon as this is dissolved, 1 to 2 drops of a dilute solution of ferric chloride are added. If sulphuretted hydrogen is present, the water (which otherwise is of a clear red colour) becomes pure blue after a time (H. Caro, E. Fischer).

The formation of lead sulphide or of methylene blue is caused by alkaline sulphides as well as by free sulphuretted hydrogen; if, therefore, the alkaline properties of the water render the presence of the former probable, and the odour does not clearly indicate the presence of sulphuretted hydrogen, its presence may be detected by the following method:—A large bottle is half filled with the water and closed with a cork to which is attached a slip of paper previously saturated with solution of acetate of lead and then moistened with carbonate of ammonia; the bottle is shaken gently from time to time, and it is noted whether the paper acquires a brownish tint in the course of a few hours.

4. A sample of the water is mixed with some tannic acid, and **248**
another with some gallic acid; if the former imparts a red-violet, the latter a blue-violet colour, ferrous oxide is present. Instead of the two acids, infusion of galls may be employed, as it contains them both. The coloration makes its appearance only after some time, and increases in intensity from the top—where the air acts on the solution—downwards.

5. Nitrous acid and fetid organic substances are **249**
tested for according to **241** and **242**. If the water contains sulphuretted hydrogen, it must be removed before testing for nitrous acid, by adding some freshly precipitated and well-washed carbonate of lead, and filtering.

b. Operations in the Laboratory.

§ 213.

As it is always desirable to obtain, even in a qualitative examination, some information as to the proportions in which the several constituents are present, it is advisable to analyse a comparatively small portion for the principal constituents, and to ascertain, as far as may be practicable, the way in which these constituents are combined, and thus to determine the character of the water; then to examine a far larger portion for the constituents which are present in small quantity; and finally a very large portion or the sinter for those constituents which are present merely in traces. For this purpose proceed as follows:—

1. Examination for those Constituents which are present in Large Quantities.

a. About 1·5 litre of the clear water, or of the water filtered at the spring, is boiled for an hour in a porcelain dish (a flask is less suitable), taking care, however, to add from time to time some distilled water, so that the quantity of liquid may remain undiminished, and that only those salts may be thrown down by the boiling which were kept in solution by the carbonic acid present. It is then filtered, and the precipitate and the filtrate examined as directed § 210. 250

b. Ammonia, organic matters, &c., are also tested for by the methods given in § 210.

If from any cause the water is not fit to be tested directly for ammonia according to 240, it should be distilled with addition of some freshly boiled potassa or soda solution, and the distillate examined. It should be specially noted that the Nessler reaction for ammonia cannot be employed if the solution contains free carbonic acid, acid carbonates, or sulphides of the alkali metals (see p. 91).

2. Examination for those Fixed Constituents which are present in Minute Quantities.

A large quantity of the water (at least 10 litres) is evaporated in a silver or porcelain dish to dryness, in a place as free as possible from dust, and with the most scrupulous cleanliness. If the water contains no carbonate of an alkali, pure carbonate of potassa is added in slight excess. The evaporation may be conducted at first over a gas-lamp, but ultimately the sand-bath must be employed. The dry mass is heated to very faint redness: if it has been evaporated in a silver dish, it can be ignited in that; but if a porcelain dish has been employed, the residue must be transferred to a silver or platinum vessel before igniting. If the mass turns black during the heating, organic matters may be assumed to be present.* 251

The residue is thoroughly mixed, and divided into three portions, *a* and *b* being each about a quarter, and *c* one half.

a. Examination for phosphoric acid.

The portion *a* is warmed with water, pure hydrochloric acid added in sufficient excess, the whole evaporated on the water-bath to dryness, and the residue warmed with hydrochloric acid; it is then diluted slightly, filtered through paper which has been washed with hydrochloric acid and water, 252

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* This inference is, however, correct only if the water has been effectually protected from dust during evaporation; if this has not been done, and it is desired to ascertain beyond doubt whether organic matters are present, a separate portion of the water must be evaporated in a retort. If organic matter is found, and it is necessary to determine whether it consists of crenic acid or of apocrenic acid, a portion of the residue is treated as directed in § 214, 3.

evaporated with repeated addition of nitric acid to a small residue, and finally tested for phosphoric acid with a nitric acid solution of molybdate of ammonia (§ 142, 10).

b. Examination for fluorine.

253 The portion *b* is heated with water, and chloride of calcium added as long as a precipitate continues to form; this, which consists chiefly of carbonates of lime and magnesia, is allowed to settle, and then collected on a filter, washed, dried, and ignited. It is now treated with water in a small dish, acetic acid added in slight excess, the mixture evaporated to dryness on the water-bath, keeping the dish on the bath until all smell of acetic acid has disappeared; water is added, the mixture heated, the solution of the acetates of the alkaline earths filtered off, and the residue washed, dried, or ignited, and tested for fluorine as directed in § 146, 5.

c. Examination for the remaining fixed constituents present in minute quantities.

254 The portion *c* is boiled repeatedly with water, filtered, and the undissolved residue washed with boiling water. In this way a residue (α), and a solution (β) are obtained.

a. The *residue* consists chiefly of carbonate of lime, carbonate of magnesia, silicic acid, and—in the case of chalybeate springs—hydrated ferric oxide. It may also contain minute quantities of baryta, strontia, alumina, oxide of manganese, and titanic acid, and must accordingly be examined for these.

It is treated with water in a platinum or porcelain dish, hydrochloric acid added in slight excess, then 4 or 5 drops of dilute sulphuric acid, and the whole evaporated to dryness on the water-bath; the residue is moistened with a little hydrochloric acid, water added, the mixture warmed gently, filtered, and washed.

255 *aa.* Examination of the residue insoluble in hydrochloric acid. This will consist mostly of silicic acid; but it may contain also sulphates of the alkaline earths, titanic acid, and carbon. It is heated in a platinum dish repeatedly with hydrofluoric acid or fluoride of ammonium with addition of sulphuric acid, until all the silicic acid is expelled. It is finally evaporated to dryness, the residue (if any) fused with bisulphate of potassa, the melt treated with cold water, filtered, and the solution tested for titanic acid by protracted boiling. If any residue is left on treating the melt with water, it must be washed and the filter incinerated. If a spectroscope is to hand, the ash is taken up on the loop of a platinum wire, exposed for some time to the reducing flame, moistened with hydrochloric acid, and examined spectroscopically for baryta. Strontia will not be found here, or only in traces. When a spectroscope is not to hand, the ash must be set aside for subsequent examination.

bb. Examination of the hydrochloric acid solution. 256 This is mixed in a flask with pure chloride of ammonium, ammonia added until the liquid is just alkaline, then sulphide of ammonium free from ammonia; the flask, filled to the neck, is closed, and allowed to remain for twenty-four hours in a moderately warm place. If, at the end of that time, a precipitate has formed, it is filtered off, dissolved in hydrochloric acid, boiled, and potassa added (§ 34, *c*) in excess; the solution is boiled again, filtered, and the *filtrate* tested for alumina by acidifying with hydrochloric acid and heating with ammonia.* The *residue* is divided into two parts, of which one is tested for manganese with carbonate of soda before the blowpipe, the other for iron by dissolving it in hydrochloric acid and adding sulphocyanate or ferrocyanide of potassium.

The filtrate from the sulphide of ammonium precipitate may contain traces of manganese and bartya, and will contain all or nearly all the strontia. This solution is first of all acidified with hydrochloric acid, concentrated by evaporation, and any sulphur which may have been precipitated is filtered off; bromine water and a slight excess of ammonia are then added, and the solution heated. If after this treatment a slight brown precipitate is formed, this is caused by a trace of manganese, which has not been precipitated by the ammonium sulphide. The solution is then filtered, ammonia and carbonate of ammonia added to the filtrate, and after some time the precipitate is collected, washed, dried, and examined by Engelbach's method, described on p. 102. If a spectroscope is to hand, the aqueous extract obtained by boiling the ignited precipitate is evaporated to dryness with hydrochloric acid, and the residue examined spectroscopically for strontia and any traces of baryta which may be present. If a spectroscope is not available, the solution obtained by boiling the ignited residue with water is evaporated nearly to dryness with sulphate of ammonia, the residue boiled with a saturated solution of sulphate of ammonia, filtered, and the precipitate washed, dried, and incinerated; the residue set aside in 255 is added to it, and the whole fused with carbonate of soda, treated with water, washed, and the residue dissolved in hydrochloric acid and tested for baryta and strontia according to § 99.

β. The *alkaline solution* contains the salts of the alkalies, 257 and usually also magnesia and traces of lime. It has now to be examined for nitric acid,† boric acid, iodine,

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* There is no use in testing for alumina unless the evaporation has been effected in a platinum or silver dish.

† The nitric acid originally present may have been destroyed by the ignition of the residue in 251, if the latter contained organic matter. If it is suspected that such is the case, and nitric acid has not been already found in 250, a larger portion of the non-ignited residue is examined, according to 258.

bromine, and lithia. It is evaporated until *very* concentrated, allowed to cool, and the dish placed in a slanting position, so that the small quantity of liquid may separate from the saline mass; a few drops of the concentrated solution are transferred to a watch-glass by means of a glass rod, rendered just acid with hydrochloric acid, and tested with turmeric-paper for boric acid (§ 144, 6). The contents of the dish are now evaporated completely to dryness with stirring, and the residuary powder divided into two portions, *aa* being about two-thirds and *bb* one-third.

aa. The larger portion is tested for nitric acid, iodine, and bromine. 258

The residue is powdered, boiled thrice with alcohol of 90 per cent. in a flask heated on a water-bath, and each time filtered hot. After a few drops of potassa have been added to the alcoholic extract, the alcohol is distilled off almost entirely, and the residue allowed to cool. If minute crystals separate, these may consist of nitrate of potassa; the liquid is poured off from them, the crystals washed with a little spirit, dissolved in a very little water, and the solution tested for nitric acid, with diphenylamine, brucine, or indigo (§ 159). The alcoholic solution is now evaporated completely to dryness. If nitric acid has not yet been found, a small portion of the residue is dissolved in a very little water, and the solution tested for the acid. The remainder or, as the case may be, the whole of the residue is treated three times with warm alcohol, filtered, and the filtrate evaporated to dryness with addition of a drop of potassa; the residue is then dissolved in a very little water, acidified slightly with sulphuric acid, some pure bisulphide of carbon added, and then tested for iodine by a drop of solution of nitrous acid in sulphuric acid, or a very small quantity of a solution of nitrite of potassa. After the mixture has been shaken, and it has been carefully noted whether the bisulphide of carbon is coloured violet or reddish, indicating the presence of iodine, the same liquid is tested for bromine by the careful addition of chlorine water as in § 157.

bb. The smaller portion is tested for lithia. 259
For this purpose, the smaller portion of the residue, which, if lithia be present, will contain it as carbonate or phosphate, is warmed with water, hydrochloric acid added until the reaction is distinctly acid, the whole evaporated *nearly* to dryness, and then mixed with pure alcohol of 90 per cent., which will separate the greater portion of the sodium and potassium compounds, leaving all the lithia in solution. The alcohol is removed by evaporation, and, if a spectroscope is to hand, the residue is tested for lithia by its means (§ 93, 3). If a spectroscope is not available, the residue is dissolved in water and a few drops of hydrochloric acid, a little ferric chloride added, and

then sufficient milk of lime to render the solution strongly alkaline; the mixture is boiled, filtered, and the filtrate precipitated with oxalate of ammonia; the solution is then filtered, and the filtrate, which is now free from phosphoric acid and alkaline earths, is evaporated to dryness, and gently ignited until the salts of ammonia are expelled; the residue, to which a few drops of hydrochloric acid have been added, is treated with a mixture of absolute alcohol and dry ether, filtered, the filtrate concentrated by evaporation, and the alcohol set on fire; if it burns with a carmine flame, lithia is present. By way of confirmation, the lithia is converted into phosphate. The residue left on evaporating the substance with phosphate of soda and caustic soda, and treating the product with ammonia and water, cannot, however, be considered as phosphate of lithia until it has been examined to ascertain whether it exhibits the characteristic properties of that substance (§ 93, 3).

3. Examination for those Constituents which are present in Very Minute Quantities.

From 100 to 150 litres of the water is evaporated in a large perfectly clean iron pot until the salts soluble in water begin to separate. If the mineral water contains no carbonate of soda, sufficient of it is added to render the liquid distinctly alkaline. After evaporation, the solution is filtered and the precipitate washed, but the washings are not added to the filtrate. **260**

a. The precipitate is examined by the method given in § 214 for sinter-deposits;

b. Hydrochloric acid is added to the solution to acid reaction; it is then heated, and the sulphuric acid which may be present is carefully precipitated with chloride of barium; the solution is filtered, the filtrate evaporated to dryness, the residue digested with alcohol of 90 per cent., and the solution examined for cæsium and rubidium according to § 93, last paragraph, pp. 92-93. The residue insoluble in alcohol is dissolved in water and ammonia, then added to the hot concentrated solution in slight excess; if a precipitate is formed, this is removed by filtration, and iodide of potassium added to the hot solution containing but little free ammonia. If a precipitate is formed either immediately or after a time, it is tested spectroscopically for thallium (§ 113, *b*).

II. EXAMINATION OF THE SINTER-DEPOSIT.

§ 214.

1. The deposit is freed from impurities by picking, sifting, elutriation, &c., and from the soluble salts adhering to it, by washing with water, and a large quantity (about 200 grams) is digested with water and hydrochloric acid (effervescence indicates carbonic acid), at a very moderate heat, until all that is soluble is com- **261**

pletely dissolved; it is then diluted, allowed to cool, filtered, and the residue washed.

a. Examination of the filtrate.

a. The larger portion is heated to 70°, and sulphuretted hydrogen passed into it for some time and also during cooling; it is then allowed to remain in a moderately warm place until the odour of the gas is almost gone, when it is filtered. 262

After the precipitate is washed and dried, the greater part of the free sulphur is removed by digesting and washing it with bisulphide of carbon; it is then warmed gently with yellow sulphide of potassium, diluted, filtered, washed with water containing sulphide of potassium, and the filtrate and washings precipitated with hydrochloric acid. The precipitate is allowed to settle, collected, washed, dried, again extracted with bisulphide of carbon, and the residue, if any, together with the filter, is treated in a small porcelain dish with pure red fuming nitric acid; the mixture is warmed until the greater part of the acid is expelled, excess of carbonate of soda added, then a little nitrate of soda, and the mixture fused; the melt is treated with cold water, filtered, washed with diluted alcohol, the aqueous solution tested for arsenic acid by **121** and **122**, and the residue for antimony and tin by dissolving it in dilute hydrochloric acid and treating the solution in a platinum capsule with zinc free from lead (**123**). 263

If there is a residue on treating the sulphuretted hydrogen precipitate with sulphide of potassium, it must be washed, removed from the filter by a jet of water, and boiled with a small quantity of dilute nitric acid; the mixture is filtered, washed, and what remains on the filter is treated with a hot solution of acetate of ammonia so as not to miss sulphate of lead which may possibly be present. The filtrate is tested for lead with sulphuretted hydrogen, whilst the residue on the filter, if there is any, is examined for baryta and strontia according to **256**. The nitric acid solution is mixed with a little pure sulphuric acid, evaporated to dryness on a water-bath, and tested according to **132** for lead, copper, and other metals of the fifth group which may be present. 264

A portion of the filtrate from the sulphuretted hydrogen precipitate is evaporated to dryness with excess of nitric acid on a water-bath, the residue treated with nitric acid and water, filtered, and the solution tested for phosphoric acid with molybdic acid solution. 265

A second portion is evaporated, nitric acid being added at the close of the operation in order to convert into ferric chloride, most of the ferrous chloride usually present; a slight excess of ammonia is then added, the solution warmed, filtered, and the precipitate washed, dried, powdered, and ignited for some time in a stream of hydrogen at a sufficiently high temperature so as to convert the ferric oxide into metallic iron; the residue is then treated with very dilute nitric acid (1 part of nitric acid to 30 of water) until the iron is dissolved. Any insoluble residue is fused with acid sulphate of potassa, the melt treated with cold water, filtered, and the filtrate boiled for some time. If a white precipitate is formed, it indicates the presence of titanic acid (§ 104, 8).

The remainder of the filtrate from the sulphuretted hydrogen precipitate is transferred to a flask, chloride of ammonium added, then ammonia until the liquid is just alkaline, and lastly sulphide of ammonium containing no free ammonia; the flask, filled to the neck, is tightly corked and allowed to remain in a moderately warm place until the supernatant fluid is yellow without a shade of green, the precipitate is then collected and washed with water containing sulphide of ammonium, treated with dilute hydrochloric acid, and examined for cobalt, nickel, iron, manganese, zinc, alumina, and silica according to **152–160**.

Carbonate and oxalate of ammonia are added to the filtrate from the sulphide of ammonium precipitate, to throw down the lime and strontia and any baryta which may be present; the precipitate is tested for strontia and baryta by Engelbach's method (p. 102). Lastly, the filtrate from the lime precipitate is tested for magnesia.

β. A portion of the hydrochloric acid solution is considerably diluted, chloride of barium added, and the mixture allowed to remain for twelve hours in a warm place; a white precipitate indicates sulphuric acid.

b. Examination of the residue.

This usually consists of sand, hydrated silicic acid, clay, **266** and organic matters; it may also contain sulphur if the water is hepatic, and sulphates of baryta and strontia. The residue is boiled with a solution of carbonate of soda and caustic soda, to dissolve and remove the hydrated silicic acid and sulphur, collected, well washed, and treated on the filter with dilute hydrochloric acid to dissolve the baryta and strontia and leave the clay and sand. The hydrochloric acid solution is tested for baryta and strontia according to **256**.

2. To test for fluorine, it is best to take a separate portion of **267** the deposit; this, if there is not too much carbonate of lime present, is mixed with about half its weight of pure hydrate of lime, and ignited (blackening indicates organic matter); water is added, and then acetic acid in excess, the whole evaporated until the excess of acid is expelled, and the residue examined as directed in **253**.

3. The deposit is boiled for a considerable time with concen- **268** trated potash or soda, and filtered.

a. A portion of the filtrate is acidified with acetic acid, ammonia added, the whole allowed to remain for twelve hours, and then the precipitate of alumina and hydrated silicic acid, which usually forms, is filtered off. Acetic acid in excess is again added to the filtrate, and then solution of neutral acetate of copper; if a brownish precipitate is formed, this consists of apocrenate of copper. To the filtrate from this precipitate carbonate of ammonia is added until the green colour has changed to blue, and the solution is warmed; if a bluish-green precipitate is produced, this is crenate of copper.

b. If arsenic has been found (263), the remainder of the alkaline liquid is used to ascertain whether the arsenic existed in the sinter as arsenious acid or as arsenic acid. (Comp. § 134, 11.)

IV. ANALYSIS OF SOILS.

§ 215.

Soils must necessarily contain all the constituents which are found in the plants growing upon them, with the exception of such as are derived from the atmosphere and the rain. When we find, therefore, a plant, the constituents of which are known, growing in a certain soil—a bare rock, for example—the mere fact of its growing there gives us some insight into the composition of that soil, and may accordingly save us, to some extent, the trouble of a qualitative analysis.

Viewed in this light, it would appear quite superfluous to make a qualitative analysis of soils still capable of producing plants, as the ashes of plants almost invariably contain the same constituents, the differences between them being caused principally by differences in the relative proportions in which the several constituents are present. But if, in the qualitative analysis of a soil, regard is had also to the proportions of the constituents, and to the state in which they are present, an analysis of the kind, if combined with an examination of the physical properties of the soil, and a mechanical separation of its parts,* may give most useful results, enabling the analyst to judge sufficiently of the condition of the soil to supersede the necessity of a quantitative analysis, which would require much time, and is a far more difficult task.

As plants can only absorb substances in a state of solution, it is a matter of especial importance, in the qualitative analysis of a soil, to know which constituents are soluble in pure water; † which require

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* With regard to the mechanical separation of the component parts of a soil, and the examination of its physical properties and chemical condition, compare F. Schulze, Jour. pr. Chem., **47**, 241; also the QUANTITATIVE ANALYSIS (fifth edition), § 263, and E. Wolff, Zeit. anal. Chem., **3**, 85; also Wolff's *Anleitung zur chem. Untersuchung landwirthschaftlich wichtiger Stoffe*, third edition (Berlin, 1875); and W. Knop, Zeit. anal. Chem., **13**, 88.

† It was formerly universally assumed that substances soluble in water, or in water containing carbonic acid, circulated freely in the soil so long as there existed agents for their solution; but since it has been discovered that arable soil possesses, like charcoal, the property of withdrawing from dilute solutions the compounds dissolved in them, this notion is exploded, and we now know that arable soil will retain with a certain force substances otherwise soluble—from which we conclude that the aqueous extract of a soil cannot be expected to contain the whole of the substances present in that soil in a state immediately available for the plant. Least of all can we expect to find these matters in the aqueous extract in the same proportion in which they are present in the soil, since the latter will readily give up to water those substances in regard to which its power of absorption has been

an acid for their solution (in nature principally carbonic acid); and, finally, which are insoluble both in water and in acids, and, consequently, are not in a position for the time being to afford nutriment to the plant. With regard to the insoluble substances, another interesting point is to ascertain whether they suffer disintegration readily, or slowly and with difficulty, or whether they altogether resist the action of disintegrating agents; and also what are the products which they yield when disintegrated.

In the analysis of soils, therefore, the constituents soluble in water, those soluble in acids, and the insoluble constituents, must be examined separately. The examination of the organic matters present also demands a separate process.

The analysis is therefore properly divided into four parts.

1. Preparation and Examination of the Aqueous Extract.

§ 216.

About 1000 grams of the air-dried soil is used for this purpose. To prepare a clear aqueous extract is somewhat difficult if, in the usual way, the earth is digested or boiled with water, and then filtered, the fine particles of clay impeding the operation by choking up the pores of the filter; they also almost invariably render the filtrate turbid, at least the portion which passes through first. The following method, proposed by F. Schulze (see note,* p. 352), is the most practical:—The necks of several middle-sized funnels are closed with small filters of strong filter-paper; these are moistened, and the paper pressed close to the sides of the funnel; the air-dried soil is then introduced, in small lumps ranging from the size of a pea to that of a walnut, but not pulverized, or even crushed, filling the funnels about two-thirds. Distilled water is now poured in in quantity sufficient to cover the soil; if the first portion of the filtrate is turbid, it must be poured back into the funnel, and the filtration allowed to proceed quietly; the funnels are again filled with water, and this process of extraction is continued until the filtrates weigh twice or three times as much as the soil used (2–3 litres). The several filtrates are mixed in one vessel, and a portion of the washed soil is kept. **269**

The aqueous solution is divided into two parts, 1 (about two-thirds) and 2 (about one-third).

1. The larger portion is evaporated in a porcelain dish to a small bulk, and tested as follows:—

> *a.* A portion is filtered, and the reaction of the filtrate tested; a part is set aside to test for organic matter (**280**), and the rest is warmed and nitric acid added; effervescence indicates an alkaline carbonate; the acid solution is then tested for chlorine with nitrate of silver. **270**

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satisfied, whilst it will more or less strongly retain others. But although, for this reason, the examination of the aqueous extract of a soil has no longer the same value as it was formerly considered to have, yet it is still useful to ascertain what substances a soil will actually give up to water. It is for this reason that the section on the preparation and examination of the aqueous extract has been retained.

b. The rest of the concentrated solution from 1, together with the precipitate which it usually contains, is transferred to a small dish, preferably of platinum, evaporated to dryness, and the brownish residue cautiously heated until the organic matter is destroyed. In the presence of nitrates, a slight deflagration will be perceptible. The gently ignited residue is examined as follows :— **271**

α. A small portion is mixed with carbonate of soda, and tested for manganese in the oxidizing flame (§ 107, 13).

β. The rest is warmed with water, hydrochloric acid added (effervescence indicates carbonic acid), the whole evaporated to dryness to separate silicic acid, then moistened with hydrochloric acid, water added, and the mixture warmed and filtered.

aa. The residue, which generally contains a little carbon, a little clay (if the aqueous extract was not clear), and also silicic acid, is washed, and the silicic acid tested for by piercing the filter, washing the residue through, boiling it with caustic soda, filtering, saturating with hydrochloric acid, evaporating to dryness, and finally taking up the residue with water, when the silicic acid will be left behind.

bb. A part of the hydrochloric acid solution is tested for sulphuric acid with chloride of barium; and a second portion is evaporated with nitric acid and tested for phosphoric acid by the nitric acid solution of molybdate of ammonia. A third portion is tested for iron with sulphocyanate of potassium, whilst a few drops of ferric chloride are added to the remainder (to remove phosphoric acid), then ammonia until slightly alkaline, the whole warmed a little, filtered, the lime thrown down with oxalate of ammonia, and the solution examined for magnesia, potassa, and soda in the usual way (§§ 196, 197). Lastly a small quantity of the pure alkaline chlorides should be examined spectroscopically for lithia.

Alumina is not likely to be found in the aqueous extract (F. Schulze never found it). If, however, it is desired to test for it, the precipitate produced by ammonia is boiled with pure potassa in a platinum or silver dish, filtered, the filtrate acidified with hydrochloric acid, and then warmed with ammonia. **272**

2. If iron has been found, part of the smaller portion (No. 2, **269**) is acidified with hydrochloric acid, half of it tested with ferricyanide of potassium, and the other half with sulphocyanate of potassium, to see in what state of oxidation the iron is present. The rest of the aqueous extract is tested for nitric acid, ammonia, and nitrous acid according to § 159, 7, 8, or 10 (also p. 341). **273**

2. Preparation and Examination of the Acid Extract.

§ 217.

About 50 grams of the soil from which the part soluble in water has been removed as far as practicable* is heated with moderately strong hydrochloric acid (effervescence indicates carbonic acid) for several hours on the water-bath, and filtered. The filtrate, which is generally yellow from the presence of ferric chloride, is examined as follows:— 274

1. A small portion is tested with sulphocyanate of potassium for ferric oxide; another with ferricyanide of potassium for ferrous oxide. 275

2. A portion is evaporated to dryness, the residue heated to a little above 100°, then moistened with hydrochloric acid, water added, and the whole warmed; more water is now added, and the silicic acid separated by filtration; this is often coloured, owing to the presence of organic matter, but becomes colourless on ignition in the air. A portion of the filtrate is tested for sulphuric acid with chloride of barium, whilst the remainder is evaporated to dryness repeatedly with nitric acid to a small bulk, and the solution tested for phosphoric acid by a solution of molybdate of ammonia in nitric acid.

3. A larger portion is employed for the detection of iron, manganese, alumina, lime, magnesia, potassa, and soda, in the usual way, proceeding according to **134** if there is only a small amount of organic matter present in the hydrochloric acid solution; otherwise the method given in **161** should be employed. 276

4. If it is a matter of interest to ascertain whether the hydrochloric acid extract contains arsenic acid, oxide of copper, &c., the remainder of the solution is treated with sulphuretted hydrogen, &c., as directed in **262–264**. 277

5. If it is thought desirable to test for fluorine, this is best done in a fresh portion of the ignited earth according to **230**.

3. Examination of the Inorganic Constituents Insoluble in Water and Acids.

§ 218.

The operation of heating the lixiviated soil with hydrochloric acid (**274**) always leaves the greater portion of it undissolved. If it is wished to submit this undissolved residue to a chemical examination, it must be washed, dried, and sifted, to separate the stones from the clay and sand, the last two being separated from each other by elutriation. The several portions are then examined by the methods given for silicates (§ 205). 278

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* Complete lixiviation is generally impracticable.

4. Examination of the Organic Constituents of the Soil.

§ 219.

The organic constituents of the soil, which have such a great influence on its fertility, both from their physical properties and chemical action, are partly portions of plants in which the structure may still be recognized, such as fragments of straw, roots, seeds of weeds, &c., partly products of the decomposition of vegetable matter usually called by the general name of humus. These differ, however, in their constituent elements and properties according to whether they result from the decay of the nitrogenous or the non-nitrogenous parts of plants—whether alkalies or alkaline earths have or have not had a share in their formation—whether they are in an incipient or in a more advanced stage of decomposition. To separate these several component parts of humus, which have been by no means thoroughly investigated, and which are not sharply characterized, would be an exceedingly difficult and unprofitable task. The following operations are amply sufficient to answer all the purposes of a qualitative analysis. 279

a. Examination of the Organic Substances Soluble in Water.

The portion of **270** reserved is evaporated on the water-bath completely to dryness, and the residue treated with water. The ulmic, humic, and geic acids, which were present in the solution in combination with bases, remain undissolved, whilst crenic and apocrenic acids are dissolved in combination with ammonia (Berzelius); for the manner of detecting the latter acids see **268**. 280

b. Treatment with Alkaline Carbonate.

A portion of the soil which has been exhausted with water is dried and sifted to separate the fragments of straw, roots, &c., and the small stones, from the finer part; the latter is digested for several hours at 80–90° with solution of carbonate of soda, and filtered; the filtrate is then acidified with hydrochloric acid, and, if brown flakes separate, these consist of ulmic acid, humic acid, or geic acid. The larger the proportion of ulmic acid present, the lighter will be the colour of the precipitate, whilst a darker brown indicates more humic or geic acid. 281

c. Treatment with Caustic Alkali.

The soil which has been boiled with solution of carbonate of soda (*b*) is washed with water, boiled for several hours with potassa, replacing the water as it evaporates, then diluted, filtered, and washed. The brown solution is treated as in *b*. The ulmic and humic acids which are thrown down have been produced by the action of the boiling potassa on ulmin and humin. 282

V. DETECTION OF INORGANIC SUBSTANCES IN PRESENCE OF ORGANIC SUBSTANCES.

§ 220.

It will be easily understood that the presence of coloured or mucilaginous organic substances may so far interfere with the analysis that it cannot be carried out until the organic matter has been totally destroyed; as, for instance, a change of colour or a precipitate cannot be distinguished in a dark-coloured liquid, whilst the presence of slimy matter may render filtration impossible. Difficulties of this kind are of constant occurrence in the examination of medicines, in the analysis of articles of food or of the contents of a stomach for inorganic poisons, as well as in the analysis of the inorganic constituents of vegetable or animal substances. In the following pages a general method will be given first, and then special cases will be considered.

1. General Rules for the Detection of Inorganic Substances in Presence of Organic Matters, which by their Colour, Consistence, or other Properties, impede the Application of the Reagents, or obscure the Reactions produced.

§ 221.

The description here is confined, of course, to the most generally applicable methods, leaving the modifications which circumstances may require in special cases to the discretion of the analyst.

1. The substance is soluble in water, but the solution is dark-coloured or of a slimy consistence. 283

a. A portion of the solution is heated with hydrochloric acid on the water-bath, and chlorate of potassa gradually added until the mixture is decolorized and perfectly fluid; it is then heated until it no longer smells of chlorine, diluted with water, and filtered. The filtrate is examined in the usual way, commencing at § 190 (compare also § 225). It is hardly necessary to say that the original state of oxidation of the metals cannot be determined, since mercurous oxide, stannous oxide, and ferrous oxide would be converted by treatment with chlorate of potassa and hydrochloric acid into mercuric chloride, stannic chloride, and ferric chloride respectively.

b. Another portion of the solution is boiled for some time with nitric acid, filtered, and the filtrate tested for silver and potassa. If the ready and complete destruction of the colouring and slimy matters, &c., can be effected by means of nitric acid, this method of treatment is often preferable to any other.

c. Alumina and sesquioxide of chromium might escape detection by this method, because ammonia and sulphide of ammonium do not precipitate these oxides from liquids containing non-volatile organic substances with certainty and completely. If there is reason to suspect the presence of these oxides, a third portion of the substance is mixed with carbonate of soda and chlorate of potassa, and the mixture thrown in small portions at a time into a red-hot crucible. When the mass is cold, it is treated with water, and the solution examined for chromic acid and alumina, the residue for alumina (§ 103).

d. A separate portion is tested for ammonia with hydrate of lime.

e. Another portion is submitted to dialysis and the dialysate is examined for acids, and also as to the state of oxidation of the metals present.

2. The substance is insoluble or only partly soluble in boiling water; the solution can be filtered. 284

It is filtered, and the filtrate treated either as directed in § 189, or, should it require to be decolorized, according to **283**. The nature of the residue may vary.

a. It is fatty or resinous. The fat or resin is removed by means of ether, light petroleum, carbon bisulphide, or other suitable solvent, but this, if possible, should not be miscible with water. The solution formed is separated from any residue, and shaken up first with water alone and then with water acidified with hydrochloric or nitric acid, and the solutions thus obtained examined in the usual way. If, after the treatment with ether or other solvent, a residue remains, it must be examined according to *b.*

b. It has a different character to the above; for example, wood-fibre, &c.

α. In this case, any substances present soluble in acids are first of all extracted by means of hydrochloric or nitric acid or by aqua regia; the solution, if necessary, may be decolorized by passing chlorine through it, or by heating with bromine or chlorate of potassa, and is then examined for bases and acids in the ordinary way. If a residue insoluble in aqua regia remains, it is washed with water, dried, and if sulphur is present it is extracted with warm carbon bisulphide and filtered. The residue is cautiously incinerated, and the ash tested according to § 203.

β. In order to test for metals whose compounds are not volatile either at a moderate red heat alone or when mixed with carbon,* a portion of the residue insoluble in water may be partially or completely incinerated in a porcelain or platinum dish, avoiding too high a temperature. The residue is then warmed with hydrochloric acid and a little nitric

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* Under these circumstances, compounds of mercury, arsenic, cadmium, and zinc are volatile, and, at a bright red-heat, lead and antimony also.

acid, the solution diluted with water, and examined according to § 190; if there is any residue, it is examined according to § 203.

γ. The remainder is tested for ammonia, by triturating with hydrate of lime.

3. The substance does not admit of filtration or any other means of separating the dissolved from the undissolved part. **285**

In this case, the same process is employed as for the residue in **284** insoluble in water.

As regards the charred mass, **284** *b*, *β*, it is often advisable to boil the mass, carbonized at a gentle heat, with water, filter, examine the filtrate, wash the residue, incinerate it, and examine the ash.

4. A method which is very generally applicable for the detection of metallic oxides when mixed with organic matter has been proposed by E. Millon.* The substance in small pieces is put into a tubulated retort with about four times its weight of pure sulphuric acid; the retort should not be more than one-third full. The mixture is then slowly heated until it is homogeneous, when nitric acid is introduced by degrees through a funnel tube placed in the tubulure of the retort, at the same time gradually increasing the temperature; the object of this first operation is to decompose the chlorides, which takes about half an hour. The contents of the retort is now heated in a platinum dish until the sulphuric acid, which by degrees loses its black colour and turns orange or red, begins to escape. More nitric acid is now added in small portions; after each addition the liquid will be decolorized, but it again turns darker on further heating. The addition of nitric acid is continued until this coloration no longer occurs, and the sulphuric acid is then expelled and a pure white saline mass is left which can be analysed in the usual way. According to Millon, if the heat is moderated towards the end, none of the arsenic or mercury will be lost; this can only be depended on, however, if the amount of chlorides present is small.

5. If salts have to be detected in the presence of organic compounds which belong to the class of colloïds, dialysis may frequently be resorted to with great advantage (§ 8).† According to circumstances, the substance may be either placed directly in the dialyser, or first warmed with hydrochloric acid or with hydrochloric acid and chlorate of potassa (comp. also § 224).

6. If colouring matters (especially aniline colours), textile fabrics, hangings, &c., have to be examined specially for arsenic, the following method may be always employed for the purpose. If the colouring matter itself is to be

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* Journ. Pharm. Chim., **46**, 33. Zeit. anal. Chem., **4**, 208. For Pouchet's modification of Millon's process, see Zeit. anal. Chem., **21**, 306.

† Compare O. Reveil, Zeit. f. anal. Chem., **4**, 266; Bizio, *ibid.*, **4**, 51; Riederer, *ibid.*, **7**, 517; H. Struve, *ibid.*, **24**, 72.

examined, it is mixed with 2 parts of carbonate of soda and 2 parts of nitrate of soda, or the fabric or hangings may be saturated with a concentrated solution of this mixture and then thoroughly dried. Some nitrate of soda is then fused in a porcelain dish, and the substance to be examined, prepared as above, is gradually added, the heating being continued, and fresh nitrate of soda added from time to time if necessary. By this means a fused mass is obtained free from carbon and organic compounds. When cold, this is digested with water, the alkaline solution filtered off, the residue washed, and sufficient dilute sulphuric acid added to the filtrate and washings to decompose all carbonates, nitrites, and nitrates present; the solution is then evaporated, at first on the water-bath, and subsequently at a higher temperature, until thick fumes of sulphuric acid begin to come off; it is then cooled, diluted, and filtered. This filtrate may now be either introduced into a Marsh's apparatus at once in order to test it for arsenic (§ 132, 10), or a few drops of hydrochloric acid may be added, sulphuretted hydrogen passed, and the precipitate obtained may be examined according to 300. It is easy to see that in many cases a more simple method may be used in order to obtain a solution which can be directly examined in a Marsh's apparatus. Of the various methods recommended for this purpose H. Fleck's[*] is the only one that will be mentioned here.

The substance to be examined is cut up and digested for from eighteen to twenty-four hours with 50 to 100 grams of pure 25 per cent. sulphuric acid, at a temperature of 50° to 60°. If, after this digestion, any coloured residue is perceived, which, however, is very rarely the case, 3 to 5 grams of pure nitric acid 1·24 sp. gr. should be added to each 100 grams of the 25 per cent. sulphuric acid, and the digestion continued until all coloured particles are destroyed. The solution is then filtered, the residue washed, and the filtrate and washings made up to 200 c.c. and tested in a Marsh's apparatus, adding it in portions of 20 c.c. at a time. If nitric acid has been employed, the solution must be evaporated until the acid is all driven off before diluting to 200 c.c.[†]

2. Detection of Inorganic Poisons in Articles of Food, in Dead Bodies, &c., in Chemico-legal Cases.[‡]

§ 222.

The chemist is sometimes called upon to examine an article of 286
food, the contents of a stomach, a dead body, &c., with a view to detect the presence of some poison, and thus to establish the fact of poisoning; but it is more frequently the case that the question put to him is of a less general nature—that of determining whether a certain substance placed before him contains a metallic poison; or, still more limited, whether it contains arsenic or hydrocyanic

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[*] Zeit. anal. Chem., **22**, 474.

[†] With respect to other methods, compare H. Hager, Zeit. anal. Chem., **11**, 478; G. Thomas, *ibid.*, **20**, 475; E. Lyttkens, *ibid.*, **22**, 147.

[‡] Compare Fresenius, Ann. Chem. Pharm., **49**, 275; and Fresenius and v. Babo, on the quantitative estimation of arsenic, Ann. Chem. Pharm., **49**, 287.

acid, or some other particular poison—as it may be that the symptoms point clearly in the direction of that poison, or that the examining magistrate has, or believes he has, some other reason to put this question.

It is obvious that the more special and pointed the question the easier it is to answer. The analyst, however, will always act more prudently, even in cases where he is simply requested to state whether a certain poison—arsenic, for example—is present or not, if he adopts a method of examination which will not only enable him to detect the one poison named, the presence of which may perhaps be suspected on insufficient grounds, but will moreover inform him as to the presence or absence of other similar poisons.

This must not be carried too far, however; for, although unquestionably we might succeed in elaborating, at the writing-desk, a method which would include all poisons, practical experience would but too speedily convince us that the complexity inseparable from such a course would be incompatible with easy execution and certainty in the results; to such an extent, indeed, that the drawbacks would be greater than the advantages derivable from it.

Moreover, the attendant circumstances usually afford at least a tolerably safe inference as to the group to which the poison belongs. From this point of view, the following processes will be described:—

1. A method which ensures the detection of the minutest traces of arsenic in medico-legal cases with certainty, allows of its quantitative determination, and permits at the same time the detection of all other metallic poisons.

2. A method for the detection of hydrocyanic acid, which leaves the original substance still fit to be examined both for metallic poisons and for alkaloïds.

3. A method of detecting phosphorus, which does not interfere with the examination for other poisons.

This part of the work does not, therefore, profess to supply a complete guide in every possible case of medico-legal investigations, but the instructions given in it have been practically tried and proved by the author. Moreover, they will generally be found sufficient, the more so as in the section on the alkaloïds a description is given of the best processes for their detection in criminal cases.

If there are no indications at all as to the kind of poison to be looked for, so that it is necessary to search for all poisons, both organic and inorganic, the substance must be carefully examined, both with the naked eye and with a microscope, noting also the odour, reaction, &c.; then, if the circumstances do not point to examining different portions for the different classes of poisons, it should be tested for hydrocyanic acid and phosphorus (a distillation usually suffices for the detection of both), afterwards for alkaloïds, and finally for metallic poisons. If there are several different substances, as food, vomit, contents of the stomach, of the intestines, the brains, and internal organs, liver, spleen, &c., they should, as a rule, be examined individually. It is always necessary as a matter of caution to reserve one-third of each, after weighing and mixing, for contingencies, and also for finally determining in what form of combination the poison is present.

I. Method for the Detection of Arsenic (with due Regard to the Possible Presence of other Metallic Poisons.)

§ 223.

Of all metallic poisons, arsenic is the most dangerous, and at the same time that most frequently used, more particularly for criminal purposes. Again, among the compounds of arsenic, arsenious acid (white arsenic) occupies the first place, because it kills even in small doses, it has little or no taste, and it is but too readily procurable. 287

As arsenious acid is only sparingly soluble in water, and—on account of the difficulty with which it is moistened—dissolves but very slowly, the greater portion of what has been swallowed usually remains in the body undissolved; as, moreover, the smallest particle of it may be readily detected by means of an exceedingly simple experiment; and lastly, as—even if arsenic is present in other forms, in ochre colouring-matters, &c.—this much is certain, that *arsenious acid in grains or powder* can never be normally present in food, in the human body, or in decayed coffins,* the analyst ought always to take especial pains to detect arsenious acid itself, and this can usually be done. Metallic arsenic, which is sometimes used for poisoning, may also be found if present.

A. Method for Detecting Undissolved Arsenic Acid or Metallic Arsenic.

1. If food, vomit, or some other matter of the kind has to be examined, it is first weighed and then mixed as uniformly as possible; one-third is put aside for contingencies, whilst the other two-thirds is stirred up in a porcelain dish with distilled water, allowed to remain a short time, and the liquid portion, together with the lighter suspended particles, is poured off into another porcelain dish. This process of lixiviation is repeated several times, if possible with the same liquid, pouring it from the second dish back into the first, and so on. Lastly, it is washed once more with pure water, best in a glass dish, and the liquid removed as far as practicable; the residue in the dish must now be carefully examined to ascertain if any small, white, hard grains are present, which feel gritty under the glass rod (arsenious acid), or any black grains or scales (metallic arsenic). If this is not the case, proceed as directed in § 224 or § 225. If anything of the kind is found, however, the grains, or some of them, must be picked out with a 288

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* The author once had to examine the completely decomposed remains of a child which had been long buried, a small coffin painted with ochre having been used. The cover of the coffin had rotted, and the decayed wood was mingled with the remains of the child. The contents of the coffin contained a small quantity of arsenic, but not more than the ochre-colour on a surface of the coffin equal to the part which had fallen in.

pair of pincers, or, if they are very minute, they may be washed in a watch-glass, dried, weighed, and a small portion heated in a glass tube. With arsenious acid, a white sparkling sublimate is formed, consisting of octahedrons and tetrahedrons, whilst metallic arsenic yields an arsenical mirror. In the former case, another small portion is heated with a charcoal splinter, as in § 132, 2, and if an arsenical mirror is formed it is certain that the grains examined consist of arsenious acid. If it is desired to determine the arsenic quantitatively, or to test for other metallic poisons, the contents of both dishes are united and examined as directed in § 224 or § 225.

2. If a stomach is to be submitted to analysis, the contents should be emptied into a porcelain dish, the stomach turned inside out, and (*a*) the inside coat carefully examined for small, white, hard, sandy grains, or for black grains or splinters. The spots occupied by such grains are often reddened, and the grains are frequently firmly embedded in the membrane. (*b*) The contents in the dish are mixed uniformly, weighed, one-third put aside for contingencies, and the other two-thirds treated as in 1. The same course is pursued also with the intestines. In other parts of the body—with the exception perhaps of the pharynx and œsophagus—arsenious acid in grains or metallic arsenic cannot be found if the poison has been introduced through the mouth. If grains of the kind described have been found, they should be examined as directed in 1; if not, or if it is desired to test also for other metallic poisons, proceed according to § 224 or § 225.

B. Method of Detecting Soluble Arsenical and other Metallic Compounds by Means of Dialysis.[*]

§ 224.

If method *A* has failed to show the presence of arsenious acid in the solid state, and the process described in § 225, in which the organic substances are totally destroyed by chlorate of potassa and hydrochloric acid, is at once resorted to, the operator must, of course, give up all notion of ascertaining, as far as the portion operated upon is concerned, in what form the arsenic has been administered; for the process will give a solution containing arsenic acid, whether the poison was originally present in that form, or as arsenious acid, or as sulphide, or in the metallic state, &c. This defect may be avoided, however, by interpolating a dialytic experiment between *A* and *C*. 289

The experiment requires the apparatus shown in fig. 5, p. 10. The hoop is made of wood or, better, of gutta-percha; it is 2 inches (60 mm.) in depth and 8 or 10 inches (200–300 mm.) in diameter. When the dialyser is prepared, the residue and fluid of § 223, *A*, having been mixed according to the circumstances with two-thirds of the stomach, intestinal canal, &c., cut small, and digested for twenty-four hours at about 32°, is poured into it to a depth of not more than half an inch (15 mm.). The dialyser is then floated in

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[*] Compare § 8.

a basin containing about four times as much water as the fluid to be dialysed amounts to. After twenty-four hours, one-half or three-fourths of the crystalloïds will be found in the external water, which is generally colourless; this is concentrated by evaporation on the water-bath, the greater part acidified with hydrochloric acid, treated with sulphuretted hydrogen, and examined as directed in 291. If an arsenical compound soluble in water (or some other soluble metallic salt) is present, the corresponding sulphide is obtained almost pure. By floating the dialyser successively on fresh supplies of water, the whole of the soluble crystalloïds present may be finally withdrawn. If arsenic is found, test the remainder of the concentrated dialysate according to § 134, 11, to ascertain whether the arsenic is present as arsenious or arsenic acid.

It is generally best to examine the exhausted contents of the dialyser at once according to § 225 for metals, but in some cases, as, for instance, when it is thought desirable to ascertain the state of oxidation or combination of the compounds of arsenic or other metals insoluble in water, it is preferable to heat the matter first with dilute hydrochloric acid and to dialyse it again.

Instead of interpolating the dialysis between § 223 and § 225 (which will naturally delay the investigation), you may wait till the close of *C*, and then if a metallic poison has been found the reserved one-third of the material may be submitted to dialysis with the view of ascertaining the state of combination or degree of oxidation of the metal (308). This is usually the most advantageous method of operating.

C. Method for the Detection of Arsenic in whatever Form it may exist, which allows also of its Quantitative Determination, and of the Detection of all other Metallic Poisons.[*]

§ 225.

If neither arsenious acid nor metallic arsenic has been found in the substance by the method described in *A*, nor an arsenic compound soluble in water or hydrochloric acid, by dialysis, the mass obtained by lixiviation is evaporated in a porcelain dish, on the water-bath, to a pasty consistence, having previously added pure carbonate of soda in slight excess if the reaction was acid; if occasion requires, two-thirds of the stomach and intestines cut small are added, provided this has not been done already in the process of dialysis. If other parts of the body (the lungs, liver, &c.) have to be examined, they are also cut into small pieces and two-thirds used for the analysis.

If the substance to be examined contains alcohol, this must, under all circumstances, be first removed by evaporation.

The process is arranged in the following divisions.[†]

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[*] This method is essentially the same as that which was published in 1844 by L. v. Babo and the author; compare Ann. Chem. Pharm., **49**, 308. Since that time, the author has had frequent occasion to test its value both personally, and by others under his immediate inspection, and *it has been found invariably to answer the purpose perfectly*. With regard to the distribution of arsenic in the animal organism after the exhibition of arsenious acid, see E. Ludwig, Zeit. anal. Chem., **26**, 608.

[†] It is evident that the reagents and vessels used in a research of this nature

1. Decolorization and Solution.

To the matters in the porcelain dish, which may amount to, say, 290
100 or 250 grams, hydrochloric acid of 1·10–1·12 sp. gr. is added, in weight about equal to or somewhat exceeding the weight of the dry substances present, and also sufficient water to give to the entire mass the consistence of a thin paste. The hydrochloric acid added should never exceed one-third of the entire liquid present.

must be most carefully examined, to ascertain that they are absolutely free from arsenic, the heavy metals, and every other impurity. The method here described requires the following reagents :—

1. Hydrochloric acid of 1·10 to 1·12 sp. gr.—Although the method of testing hydrochloric acid to ascertain its purity has already been treated of in § 28, it should be noted that, as this acid has to be used in relatively large quantities, the greatest care must be taken to insure the absence of arsenic. The following methods are particularly adapted for delicate tests. (*a*) Pure ferrous chloride is added to 1 litre of the acid, and 50 c.c. distilled off; this must be tested in the apparatus described in § 132, 10, zinc free from arsenic being employed: it should yield no trace of arsenical deposit in the glass tube even after prolonged heating. In researches of this kind, and especially if a hydrochloric acid solution is introduced into the Marsh's apparatus, the chloride of calcium tube should be filled with small pieces of potassa. (*b*) A few grains of chlorate of potassa and a small quantity of water are added to 1 litre of the acid, and the whole evaporated to a small bulk in a porcelain dish, water being added from time to time; the residue is then tested in a Marsh's apparatus as described under *a* (R. Otto in F. J. Otto's *Anleitung zur Ausmittelung der Gifte*, sixth edition, p. 146). The ferrous chloride required for the method described under *a* may be prepared by dissolving iron wire in pure hydrochloric acid of from 1·10 to 1·12 sp. gr. and heating the solution for some time in a small distillation apparatus. As soon as no trace of arsenic can be detected in the distillate, the ferrous chloride may be considered to be free from arsenic.

2. Chlorate of potassa.—This may be most readily tested by heating a large quantity to boiling with twice its weight of water, and allowing it to crystallize with constant stirring up. The mass of crystals is then placed on a filter, and the mother liquor allowed to run off; this is decomposed by warming with dilute hydrochloric acid free from arsenic, a small quantity of the solution thus obtained is tested for the heavy metals with sulphuretted hydrogen and sulphide of ammonium, a second portion is evaporated to a small bulk, water being added from time to time, and the residue tested in a Marsh's apparatus.

3. Sulphuretted hydrogen gas.—The sulphuretted hydrogen prepared by the action of hydrochloric or sulphuric acid on ferrous sulphide frequently contains arseniuretted hydrogen gas derived from the materials employed; the gas prepared by this method, therefore, must not be employed in chemico-legal investigations, or at least not without previous purification. The gas must either be evolved from materials free from arsenic, or, if prepared according to the usual method, it must be purified before being used. Although several methods for purification have been recommended recently—combination of the sulphuretted hydrogen with magnesia, the sulphydrate being formed (Divers and Shimidzu, Jour. Chem. Soc. Trans. 1884, p. 699, or passing the gas over sulphide of potassium heated at 350° (O. v. d. Pfordten, Ber. deut. chem. Ges., 17, 2897)—it is more satisfactory to prepare the gas from materials free from arsenic, from the sulphides of calcium or barium which may be prepared by igniting gypsum or heavy spar with carbon. According to Kosmann, sulphide of barium has been employed for the preparation of sulphuretted hydrogen in the laboratory of the *Ecole des Mines*, at Paris, under Rivot's direction, for at least twenty years. Calcium sulphide has been especially recommended by R. Otto (F. J. Otto's *Anleitung zur Ausmittelung der Gifte*, sixth edition, p. 158), the preparation of the sulphide and the evolution of the gas being conducted in the following manner:—7 parts of anhydrous gypsum, 3 parts of powdered charcoal, and 1 part of rye meal are mixed with water to a stiff paste, the mixture rolled into balls or cylinders, completely dried, and ignited at a strong red heat in a well-covered Hessian crucible. The sulphide of calcium is then broken up into small pieces and introduced into a Woulfe's bottle, one tubulus of which is fitted with a separating funnel with a glass tap, whilst in the

The dish is now heated on the water-bath, adding every five minutes from 0·5 to 2 grams of chlorate of potassa to the hot liquid, stirring at the same time until the contents of the dish are light yellow and tolerably homogeneous and fluid; the water must be replaced from time to time as it evaporates. When this point is attained, some more chlorate of potassa is added and the dish removed from the water-bath. When quite cold, the contents of the dish are cautiously poured on to a linen strainer or a filter, according to the quantity; the whole of the liquid is allowed to pass through, and the filtrate heated on the water-bath with renewal of the water as it evaporates, until the odour of chlorine has gone off or nearly so. The residue is washed well with hot water and dried; it is then marked I., and reserved for further examination, according to **302**. The washings are evaporated on the water-bath to about 100 grams, and added, together with any precipitate that may have formed therein, to the principal filtrate.

2. Treatment of the Solution with Sulphuretted Hydrogen (Separation of the Arsenic as Sulphide, and of all the Metals of Groups V. and VI. in the form of Sulphides). 291

The solution obtained in 1, which amounts to three or four times the quantity of the hydrochloric acid used, is put into a flask, heated on the water-bath to 70°, and a slow current of washed sulphuretted hydrogen passed through it for about twelve hours; it is then allowed to cool without discontinuing the passage of the gas; the gas-delivery tube is rinsed out with some ammonia, the ammoniacal solution thus obtained, after being acidified, is added to the principal portion of the liquid, the flask lightly covered with filter-paper, and put in a moderately warm place (about 30°) until the odour of sulphuretted hydrogen has nearly disappeared. The precipitate obtained in this manner is collected

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other is inserted a tube for delivering the gas. If hydrochloric acid free from arsenic is allowed to drop from the funnel on to the calcium sulphide covered with a layer of water, a tolerably steady stream of pure sulphuretted hydrogen is evolved if the vessel be shaken occasionally. In regard to other methods for the preparation of sulphuretted hydrogen free from arsenic, see Zeit. anal. Chem., **23**, 280, and also O. v. d. Pforten, Ber. deut. chem. Ges., **17**, 2898.

4. Red fuming nitric acid.—In order to test this, a large sample is evaporated to dryness on the water-bath, and the aqueous solution of any residue which may remain is tested with sulphuretted hydrogen and ammonium sulphide, and in a Marsh's apparatus.

5. Concentrated sulphuric acid.—The method of testing this reagent has already been described in § 24. The examination by means of Marsh's apparatus must be carried on for a long time if a trustworthy result is to be obtained.

6. Carbonate of soda.—For the method of testing this reagent see § 46.

7. Nitrate of soda.—This must dissolve in water without turbidity, and the solution must yield no yellow precipitate when heated with molybdate of ammonia and nitric acid (§ 133, 9). Sulphuretted hydrogen should give no precipitate in an acid solution, nor ammonium sulphide in an alkaline solution.

8. Cyanide of potassium.—For the method of testing this reagent, see § 54. It should always be carefully seen that on mixing it with pure carbonate of soda in a porcelain boat, and heating for some time in the apparatus described in § 132, 12, no dark coating is formed in the glass tube.

9. The washed filter-paper which is to be employed is also tested by moistening a number of the filters with hydrochloric acid, washing out the acid with water after the lapse of some time, and testing the dilute hydrochloric acid thus obtained as described in No. 1 of this note.

on a filter, which should not be too large, and washed with water containing sulphuretted hydrogen until the washings are quite free from chlorine. The filtrate and washings are evaporated after being several times saturated with sulphuretted hydrogen; if a precipitate is formed, it is collected, washed, and added to the principal sulphuretted hydrogen precipitate. The filtrate concentrated by evaporation is mixed with ammonia in a proper sized flask until the reaction is alkaline; sulphide of ammonium is then added, and the flask, which must now be nearly full, is closely corked and kept for further examination according to **306**.

3. Purification of the Precipitate produced by Sulphuretted Hydrogen. **292**

The precipitate obtained in 2, which contains the whole of the arsenic and all the other metals of the fifth[*] and sixth groups, in the form of sulphides, also organic matter and free sulphur, is dried with the filter completely in a small dish over the water-bath; pure fuming nitric acid, free from chlorine, is then added, drop by drop, until the mass is thoroughly moistened, the whole evaporated on the water-bath to dryness, and this treatment with nitric acid is repeated several times if necessary. The residue is moistened uniformly with pure concentrated sulphuric acid, previously warmed, heated for two or three hours on the water-bath, and finally with an air-, sand-, or oil-bath at a somewhat higher, though still moderate, temperature (170°), until the charred mass becomes friable, and a small sample of it—to be returned afterwards to the mass—when stirred up with water and allowed to subside, yields a colourless or almost colourless solution; should the aqueous solution be brownish, or should the residue consist of a brown oily liquid, some cuttings of pure, well washed and dried Swedish filtering-paper are added to the mass, and the application of heat continued. The temperature can be safely raised until fumes of sulphuric acid begin to escape, without fear of any loss of arsenic. By attending to these rules, the destruction of the organic substances, without loss of any of the metals, can always be accomplished safely and satisfactorily. The residue is warmed on the water-bath with a mixture of 8 parts of water and 1 part of hydrochloric acid, filtered, and the undissolved part washed thoroughly with small quantities of hot distilled water, containing a little hydrochloric acid; the washings, concentrated if necessary, are added to the filtrate and the first washings.

The washed carbonaceous residue is dried, marked II., and reserved for further examination according to **303**.

4. Preliminary Examination for Arsenic and other Metallic Poisons of Groups V. and VI. (Second Precipitation with Sulphuretted Hydrogen.) **293**

The clear and colourless or, at the most, somewhat yellowish solution obtained in 3 contains all the arsenic in the form of

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[*] Sulphide of lead and sulphide of cadmium are not precipitated from very acid solutions. If, on this account, lead or cadmium remains in solution, it will be found in the precipitate produced by sulphide of ammonium (**306**).

arsenious acid, and may contain also tin, antimony, mercury, copper, bismuth, and cadmium. A small portion is gradually and cautiously supersaturated with a mixture of carbonate of ammonia and ammonia to see whether a precipitate is produced or not. The solution is then acidified with hydrochloric acid, which will re-dissolve the precipitate that may have been produced by ammonia, and the sample is returned to the bulk of the solution. The whole is treated with sulphuretted hydrogen, first at a gentle heat, afterwards without heat, according to **291**.

This treatment may lead to three different results, which are to be carefully distinguished.

a. Sulphuretted hydrogen passed for a long time produces no precipitate; but on standing a trifling white or yellowish-white precipitate separates. In this case probably none of the metals of Groups V. and VI. are present. Nevertheless, the filtered and washed precipitate should be treated as directed in **297**, to guard against overlooking even the minutest trace of arsenic, &c. **294**

b. A pure yellow precipitate is formed, of the colour of sulphide of arsenic. A small portion of the liquid is taken, together with the precipitate suspended in it, some carbonate of ammonia added, and the whole shaken for some time without heating. If the precipitate dissolves readily, and, with the exception of a trace of sulphur, completely, and if in the preliminary examination (**293**) carbonate of ammonia produced no precipitate, arsenic alone is present, and no other metal (at least, if any tin or antimony is present, it is no worth mentioning). The solution of the small sample in carbonate of ammonia is acidified with hydrochloric acid, and then returned to the liquid containing the principal precipitate, which is examined as directed in **297**. If, on the other hand, the precipitate does not dissolve or only incompletely, or if, in the preliminary examination (**293**), carbonate of ammonia has produced a precipitate, there is reason to suppose that another metal is present, perhaps along with arsenic. In the latter case also, hydrochloric acid is added to the sample in the test-tube to acid reaction, and it is returned to the liquid containing the principal precipitate, which is treated as directed in **298**. **295**

c. A precipitate is formed of another colour. In that case, it must be assumed that other metals are present, perhaps along with arsenic. Proceed as directed in **298**. **296**

5. Treatment of the pure Yellow Precipitate produced by Sulphuretted Hydrogen, when the Results of 295 lead to the Assumption that Arsenic alone is Present. (Quantitative Determination of the Arsenic.) **297**

As soon as the solution precipitated according to **293** has nearly lost the smell of sulphuretted hydrogen, the yellow precipitate is collected on a small filter, and washed thoroughly, first with water, then with absolute alcohol, and lastly with bisulphide of carbon, to remove the sulphur mixed with the sulphide of arsenic. After the bisulphide of carbon has been displaced by absolute alcohol, and this again washed out with water, ammonia is poured on to the still moist precipitate, and the filter—on which, in this case, nothing should remain undissolved—is washed thoroughly with dilute ammonia; the filtrate is evaporated in a small accurately tared porcelain dish, on the water-bath, and the residue dried at 100° until the weight is constant. The final weight represents the amount of sulphide of arsenic if this is found to be pure on subsequent reduction; in that case, the weight is multiplied by 0·8049 to obtain the corresponding amount of arsenious acid, or by 0·6098 to obtain the corresponding amount of metallic arsenic. The residue in the dish is treated according to **300**.

6. Treatment of the Yellow Precipitate produced by Sulphuretted Hydrogen, when the Results of **295** or **296** lead to the Assumption that another Metal is present—perhaps with Arsenic. (Separation of the Metals from each other. Quantitative Determination of the Arsenic.) **298**

If there are grounds for supposing that the solution precipitated according to **293** contains other metals, perhaps along with arsenic, the precipitate is collected on a small filter, as soon as the precipitation is thoroughly accomplished and the smell of sulphuretted hydrogen has nearly gone off, and washed thoroughly; the point of the filter is then pierced, and all the precipitate washed into a small flask, using the smallest possible quantity of water; to the liquid in which the precipitate is now suspended, ammonia is first added and then some yellow sulphide of ammonium, allowing the mixture to digest for some time at a gentle heat. Should part of the precipitate remain undissolved, this is filtered off, washed, rinsed off the pierced filter, and marked III., reserving it for further examination according to **304**. The filtrate, together with the washings, is evaporated to dryness in a small porcelain dish; the residue is treated with some pure fuming nitric acid free from chlorine, and evaporated until nearly the whole of the acid is driven off, and a solution of pure carbonate of soda, as C. Meyer was the first to recommend, is then added in small portions at a time until in excess. A mixture of 1 part of carbonate with 2 of nitrate of soda is now added in sufficient, yet not excessive, quantity, the whole evaporated to dryness, and the residue heated very gradually to fusion; when cold, the fused mass is extracted with cold water. If a **299** residue remains undissolved, it is collected, washed with a mixture of equal parts of spirit of wine and water, marked IV., and reserved for further examination according to **305**; the filtrate, which contains all the arsenic as arsenate of soda, is added to the washings, previously freed from alcohol by evaporation; it is then gradually and carefully acidified with pure dilute sulphuric acid until the liquid has a strongly acid reaction, and evaporated in a small porcelain dish. When the solution is highly concentrated, sulphuric acid is again added to see whether sufficient had been previously added to expel all nitric acid and nitrous acid, and the mixture is cautiously heated until heavy fumes of hydrated sulphuric acid begin to escape; when the liquid is cold, from 5 to 10 c.c. of an aqueous solution of sulphurous acid is added to reduce the arsenic acid to arsenious acid, the mixture heated on a water-bath to expel the excess of sulphurous acid, diluted with water, and the solution transferred to a small flask; this is kept at a temperature of 70°, a slow current of washed sulphuretted hydrogen passed into it for at least six hours, finally allowing it to cool whilst the gas is still passing. If arsenic is present, a yellow precipitate will be formed. When the precipitate has completely subsided, and the solution has nearly lost the smell of sulphuretted hydrogen, the precipitate is collected, washed in the manner described in **297**, dissolved in ammonia, and the solution treated according to **297** in order to determine the weight of the arsenic.

7. Reduction of the Sulphide of Arsenic.

300 The production of metallic arsenic from the sulphide, which may be regarded as the keystone of the whole process for detecting the arsenic, must be carried out with the greatest care. The method recommended in § 132, 12—namely, that of fusing the arsenical compound, mixed with cyanide of potassium and carbonate of soda in a porcelain boat, in a slow stream of carbonic acid gas—is the best and safest, affording, besides the advantage of great accuracy, also a positive guarantee against the chance of confounding the arsenic with any other element, particularly antimony; on this account, it is more especially adapted for medico-legal investigations.

Care must be taken that the whole apparatus is filled with carbonic acid, that the contents of the boat is quite dry, that no spirting takes place on heating, and that the stream of gas is passing at the proper rate before applying heat. Heating the mixture of cyanide of potassium, carbonate of soda, and the supposed arsenical compound directly in a glass tube is to be carefully avoided until tubing free from arsenic can be obtained again (see p. 174). A gas generating apparatus which does not allow of the current being regulated is not adapted for the present purpose.

The sulphide of arsenic can be at once submitted to reduction, if possible, however, the whole of the residue obtained by the evaporation should not be used in one operation, but only a small part of it, so that, if necessary, the reduction may be repeated several times. If there is too little sulphide of arsenic to be divided, it should be dissolved in a few drops of ammonia, a small quantity of carbonate of soda added, the mixture evaporated to dryness on the water-bath with stirring, and a portion of the dry residue used for the reduction.*

301 When the operation is finished, the reduction tube is cut off between the narrow part and the place where the boat is (fig. 44),

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* A distinct mirror can be obtained from a quantity of sulphide of arsenic corresponding with 0·01 mgrm. of arsenious acid (W. Fresenius, Zeit. anal. Chem., **20**, 531).

the fore part, which contains the arsenical mirror, is set aside, and the porcelain boat is put into water and allowed to remain some time, until the saline mass is dissolved; the solution is then filtered, and the filtrate acidified with hydrochloric acid; sulphuretted hydrogen is then passed through it, and it is noted whether a precipitate is produced. In cases where the reduction of the sulphide of arsenic has been effected directly, without previous conversion into arsenic acid, a trifling yellow precipitate of sulphide of arsenic may be formed;* if traces of antimony are present, the precipitate will be orange-coloured and insoluble in carbonate of ammonia. After all the soluble salts of the fused mass have been dissolved out, the metallic residue which may be left is examined for traces of tin and antimony (nothing but traces of these two metals could be present here if the instructions given have been strictly followed). Should appreciable traces of these metals, or either of them, be found, proper allowance must be made for this in calculating the weight of the arsenic.

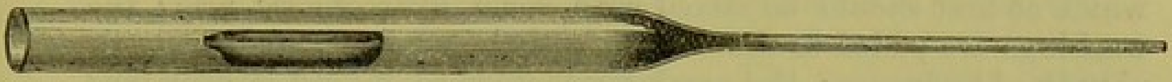

Fig. 44.

8. Examination of the reserved Residues, for other Metals of the Fifth and Sixth Groups.

a. Residue I. (see 290).

302 This may contain chloride of silver and sulphate of lead;† possibly also stannic oxide and sulphate of barium. It is incinerated in a porcelain dish, the carbon burned with the aid of nitrate of ammonia, the residue completely extracted with water, and the insoluble residue dried and fused with carbonate of soda and cyanide of potassium in a porcelain crucible. When cold, it is exhausted with water, and then treated with dilute acetic acid to extract any carbonate of baryta; the residue which usually remains is warmed with nitric acid, and the solution examined according to 109, the residue, if any, according to § 203. The aqueous extract from the fusion with cyanide of potassium is acidified with nitric acid. If a turbidity is produced, it is allowed to settle, collected, and tested for silver by § 115, 8, as traces of silver may pass over into the cyanide of potash solution. A small portion of the acetic acid solution is then treated with sulphuretted hydrogen in order that any traces of lead present may not be overlooked, and after filtering, if necessary, to remove

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* No perceptible precipitate is produced on the reduction of a quantity of sulphide of arsenic corresponding with 0·10 mgrm. of arsenious acid (Zeit. anal. Chem., **20**, 533).

† With regard to the special examination of animal matters for silver, see Nickles, Zeit. anal. Chem., **2**, 114, and V. Lehmann, *ibid.*, **21**, 470. For lead, see A. Gusserow, *ibid.*, **1**, 120, and V. Lehmann, *loc. cit.*

any lead sulphide, the solution is tested for baryta by the addition of a solution of sulphate of lime.

b. Residue II. (see **292**).

303 The carbonaceous residue left in the purification of the sulphuretted hydrogen precipitate with nitric and sulphuric acids may contain lead,* mercury,† and tin, possibly also bismuth, antimony, and sulphate of baryta. It is gently heated for some time with nitro-hydrochloric acid, filtered, and the residue washed with water, which at first should be mixed with some hydrochloric acid; the washings are added to the filtrate, and the whole treated with sulphuretted hydrogen; if a precipitate is formed, it must be examined according to § 191. The residue insoluble in nitro-hydrochloric acid is incinerated, the ash fused with cyanide of potassium, and the melt treated as directed in **302**.

c. Residue III. (see **298**).

304 The precipitate insoluble in sulphide of ammonium is examined for the metals of the Fifth Group according to § 193.‡

d. Residue IV. (see **299**).

305 This may contain tin and antimony, perhaps also copper. It is treated as directed in **123**.

9. Examination of the Sulphide of Ammonium precipitate for Metals of the Third and Fourth Groups, especially for Zinc, Chromium, and Thallium.‖

306 *a.* The filtrate from the sulphuretted hydrogen precipitate (**291**) has already been mixed with sulphide of ammonium; this usually throws down a precipitate consisting of sulphide of iron and phosphate of lime, but it may also contain other metals of the third and fourth groups, especially sulphide of zinc, sulphide of thallium, and hydrated oxide of chromium. Moreover, it may contain lead and cadmium sulphides if the solution from which it has been thrown down by sulphuretted hydrogen were too acid. The solution is filtered, and the filtrate examined according to **307**; whilst the precipitate is first washed with water containing ammonium sulphide, the mouth of the funnel is then closed, and a mixture of 1 part of hydrochloric acid with 4 to 5 parts of sulphuretted hydrogen water is poured on to the precipitate, and allowed to remain for some time. The solution is then allowed to run through, and, if necessary, the residue remaining on the filter

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* See note ‡, *ante*, p. 371.

† For the special examination of animal matters for mercury, see L. Riederer, Zeit. anal. Chem., **7**, 517; Mayençon and Bergeret, *ibid.*, **13**, 103; E. Ludwig, *ibid.*, **17**, 395, and **20**, 475; A. Meyer, *ibid.*, **17**, 402; P. Fürbringer, *ibid.*, **17**, 526; V. Lehmann, *ibid.*, **21**, 470, and **23**, 109; H. Paschki, *ibid.*, **22**, 295.

‡ With regard to the distribution of copper in the animal kingdom, and the special examination of animal matters for copper, see Ulex, Zeit. anal. Chem., **5**, 260, and **21**, 480; also H. Lossen, *ibid.*, **5**, 261.

‖ With reference to the poisonous action of thallium, compare Lamy, Jour. pr. Chem., **91**, 366. And for the electrolytic method of discovering thallium in chemico-legal cases, see Marmé, Zeit. anal. Chem., **6**, 503.

is again treated with sulphuretted hydrogen water containing hydrochloric acid. If it is inferred that metals of the fifth group are present, the filtrate should be sufficiently diluted, sulphuretted hydrogen passed through it, and any precipitate formed collected on the filter still containing the residue; this is well washed, and the precipitate examined for lead, cadmium, nickel, and cobalt. For this purpose, it is dissolved in dilute nitric acid, and any lead which may be present is separated by evaporating the solution with excess of dilute sulphuric acid. After adding a little hydrochloric acid to the filtrate, any cadmium present is precipitated, and the nickel and cobalt are then thrown down by the addition of ammonium sulphide. The acid filtrate, free from nickel, cobalt, cadmium, and lead, is rendered faintly alkaline with ammonia, yellow sulphide of ammonium added, and the solution allowed to stand for twenty-four hours at a gentle heat. If a precipitate is formed, it is collected and washed with water containing ammonium sulphide; it is then dissolved in dilute hydrochloric acid, filtered, and a solution of iodide of potassium added to a small portion. If a pale yellow precipitate of thallium iodide is obtained, the whole solution must be precipitated by means of iodide of potassium. The precipitate must then be further tested for thallium by means of the spectroscope. The solution, free from thallium, is evaporated to a small bulk with a little nitric acid, and this is tested for zinc and chromium according to **144**.

10. Examination of the Filtrate from the Sulphide of Ammonium Precipitate.

The filtrate separated from the sulphide of ammonium precipitate in **306** may possibly contain all the chromium, as ammonia and sulphide of ammonium do not throw down the whole of the oxide of chromium from solutions containing certain organic substances. It may also contain baryta, for, when a soluble salt of baryta is present, the residue I. will only contain as much baryta as the sulphuric acid originally present, or that subsequently formed by the oxidizing action of hydrochloric acid and chlorate of potassa, can precipitate, and the precipitate thrown down by sulphuretted hydrogen will only contain so much sulphate of baryta as is due to the sulphuric acid formed by the action of the air on the sulphuretted hydrogen. In order, therefore, to detect baryta and chromium, sufficient dilute sulphuric acid is added, and the solution evaporated until fumes of sulphuric acid begin to come off. When cold, the solution is diluted, and the precipitate collected, washed, and heated to drive off the sulphur. Should a residue remain, it must be tested for baryta according to **208**. The sulphuric acid filtrate is neutralized with carbonate of soda, evaporated to dryness, the residue, which consists principally of sulphate of soda, is ignited to drive off sulphate of ammonia, fused with carbonate of soda and chlorate of potassa, and finally the aqueous extract of the melt is tested for chromium. **307**

11. Determination of the State of Combination in which the Metals Detected existed in the Original Mixture.

308 If arsenic has been detected in 300, or if in the examination of the residues I. II. III. IV. (302 to 305) any of the metals in question are found in the precipitate from ammonium sulphide, or in the filtrates therefrom, the state of combination in which they existed in the original substance must be determined. The solution of this problem is always of importance, and specially so in the case of metals which are poisonous in some of their compounds, but innocuous in others, as with barium for instance, which is poisonous in the form of chloride of barium or carbonate of baryta, but harmless as sulphate (heavy spar); or, again, chromium, which is poisonous as chromate of potassa, but harmless in the form of chromium oxide.

Dialysis usually offers a suitable method for determining such questions. If, therefore, dialysis has not been employed between A. § 223 and C. § 225, the third of the substance which has been reserved must be treated according to § 224 in order to obtain a solution fitted for determining the state of combination of the suspected metals whose presence has been detected.

D. *Modification of the Method Described under* C.*

309 Naturally, various modifications of the method described in C. may be employed, but it is unnecessary to describe them, as the circumstances under which they offer advantages over that already given above cannot readily be foreseen. It will be advantageous, however, to describe two modifications which depend on a difference in the method of reducing the arsenic to the metallic state.

1. J. Otto and R. Otto † recommend that, instead of reducing a portion of the weighed arsenious sulphide by fusing it with carbonate of soda and cyanide of potassium as described in 300, the arsenic acid obtained from the arsenic sulphide should be reduced by cyanide of potassium. For this purpose, the sulphide of arsenic is boiled down with concentrated nitric acid, and, if necessary, the operation is repeated; every trace of nitric acid is then removed by repeatedly moistening the residue with water, and evaporating to dryness. The product thus obtained is treated with a few drops of water, and powdered carbonate of soda added until the mixture is alkaline; this is thoroughly dried in the dish, with constant stirring, care being taken to keep the mixture in as small a heap as possible in the middle of the dish. Thus prepared, the mixture is obtained in a form very suitable for reduction. The greatest care must be taken that the whole of the nitric acid is removed, and that absolutely *no traces* either of the acid itself or

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* With regard to the separation of arsenic as chloride by Schneider and Fyfe's distillation method, see Selmi, Ber. deut. chem. Ges., **5**, 289; H. Hager, Pharm. Centralhalle, **22**, 169; J. A. Kaiser, Zeit. anal. Chem., **14**, 250, and **22**, 478; E. Fischer, *ibid.*, **21**, 266; Hufschmidt, *ibid.*, **24**, 255; Beckurts, Pharm. Centralhalle, **25**, 488.

† F. J. Otto's *Anleitung zur Ausmittelung der Gifte*, sixth edition by Rob. Otto, p. 190.

of a nitrate remain in the residue, as, if this precaution is neglected, deflagration will ensue when it is fused with the cyanide of potassium, and the estimation be spoilt.

2. Instead of precipitating with sulphuretted hydrogen the solution obtained in **299**, it may be directly tested in Marsh's apparatus, as described at § 132, 10.[*] If arsenic is present in any considerable quantity, a portion of the weighed or measured solution will be sufficient to yield a distinct arsenical mirror, and the remainder of the solution can then be used for the quantitative estimation of the arsenic. If, however, a minute quantity only of arsenic is present, so that it is necessary to introduce the whole of the solution into the Marsh's apparatus in successive portions in order to obtain a distinct arsenical mirror, the quantitative estimation of the arsenic must be omitted. In order that the arsenic carried off as arseniuretted hydrogen may not be lost, the gas issuing from the heated tube is passed through a solution of silver nitrate acidified with nitric acid (§ 134, 6).

It has already been pointed out (§ 132, 10) how important it is that the zinc used should be absolutely free from arsenic. It should be noted, moreover, that in chemico-legal investigations the zinc employed must be free from sulphides, and that when a quantity equal to that to be employed in the actual experiment is completely dissolved in some of the pure sulphuric acid to be employed, as described in § 132, 10, it must yield no trace of an arsenical mirror in the heated glass tube. As all glass tubing contains arsenic, it is not an unwise precaution, when testing the zinc and sulphuric acid, to employ a portion of the same piece of glass tubing, as is to be used in the actual investigation. In order to obtain the necessary confirmation that the mirror obtained is actually an arsenical deposit, it should be treated with sulphuretted hydrogen, &c. (see p. 173).

II. Method for the Detection of Hydrocyanic Acid.

§ 226.

In an actual or a supposed case of poisoning with hydrocyanic **310**
acid or cyanide of potassium (the latter acts similarly to hydrocyanic acid, and is more readily obtainable, as it is employed for many technical purposes), if the hydrocyanic acid is to be separated from and detected in food or the contents of the stomach, it is above all things necessary that the examination should be made at once, as hydrocyanic acid is an unstable compound, and is readily decomposed;[†] moreover, according to some investigators, cyanogen compounds may be formed by the putrefaction of animal

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[*] In this case, the reduction of the arsenic acid by means of sulphurous is unnecessary.

[†] The decomposition of hydrocyanic acid in a dead body occurs after a period which may vary in duration; as a rule, however, a considerable time elapses before *all* the hydrocyanic acid in the organism is decomposed. With regard to experiments made on this question, see Dragendorff, *Die gerichtlich-chemische Ermittelung von Giften*, p. 59, second edition (St. Petersburg: Schmitzdorff); Buchner, Jour. pr. Chem., **104**, 338; Bonjean, Pharm. Centralhalle, 1871, 199; H. Struve, Zeit. anal. Chem., **12**, 14, and 19; Rennard (*ibid.*, **13**, 110), Reichard, Arch. Pharm., **219**, 204; Sokoloff, Zeit. anal. Chem., **14**, 423.

matters; this, however, cannot as yet be received as definitely proved.* If a dead body is to be examined, not only must the stomach and the intestinal canal be tested, but also the blood, the brain, the liver, and the urine.

Besides the poisonous cyanogen compounds, prominent among which stand hydrocyanic acid and cyanide of potassium, there are others which are innocuous, of which ferrocyanide and ferricyanide of potassium and prussian-blue are the best known; as, however, the action of weak acids even on these sets free a small portion of their cyanogen as hydrocyanic acid, it is most necessary to make a preliminary examination, so as to determine the most suitable method to adopt to ascertain with certainty whether hydrocyanic acid or cyanide of potassium was originally present or not.

A. Preliminary Examination.

1. The odour of the substance to be examined is noted. By this means, if hydrocyanic acid is present in any considerable quantity in a mixture free from any other compounds having a distinct odour, it may be immediately recognized. If, however, the part of the body under examination has begun to putrefy, the odour of the hydrocyanic acid may be completely masked by that of the decomposing substances. The odour alone, moreover, can never be considered as sufficient proof of the presence of hydrocyanic acid, since both benzaldehyde and nitrobenzene have somewhat similar odours. 311

2. A portion of the substance, which, if necessary, may be diluted with water, is placed upon a moistened filter; the filtrate is acidified with hydrochloric acid and tested with ferric chloride for ferrocyanides, and with ferrous sulphate for ferricyanides. The ferric chloride will also indicate whether any soluble thiocyanates are present. If there is any prussian-blue in the mixture under examination, its presence is indicated, as a rule, by the colour. Should the presence of a ferrocyanide, a ferricyanide, or a thiocyanate be indicated, the testing for any simple cyanogen compound (hydrocyanic acid or cyanide of potassium) which may also be present requires the greatest caution, the examination being made according to B. 2.† 312

3. If ferrocyanides, ferricyanides, and thiocyanates are all absent, the substance under examination is next tested with guaiacum-paper containing copper. The substance is tested with 313

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* On this question, see Taylor in Dragendorff (*op. cit.*, p. 60), Bonjean (Pharm. Centralhalle, 1871, 199), and W. Preyer (Zeit. anal. Chem., **12**, 23).

† As both ferrocyanide and ferricyanide of potassium are decomposed even in cold aqueous solutions, and more rapidly and more abundantly in acid or warm solutions, it can never be concluded, according to Almén (Chem. Centralbl., 1872, 439), that poisoning with hydrocyanic acid or cyanide of potassium has taken place when hydrocyanic acid is found in a dead body in the presence of ferrocyanides and ferricyanides. The author is of opinion that under certain circumstances it may be fairly considered that hydrocyanic acid or cyanide of potassium is the cause of death, as, for instance, when a relatively large quantity of hydrocyanic acid is found in a body immediately after death in the presence of a little ferrocyanide of potassium. See also Ludwig and Mauthner (Zeit. anal. Chem., **20**, 604).

this reagent, adding a little water if it is not a liquid. If it has an acid reaction, the further examination of the substance may be at once proceeded with, but if it is alkaline or neutral it must be rendered acid by the addition of a solution of tartaric acid. The air in the vessel over the substance is then tested by suspending in it a piece of guaiacum-paper containing copper, as described in § 155, 9. If the paper becomes blue, it is a very strong indication, although not a conclusive proof, of the presence of either hydrocyanic acid or potassium cyanide. Cyanide of mercury, if present, does not yield this reaction. Pass on to B. 1 (**315**).

4. If the preliminary tests under 1, 2, and 3 have yielded negative results, cyanide of mercury may yet be present. Pass on to B. 3 (**320**). **314**

B. Separation and Detection of Hydrocyanic Acid and Cyanogen in Poisonous Cyanides.

1. If the preliminary tests (A. 2) indicate the absence of ferrocyanides, ferricyanides, and thiocyanates, and if the guaiacum-paper is turned blue (A. 3), the substance is mixed with water if necessary, and, if the reaction is not acid, tartaric acid must be added until litmus-paper is strongly reddened; the whole is then transferred to a retort, the body of which is placed in an iron or copper vessel so that it does not touch the bottom, and this, as a precaution, should be covered with a cloth; the bath is then filled either with a solution of chloride of calcium or with high boiling paraffin oil, and cautiously heated, so that the contents of the retort boil gently, the neck of the retort sloping upwards. The vapours which come off are passed through a Liebig's condenser* by means of a tightly fitting tube, bent at a very obtuse angle, and the distillate is received in a graduated cylinder or small weighed flask. When about 12 c.c. of distillate has passed over, the receiver is removed and replaced by a somewhat larger cylinder or tared flask. **315**

The contents of the first receiver are now measured or weighed, and tested as follows:— **316**

a. One-fourth is treated as directed in § 155, 7, to convert the hydrocyanic acid into sulphocyanate of iron. As the distillate, however, may very possibly contain acetic acid, care must be taken at the end of the experiment to add a little more hydrochloric acid, so as to destroy the influence of the acetate of ammonia.

b. One-fourth is treated as directed in § 155, 6, to convert the cyanogen of the hydrocyanic acid into prussian-blue.

c. If the experiments *a* and *b* have proved the presence of hydrocyanic acid, and it is considered desirable also to approximately determine its quantity, the distillation is continued so long as the distillate contains hydrocyanic acid; one-half of

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* In testing for phosphorus at the same time, the condenser must be entirely of glass, and the operation must be conducted in a perfectly dark room. Compare § 227.

the contents of the second receiver are added to the remaining half of the contents of the first, poured into a retort, and again distilled with the addition of borax or bicarbonate of soda to retain any hydrochloric acid, until nearly the whole has passed over. The distillate thus obtained, which is now free from hydrochloric acid, and contains the whole of the hydrocyanic acid, is mixed with nitrate of silver, ammonia added in excess, and then nitric acid to strongly acid reaction. The precipitate which forms is allowed to subside, collected on a tared filter dried at 100°, well washed, dried thoroughly at 100°, and the cyanide of silver weighed. The weight of this multiplied by 0·2018, gives the corresponding amount of anhydrous hydrocyanic acid; and this multiplied again by 2—as only one-half of the distillate was used for the estimation—gives the total quantity of hydrocyanic acid which was present in the mass examined, or that has been produced by the decomposition of cyanide of potassium.

2. If the preliminary examination has shown the presence of ferrocyanides or ferricyanides or of thiocyanates, the method described in 1 (315) cannot be used for the separation of the hydrocyanic acid. In that case, one of the following methods must be substituted for it. 317

a. Method which may be employed when either ferrocyanides, ferricyanides, or thiocyanates are present. If the substance to be examined is acid, a solution of pure potassa is added until the reaction is neutral, and then a cold concentrated solution of bicarbonate of soda. The mixture is distilled in the apparatus described in 1 (315), and the distillate examined for hydrocyanic acid. The addition of a very large amount of bicarbonate of soda may be avoided by adding only a small quantity of the bicarbonate to the neutral or slightly alkaline contents of the retort, and passing a regulated stream of carbonic acid through the retort during the distillation. Neither ferrocyanide, mercuric cyanide, nor thiocyanates yield any hydrocyanic acid when treated in this way. (Jaquemin,[*] Beckurts and Schönfeld,[†] R. Otto,[‡] Taylor,[‖] H. Struve.[¶]) If ferricyanide of potassium is present, however, the distillation should not be continued for more than half an hour, so as to be absolutely certain that no hydrocyanic acid has been produced by its decomposition. (Barfoed.)

b. Methods which serve to obviate the disturbing effect of ferrocyanides and ferricyanides, but not that of thiocyanates.

α. If ferrocyanide of potassium is present, ferric chloride is added in slight excess to the substance to be tested, diluted with water if necessary, and slightly acidified with hydro- 318

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[*] Ann. Chim. Phys., [5], 4, 135.

[†] Arch. Pharm., **21**, 576; Zeit. anal. Chem., **23**, 116.

[‡] F. J. Otto, *Ausmittelung der Gifte*, sixth edition, p. 34.

[‖] Zeit. anal. Chem., **24**, 256.

[¶] *Ibid.*, **12**, 24.

chloric acid—if ferricyanide of potassium is present, ferrous sulphate must be used—the precipitate is separated by filtration if possible, and the solution, now free from ferrocyanides and ferricyanides, is treated as in 1 (315) (v. Pöllnitz, Dragendorff, Almèn,* Ludwig, and Mauthner†). If the precipitate cannot be separated, the whole is transferred to a flask, and a current of air is passed through it at the ordinary temperature, and then into dilute soda solution. A portion of the latter is subsequently tested for cyanide of sodium and hydrocyanic acid as in § 155, 6, 7, and 9, and the remainder reserved for the estimation of the cyanogen as in 1.

β. The substance, diluted with water if necessary, is slightly acidified with tartaric acid and well shaken with its own volume of ether; the layer of ether is then removed, and the aqueous liquid again shaken with ether. The ethereal extracts are free from hydroferrocyanic and hydroferricyanic acid, but contain the hydrocyanic acid originally present in the cyanide of potassium. This hydrocyanic acid can be removed from the ethereal extract by shaking it up with water containing a little soda, and may then be tested as in 2, *b*, *a* (318). (Barfoed, Beckurts, and Schönfeld.‡) This method, however, cannot be recommended when cyanide of mercury is present, as, although some of it is taken up by the ether on agitating its aqueous solution with the latter, the proportion is but small. 319

3. If the preliminary tests A. 1, 2, and 3 have given negative results, and it is undesirable to rely on the guaiacum test alone to prove the absence of hydrocyanic acid, the substance may be treated as in 2, *a* (317), and the distillate tested for hydrocyanic acid. In order to test for cyanide of mercury in the residue, chloride of sodium and excess of oxalic acid are added, and the distillation continued; the cyanogen in the cyanide of mercury, or at all events most of it, will then pass over with the distillate as hydrocyanic acid. 320

III. METHOD FOR THE DETECTION OF PHOSPHORUS.

§ 227.

Since phosphorus paste has been employed to poison mice, &c., and the poisonous action of lucifer matches has become more extensively known, phosphorus has not unfrequently been resorted to as a means of committing murder. The chemist is therefore occasionally called upon to examine some article of food, or the contents of a stomach, for this substance. It is obvious that, in cases of the kind, his whole attention must be directed to the separation of the phosphorus in the *free state*, or to the obtaining of reactions which will enable him to infer the presence of *free phosphorus;* the mere finding of phosphorus in the form of phosphates would prove nothing, as phosphates are invariably constituents of animal and vegetable substances. 321

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* Chem. Centr., 1872, 439.

† Zeit. anal. Chem., 20, 604.

‡ *Ibid.* 23, 117.

All unnecessary delay must be avoided, as any free phosphorus which may be present will be oxidized by the action of the air, first of all to phosphorous acid, and then to phosphoric acid, in which case no opinion can be formed as to whether the phosphorus was originally present in the free state or not. As, however, small particles of phosphorus when inclosed in mucilaginous organic substances may remain for a considerable time before they are completely oxidized to phosphoric acid, free phosphorus can often be detected in dead bodies even when examined several weeks after death (Neumann,[*] Dragendorff,[†] Fischer and J. Müller,[‡] Elvers,[‖] Medicus[¶]. The evidence afforded by some of the methods now about to be described may be inconclusive, however, as v. Selmi's[**] researches have proved that volatile phosphorus compounds are formed in the putrefaction of albumin, brain-substance, and portions of dead bodies, especially the intestines, and that, even when preserved in spirit; these phosphorus compounds are soluble in ether and bisulphide of carbon, and turn solutions of nitrate of silver brown.

In the examination of dead bodies, the liver, brain,[††] blood, and urine[‡‡] must all be tested as well as the stomach and intestines.

A. *Detection of Unoxidized Phosphorus.*

1. Preliminary Examination.

322 *a.* In the first place, it must be ascertained whether the substance contains free phosphorus as indicated by its odour or by its luminosity in the dark,[‖‖] and to this end the contact of the phosphorus with the air must be increased by rubbing, stirring, or shaking.

323 *b.* A little of the substance is put into a flask, into which a cork is loosely inserted having fastened to its under side a strip of filtering-paper moistened with a neutral solution of nitrate of silver, and the whole heated to 30° or 40°. If the paper does not turn black, even after some time, no unoxidized phosphorus is present; it is therefore scarcely necessary to try the methods given in 2, and the operator may at once pass on to 336. If, on the other hand, the paper turns black, this is not a positive proof of the presence of phosphorus, as sulphuretted hydrogen (this may be tested for by a strip of paper moistened with lead solution or with chloride of antimony), formic acid, putrefying matters, &c., will also cause blackening of the paper; the bulk of the substance is

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[*] Taylor-Seideler, Gifte, II. 179.

[†] His *Ermittelung von Giften*, p. 102, second edition (St. Petersburg).

[‡] Zeit. anal. Chem., **15**, 57.

[‖] Chem. Centr., 1877, 70.

[¶] Zeit. anal. Chem., **19**, 94.

[**] Ber. deut. chem. Ges., **9**, 1127, and **11**, 1691.

[††] As the brain is rich in phosphorus, and putrefied brain-substance when distilled with water always gives a distillate containing phosphorus, it is better to examine it separately.

[‡‡] In regard to the peculiar character and behaviour of urine in cases of phosphorus poisoning, see Selmi, Zeit. anal. Chem., **14**, 232, and **21**, 481, and v. Mering, *ibid.*, **15**, 507.

[‖‖] It should be remembered that the presence of free phosphorus cannot be inferred with certainty by its luminosity in the dark, as there are many other substances which have a phosphorescent appearance.

treated by the methods given in 2, *a* and *b*, or by one of the other methods in 2 (T. Scherer, Ann. Chem. Pharm., **112**, 214).

2. Complete Examination.

a. By Distillation with Water.

This excellent and approved method, recommended by E. Mitscherlich,* is founded on the fact that phosphorus is volatile with water vapour and becomes luminous. 324

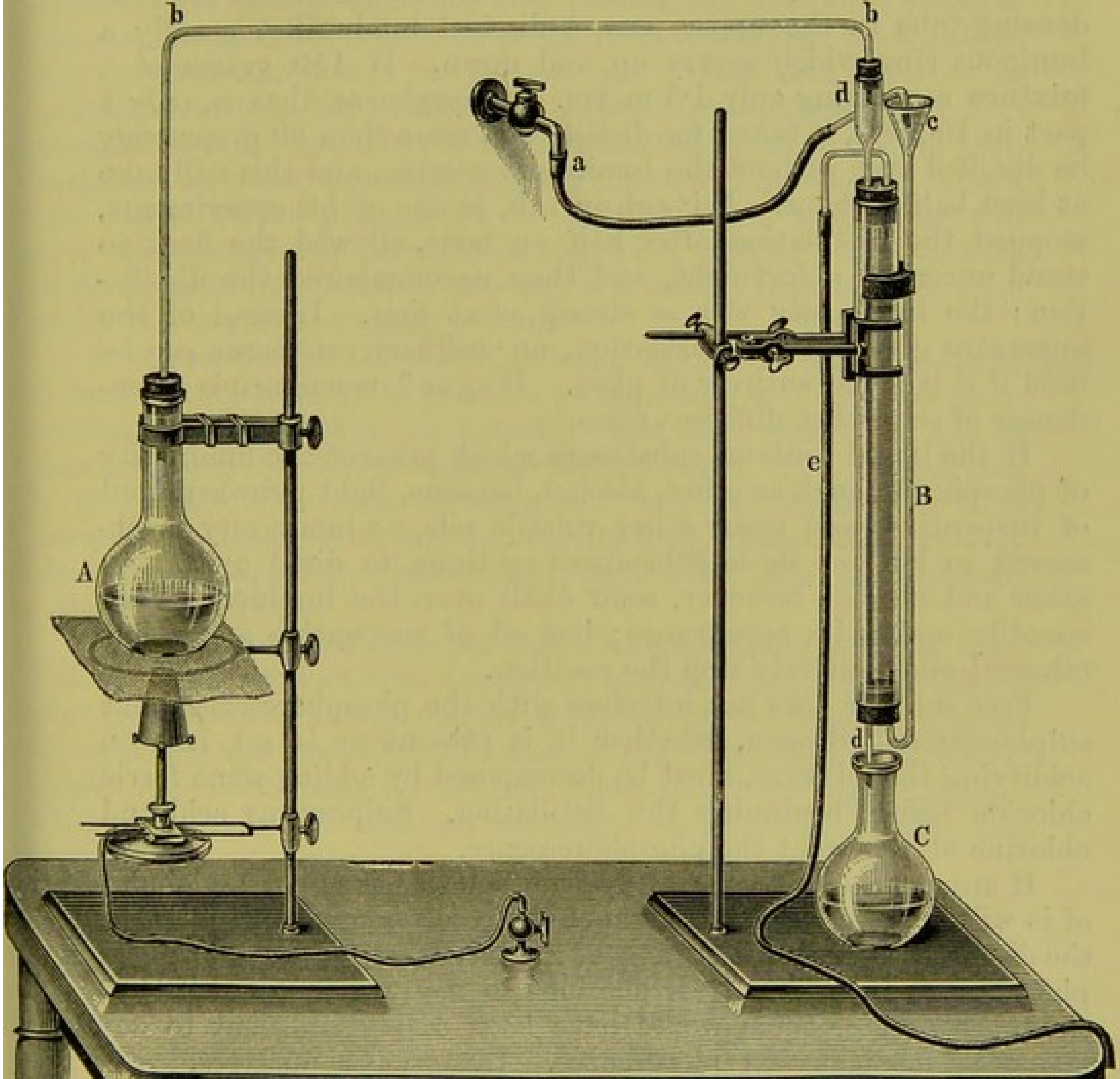

Fig. 45.

The larger portion of the substance is mixed with water and some sulphuric acid† or—if hydrocyanic acid is being tested for at

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* Jour. pr. Chem., **66**, 238.

† If it is suspected that the phosphorus occurs in the form of lucifer matches, Hager (Zeit. anal. Chem., **10**, 255) recommends the addition of ferrous chloride or sulphate, so as to neutralize the effect of the oxidizing substance present in the matches.

the same time—tartaric acid, and the mixture submitted to distillation in a flask *A* (fig. 45); it is best to heat it in a paraffin-bath, and to keep it in gentle ebullition. This flask is connected with an evolution tube *bb*, and the latter again with a glass condensing-tube *dd*, which passes through the wider glass cooling-tube, in which it is fastened by means of india-rubber corks and opens into the small flask *C*. Cold water is made to run from the stopcock *a* into a funnel *c*; the warm water flows off through *e*.

Now, if the substance in *A* contains phosphorus, there will appear, in the dark, at the point where the steam enters the condensing-tube in the upper part, a distinct luminosity, usually a luminous ring which moves up and down. If 150 grams of a mixture containing only 1·5 mgrm. of phosphorus, that is, only 1 part in 100,000, is taken for distillation, more than 90 grams may be distilled over without the luminosity ceasing, and this will take at least half an hour. Mitscherlich, in one of his experiments, stopped the distillation after half an hour, allowed the flask to stand uncorked a fortnight, and then re-commenced the distillation: the luminosity was as strong as at first. Instead of the apparatus given in the illustration, an ordinary condenser can be used if it is made entirely of glass. Hager* recommends a condenser of somewhat different form.

If the liquid contains substances which prevent the luminosity of phosphorus, such as ether, alcohol, benzene, light petroleum, oil of turpentine, and many other volatile oils, no luminosity is observed so long as these substances continue to distil over. As ether and alcohol, however, soon distil over, the luminosity very speedily makes its appearance; but oil of turpentine and other ethereal oils positively stop the reaction.

Free sulphur does not interfere with the phosphorescence, but sulphuretted hydrogen, whether it is present or is set free on acidifying the mixture, must be decomposed by adding some ferric chloride before beginning the distillation. Sulphurous acid and chlorine also prevent the phosphorescence.

If any considerable quantity of phosphorus is present, globules **325**
of it will be found at the bottom of the receiver used for collecting the distillate. From 150 grams of a mixture containing 0·02 gram phosphorus, Mitscherlich obtained so many globules of it that the tenth part of them would have been amply sufficient to demonstrate that it was phosphorus. In forensic analyses, these globules should first be washed with alcohol, then weighed. A portion may afterwards be subjected to a confirmatory examination, to make quite sure that it really is phosphorus; the remainder, together with a portion of the liquid which exhibits the luminosity when distilled, should be sent in with the report.

The operation should be conducted in a perfectly dark room, best in the evening. Where it is performed in the daytime, care should be taken that no light whatever enters the darkened room, as, otherwise, the rays of light entering through some chink or crevice may chance to be reflected by the glass vessel or by the liquids, and thus lead to deception. It is advisable to pass the evolution-tube at *b* through the aperture of a screen, so as to

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* Pharm. Central., 1870, 465; Zeit. anal. Chem., **10**, 255.

guard effectively against any reflection of light from the spirit-lamp or gas-lamp. These precautionary measures are of course necessary only when very minute traces of phosphorus are to be detected.

326 The residue left in the flask is then examined for phosphorous acid as directed **336**. The distillate also may be further examined in the same way, to confirm the presence of phosphorus, or to show the presence of phosphorous acid formed by the oxidation of phosphorus fumes.* If, however, this is to be employed merely for an approximate estimation of the free phosphorus originally present, the distillation is continued until the luminous appearance ceases, and then the contents of the receiver are treated with chlorine so as to convert both the phosphorus and the phosphorous acid into phosphoric acid ; the latter is then estimated by precipitation with magnesia mixture, concentrating the solution if necessary. Twice the weight of the phosphorus in the phosphoric acid found will give the quantity of phosphorus originally present ; the amount of phosphorus calculated in this way is generally rather below than above the quantity actually present.†

327 If the nature of the material being examined for phosphorus is such that it is likely to give rise to bumping, it is convenient to conduct the distillation in a flask heated on a sand-bath, and to pass a current of steam through the boiling liquid. If the apparatus is previously filled with carbonic acid, and the distillation in a current of steam continued sufficiently long, almost the whole of the free phosphorus present will pass over into the receiver (M. Buchner‡).

It should be noted that the fact that phosphoric acid has been found in the distillate after treatment with chlorine is not evidence that free phosphorus was originally present in the substance, even disregarding the possibility of traces of any phosphoric acid which might be present being carried over mechanically through spirting. This will easily be seen on referring to Selmi's researches mentioned on p. 380.

b. By Distilling off the Phosphorus in a Current of Carbonic Acid.

328 As in the process described in *a* the phosphorescent appearance is often prevented by the presence of certain substances, it is always advisable to treat another portion by the method devised by Neubauer and the author.|| For this purpose, the substance, with the addition of water if necessary, is introduced

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* If the substance contains both hydrocyanic acid and phosphorus, the former will pass over first, whilst the phosphorus is found in the latter portions of the distillate ; it is better, therefore, to collect the first 15 c.c. of the distillate separately, and to examine this for hydrocyanic acid, the subsequent portions for phosphorus.

† If the apparatus used is not too large, and the distillate is conducted so that the phosphorescent light is always in the condenser and never in the flask or leading tube, and moreover is continued until there is no luminous appearance in a perfectly dark room, at least one-half of the free phosphorus distils over, and under peculiarly favourable circumstances, three-fourths (L. Meyer, O. Schifferdecker, Zeit. anal. Chem., 11, 279).

‡ Zeit. anal. Chem., 14, 165.

|| *Ibid.*, 1, 336.

into a flask with a doubly perforated cork, acidified with dilute sulphuric acid, and a slow current of washed carbonic acid from a Kipp's apparatus (fig. 38, p. 175) passed into the flask, through a glass tube reaching nearly to the bottom, whilst the gas issuing from the other glass tube is passed through one or two U tubes containing a neutral solution of nitrate of silver. When the flask if filled with carbonic acid, it is gently warmed on the water-bath. The operation should be continued for several hours, and if free phosphorus is present, it will volatilize unoxidized in the carbonic acid stream, then pass into the silver solution, where it will be partly converted into black phosphide of silver, partly into phosphoric acid and metallic silver. If no precipitate is formed, it may be safely concluded that no unoxidized phosphorus is present, but, on the other hand, the formation of a precipitate is not sufficient proof of the presence of phosphorus, as the precipitate may be due to the action of volatile reducing agents or to sulphuretted hydrogen.

329 If a precipitate is formed, it is collected on a filter which has been well washed with dilute nitric acid and water, and washed. The phosphide of silver in it may be detected by Blondlot's improved modification of Dusart's method,* substituting, however, for the apparatus used by Blondlot, the one shown in fig. 46, which may be easily constructed.

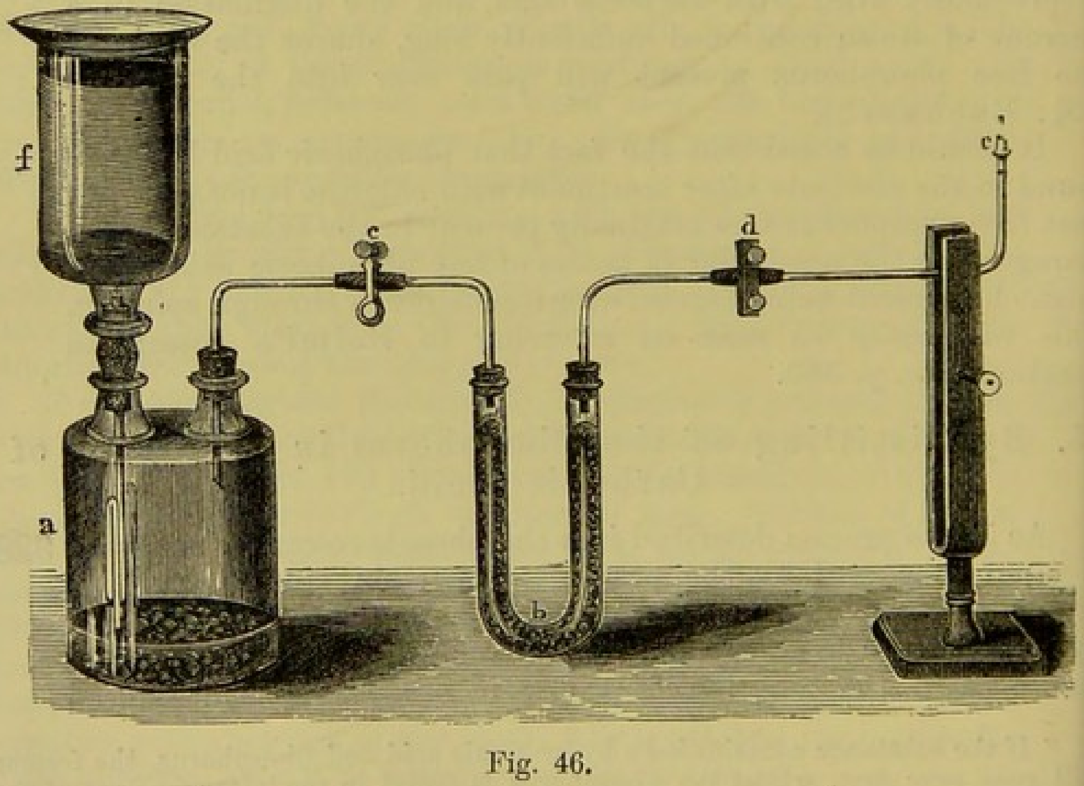

Fig. 46.

a is a hydrogen apparatus, *b* contains pumice-stone moistened with concentrated solution of potassa to absorb any sulphuretted hydrogen, *c* is a common clip, *d* a screw clip, *e* a platinum jet which is kept cool by tying moistened cotton round it. This platinum jet

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* Zeit. anal. Chem., 1, 129. According to Blondlot, the organic matter to be tested is treated directly with zinc and sulphuric acid (this cannot be recommended), and the evolved gases passed into a silver solution.

is indispensable to the production of a colourless hydrogen flame, as the soda in the glass will always colour the flame yellow.*

To ascertain whether the zinc and sulphuric acid will give a gas quite free from phosphuretted hydrogen, the evolution is allowed to go on a short time, then *c* is closed until the liquid has ascended from *a* to *f*; *d* is now closed, *c* opened, and *d* regulated by means of the screws so as to obtain a suitable flame. If the flame, viewed in a dark place, is colourless, showing no trace of a green cone in the centre, and no emerald-green coloration when the flame is allowed to impinge upon a piece of porcelain as in Marsh's experiment, the hydrogen may be considered pure; it is advisable to repeat this experiment. The precipitate under examination is now rinsed into *f* with a little water, taking care that every particle of it reaches *a*, and the experiment is repeated as before. If the precipitate contains even a minute trace of phosphide of silver, the green cone in the centre of the flame and the emerald-green coloration will be distinctly visible.

The excess of silver in the filtrate from the silver precipitate is **330** removed by hydrochloric acid, and the solution filtered through a filter which has been well washed with acid and water; the hydrochloric acid is then removed by repeated evaporation with nitric acid on the water-bath, and the residue is taken up with nitric acid, and tested for phosphoric acid with a nitric acid solution of molybdate of ammonia, or with a mixture of sulphate of magnesia, chloride of ammonium, and ammonia.

By the employment of this method, the author has been able to detect phosphorus with the greatest certainty in the head of a single lucifer match which had been mixed with a large quantity of putrefying blood, and also in the presence of such substances as prevent the appearance of phosphorescence in Mitscherlich's method. The green flame coloration and the detection of phosphoric acid in the filtrate from the phosphide of silver, however, is not such conclusive evidence of the presence of phosphorus as the appearance of phosphorescence in Mitscherlich's process, at all events when examining decomposing animal matter. (See Selmi's experiments, p. 380).

If there is sufficient phosphorus present to allow of a quan- **331** titative determination being made, Scherer's modification of Mitscherlich's method † may be employed, as the process described in **326** gives only approximate results. For this purpose another portion of the substance is acidified with sulphuric acid, and distilled in an atmosphere of carbonic acid, ferrous sulphate being added if necessary (see note †, p. 381). With respect to this, the author suggests that the distilling flask should be furnished with a doubly perforated cork, a current of pure carbonic acid being passed in until the apparatus is filled with it, when the passing the carbonic acid should be discontinued. A flask with doubly perforated cork is used as a receiver; the mouth of the condensing-tube passes through one of the openings, whilst into the other is

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* With regard to the manner in which hydrogen containing phosphorus burns, and which renders the use of the platinum jet indispensable, see **332**.

† Ann. Chem. Pharm., **112**, 216.

inserted a bent glass tube, which leads to a U tube containing a solution of pure nitrate of silver.

When the distillation is over, minute globules of phosphorus are found in the receiver. A moderate stream of carbonic acid is now once more passed through the apparatus, and a gentle heat applied, with the object of causing the phosphorus to agglomerate in larger globules; they are then washed and weighed as in Mitscherlich's method. The liquid poured off the phosphorus globules is luminous in the dark when shaken. It requires, however, a larger proportion of phosphorus to obtain distinct luminosity in this way than when it is distilled with water as in 324. The phosphorus in this liquid may be oxidized by nitric acid or chlorine, and determined as phosphoric acid. To estimate quantitatively the whole of the phosphorus, the contents of the U tube is also treated with nitric acid, the silver thrown down by hydrochloric acid, filtered through a washed filter, concentrated in a porcelain dish, the phosphoric acid precipitated as phosphate of magnesia and ammonia, and finally weighed as pyrophosphate of magnesia. The phosphoric acid from the liquid or from the contents of the U tube can only be considered with certainty as being derived from free phosphorus, when care has been taken that none of the boiling liquid has spirted over, and if there are no putrid brains, &c., in the substance examined. (See Selmi, p. 380.)

c. By Distilling off the Phosphorus in a Current of Hydrogen.

As in Blondlot's method, where the substance to be tested 332 for phosphorus is treated with zinc and sulphuric acid, it is difficult to test the residue for other poisons. Dalmon[*] proposes to pass a current of pure hydrogen through the organic mixture containing phosphorus; under these circumstances, the hydrogen takes up phosphorus. The gas is allowed to escape through a tube bent upwards at right angles and drawn out to a jet, a moderately long and narrow glass tube being placed over the flame as with a singing flame. If phosphorus is present, the flame contracts and becomes green, but without emitting any sound. Neubauer,[†] who confirms Dalmon's statement, remarks that the escaping phosphorized hydrogen (not ignited) appears luminous in a dark room.

d. By Distillation with Alcohol.

If the substance to be examined has been preserved in spirit, it 333 is better to employ H. Hager's[‡] method. Some sulphuric acid is added to the mixture, and, if lucifer matches are suspected, some ferrous chloride also, and the spirit then distilled off on a water-bath. There is no phosphorescence, but the alcoholic distillate contains phosphorus if it was originally present in the mixture. By repeating the distillation with fresh quantities of spirit, and if

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[*] Jour. Chim. Med. 1870, 123.

[†] Zeit. anal. Chem., **10**, 132.

[‡] Pharm. Centralhalle, 1870, 465, and Zeit. anal. Chem., **10**, 256.

the amount of the free phosphorus is but small, the whole of it will be found in the distillate. A test-tube is then filled one-third with water, 10 drops of the first alcoholic distillate added, and the whole shaken in the dark; the presence of phosphorus is indicated by the empty space in the tube appearing luminous. The phosphorized spirit turns a solution of nitrate of silver or sulphate of copper brown or black, with separation of the metal or a metallic phosphide, and formation of phosphorous acid. By means of lead-paper, it is easy to ascertain whether the blackening is due to sulphuretted hydrogen or not.

c. By Agitation with Solvents which are Immiscible with Water.

334 If organic substances containing free phosphorus are suspended in water and agitated with solvents of phosphorus immiscible with water, the phosphorus is taken up by the solvent, and remains behind on cautiously evaporating the latter; it is advisable to add a little water before evaporating, so as to protect the phosphorus from the oxidizing action of the atmosphere. Selmi* recommends bisulphide of carbon; v. Lassaigne † and, more recently, van Bastelaer,‡ ether; whilst H. Hager || proposes the use of light petroleum. When the solvent has been almost entirely removed by spontaneous evaporation at the ordinary temperature, and the residue is poured out on to a flat plate in the dark, as a rule it at once shows phosphorescence. The residue can also be further tested by one of the methods already given. In order to obtain the phosphorus as pure as possible, van Bastelaer recommends that the fatty residue left on evaporating the ethereal extract along with a little water should be heated to 50°–60°; the melted fat containing the phosphorus is then repeatedly agitated with concentrated aqueous ammonia to dissolve and remove the former, and the phosphorus, which is scarcely acted on by the ammonia, is washed first with water containing a little sulphuric acid, and lastly with water.

335 Dusart's method,¶ in which the substance to be examined is extracted with a mixture of equal volumes of bisulphide of carbon, ether, and alcohol containing sulphur, so far resembles those of Lipowitz ** and E. Mulder ††; but it differs from theirs in the subsequent treatment of the residue of sulphur containing phosphorus which is left on the evaporation of the solvent. For details of these little-used methods, the reader is referred to the original papers.

B. *Detection of Phosphorous Acid.*

336 If the attempts to detect phosphorus have failed, the substance must be examined to see whether the first product of its oxidation, that is, phosphorous acid, is present or not. For this

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* Ber. deut. chem. Ges., **5**, 289. † Pharm. Centralbl., 1850, 360.
‡ Zeit. anal. Chem., **13**, 350. || *Ibid.*, **20**, 321. ¶ *Ibid.*, **15**, 505.
** Ann. Phys. Chem., **90**, 600, and Chem.-pharm. Centralbl., 1854, 157.
†† Zeit. anal. Chem., **2**, 111.

purpose, the residue left in the distilling flask in **326** or from **328**, **331**, or **329**, is transferred to the apparatus, fig. 46, p. 384, and note taken as to whether the coloration of the hydrogen flame (**329**) reveals the presence of phosphorus (Wöhler). Should this be the case, the end in view is attained; if not, the presence of organic substances may be the preventive cause. If, therefore, the flame remains uncoloured, the pinch-cock should be shut at once, and the apparatus connected with a U tube containing solution of neutral nitrate of silver; the clip is again opened, and the gas allowed to pass for many hours, in a slow stream, through the silver solution. If phosphorous acid is present, a precipitate containing phosphide of silver will separate in the silver solution; this must be examined according to **329**.*

3. Examination of the Inorganic Constituents of Plants, Animals, or Parts of the same, of Manures, &c. (Ash Analysis.)

§ 228.

A. Preparation of the Ash.

It is sufficient for the purposes of a qualitative analysis to incinerate a comparatively small quantity of the substance, which must previously be most carefully cleaned. The incineration is effected best in a small clay muffle, but the substance may be burned also in a Hessian crucible placed in a slanting position, or, under certain circumstances, even in a porcelain or platinum dish, with the aid of a wide glass tube or lamp-glass, to increase the draught. The heat must always be moderate, to prevent the volatilization of certain constituents, especially of chlorides, and it is not always necessary to continue the combustion until all the carbon is consumed. With ashes containing a large proportion of fusible salts, such as the ash of beet-root molasses, it is best, after it has been thoroughly carbonized, to boil the charred mass with water, and finally to incinerate the washed and dried residue. For further particulars, see Quantitative Analysis, sixth edition, § 284. **337**

B. Examination of the Ash.

As the qualitative analysis of an ash is undertaken, either as a practical exercise, or for the purpose of determining its general character and the state in which any given constituent may happen to be present, or also with a view to make, as far as practicable, an approximate estimation of the quantities of the several constituents, it is usually the best way to examine separately the part soluble in water, the part soluble in hydrochloric acid, and the residue which is insoluble in both. This can be done the more readily, as the number of substances to be looked for is but small. **338**

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* W. Herapath's statement (Pharm. Journ., 1865, **7**, 573), that phosphoric acid is also reduced by zinc and dilute sulphuric acid, is not in accordance with the facts; compare the author's paper in the Zeit. anal. Chem., **6**, 203.

a. Examination of the Part Soluble in Water.

The ash is boiled with water, filtered, and, whilst the residue is being washed, the filtrate is examined as follows :—

1. Hydrochloric acid in excess is added to a portion, after it has been ignited, the whole warmed and allowed to stand. Effervescence indicates carbonic acid in combination with alkalies; the odour of sulphuretted hydrogen indicates the sulphide of an alkali metal, formed from an alkaline sulphate by the reducing action of the carbon. Turbidity from separation of sulphur, with odour of sulphurous acid, denotes a hyposulphite (which occurs occasionally in the ash of coal). The solution is filtered if necessary, and chloride of barium added ; a white precipitate indicates sulphuric acid. **339**

2. Another portion of the extract is evaporated to a small volume, hydrochloric acid added to acid reaction (effervescence indicates carbonic acid), a few drops tested for boric acid with turmeric (§ 144, 6), and the rest evaporated to dryness, and the residue treated with hydrochloric acid and water; if anything remains undissolved, it is silicic acid. The solution is filtered, evaporated to dryness repeatedly with nitric acid, and tested for phosphoric acid with molybdic acid solution (§ 142, 10). **340**

3. Nitrate of silver is added to another portion as long as a precipitate is formed; it is then warmed gently, and ammonia cautiously added ; if a black residue is left, this consists of sulphide of silver, formed from the sulphide of an alkali metal or from a hyposulphite. The ammoniacal solution is filtered if necessary, nitric acid added in slight excess to dissolve the phosphate of silver thrown down, leaving the chloride (iodide, bromide) of silver. This is filtered off, and the filtrate carefully and exactly neutralized with ammonia. If a light yellow precipitate is produced, the phosphoric acid found in **340** was present in the tribasic, if a white precipitate, it was present in the bibasic form. A portion of the aqueous solution of the ash is tested for iodine, bromine, and chlorine, according to **178** and **180**.* **341**

4. Another portion is heated with hydrochloric acid, then made alkaline with ammonia, oxalate of ammonia added, and the mixture allowed to stand; a white precipitate indicates lime. This is filtered off, and the filtrate mixed with ammonia and phosphate of soda; a crystalline precipitate, which often becomes visible only after long standing, indicates magnesia. (Magnesia is often found in distinctly appreciable, lime only in exceedingly minute quantity, even where alkaline carbonates and phosphates are present.) **342**

5. Potassa and soda are tested for as directed in **168**, *α* or *β*, according as to whether magnesia is present or not.

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* In order to test with certainty for halogens in animal or vegetable matter, a separate sample should be charred with the addition of carbonate of soda, and the aqueous extract of the residue examined (see QUANTITATIVE ANALYSIS, sixth edition, vol. II.).

6. Lithia, which is much more frequently found in ashes than has hitherto been believed, and oxide of rubidium, which almost constantly accompanies potassa, may be most readily detected by means of the spectroscope in the residue consisting of the alkali salts (§ 93).

b. Examination of the Part Insoluble in Water.

The greater part of that portion of the ash which is insoluble in water is warmed with hydrochloric acid (if it contains much carbonaceous matter, it should be incinerated first): effervescence indicates carbonic acid combined with alkaline earths; evolution of chlorine denotes oxides of manganese. The whole is evaporated to dryness with a few drops of dilute sulphuric acid, heated a little more strongly to separate the silicic acid, the residue moistened with hydrochloric acid and some nitric acid, water added, and the solution warmed and filtered from the insoluble residue; this and the solution are then examined as follows :— 343

a. Solution.

aa. A portion is tested with sulphuretted hydrogen; if this produces any other than a pure white precipitate, it must be examined in the usual way. (The ashes of plants occasionally contain copper; if the plant has been manured with excrements deodorized by nitrate of lead, they may contain lead, and so on.) 344

bb. Ammonia is added to a portion of the solution until the precipitate formed no longer re-dissolves on stirring; then acetate of ammonia and some acetic acid until the solution is distinctly acid. This produces, in most cases, a white precipitate of ferric phosphate, mixed occasionally with phosphate of alumina. The precipitate is collected, washed, heated with pure potash, filtered, and the filtrate tested for alumina by acidifying with hydrochloric acid, adding ammonia, and warming; the residue insoluble in potash may, if necessary, be dissolved in hydrochloric acid, and the solution tested for iron with sulphocyanate of potassium. If the filtrate from the ferric phosphate is reddish, there is more iron present than corresponds with the phosphoric acid; if it is colourless, ferric chloride is added drop by drop until the solution has a reddish tint. (The quantity of the precipitated ferric phosphate here formed will give some idea of the amount of phosphoric acid present.) The original reddish solution, or that which has become reddish on the addition of more ferric chloride, is heated to boiling; if it does not become colourless, more acetate of ammonia must be added, and it must be boiled again, filtered hot, the filtrate neutralized with ammonia, avoiding any great excess, and filtered again if necessary. Sulphide of ammonium is added to the filtrate in a flask which should be nearly filled with the mixture, then closed and allowed to stand for some time. The precipitate is collected and tested for manganese and zinc (the latter is seldom present), according to **139**. The liquid which is not precipitated by sulphide of ammonium, or which has been filtered from the sulphide of ammonium precipitate, is tested for lime (which may contain a little strontia) and magnesia, according to § 195 and § 196.

β. Residue.

The residue insoluble in hydrochloric acid may contain the **345** silicic acid which has separated on treating with hydrochloric acid, any baryta which may be present, the greater part of the strontia, also some lead in the form of sulphate of lead, and lastly those ingredients of the ash which are insoluble in hydrochloric acid. These are, in most ashes, sand, clay, carbon—substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. It is only the ashes of the stalks of cereals and others abounding in silicic acid that are not completely decomposed by hydrochloric acid.

The washed residue is boiled for a long time with solution of carbonate of soda in excess, filtered hot, the residue washed with boiling water, and the filtrate tested for silicic acid by evaporation with hydrochloric acid (§ 150, 2). The portion of the residue which is not dissolved by this treatment is heated with very dilute nitric acid, and the solution tested in the ordinary way for lead, baryta, and strontia.

If the ash was of a kind to be completely decomposed by hydrochloric acid, the analysis may be considered finished—for the accidental admixture of clay and sand will rarely interest the analyst sufficiently to warrant a more minute examination by fusing. But if the ash is very rich in silicic acid, and it is suspected that it has not been completely decomposed by the hydrochloric acid, half of the residue insoluble in solution of carbonate of soda (and which has been exhausted with dilute nitric acid and washed with water) is boiled down to dryness with excess of pure soda solution in a silver or platinum dish. This decomposes the silicates of the ash, whilst it attacks the sand but little. It is now acidified with hydrochloric acid, evaporated to dryness, and examined as in **343**. For the detection of the alkalies in the portion insoluble in water, the other half of the washed residue is employed, treating it according to **228**. If alkalies are found, these can only be regarded as derived from the ash if the latter was free from clay and other impurities which might contain alkalies.

2. The remainder of the ash which has been exhausted with water may be tested for fluorine according to § 146, 6. As, however, fluorine is lost during the incineration of organic substances containing fluorine (Tammann*), and that which remains may, under certain circumstances, pass into the aqueous solution, a separate sample must be examined for fluorine if it is desired to ascertain with certainty whether that element is present in the vegetable or animal substance. For this purpose, the sample must be boiled down to dryness with pure potash or soda solution, incinerated, and the ash tested according to § 146, 6.

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* Zeit. anal. Chem., **24**, 342.

SECTION III.

EXPLANATORY NOTES AND ADDITIONS

TO THE

SYSTEMATIC COURSE OF ANALYSIS.

I. REMARKS ON THE PRELIMINARY EXAMINATION.

To §§ 176–178.

A CONSIDERATION of the physical properties of a substance, especially if it is not a mixture, may, as already stated, in many cases enable the analyst to draw some general inference as to its nature. Thus, for instance, if the substance is white, it may be at once concluded that it is not cinnabar, or if a light substance, that it is not a compound of lead, &c. Inferences of this kind are quite admissible and advisable to a certain extent; but, if carried too far, they are apt to prejudice the operator and mislead him by blinding him to reactions which are not exactly in accordance with his preconceived notions.

As regards the examination of substances at a high temperature, platinum foil or small iron spoons may also be used in the process; the glass tube, however, in most cases gives results more clearly evident, and has the advantage that the nature of volatile substances can be more easily ascertained, and they are less likely to escape detection. It is sometimes advisable also to heat the substance in a short glass tube, open at both ends, and held in a slanting position to ascertain what the products of its oxidation may be; small quantities of a metallic sulphide, for instance, may be readily detected by this means (§ 156, 7). If a sublimate is formed when the substance is heated in the glass tube (**9**), care must be taken when heating it on charcoal (**11**) not to inhale, to any extent, the noxious vapours evolved from mercury salts or other volatile and poisonous metallic compounds.

With respect to the preliminary examination by means of the blowpipe, the student cannot be too strongly impressed that he must avoid drawing positive conclusions until he has acquired considerable experience. A slight incrustation of the charcoal, which may seem to denote the presence of a certain metal, is not always a conclusive proof of its presence; neither is it safe to assume the absence of a substance simply because it is not reduced in the blowpipe flame, or because nitrate of cobalt does not impart a colour to the ignited mass. The blowpipe reactions are, indeed, in most cases unerring, but it is not always easy to produce them, and they are moreover liable to be modified by accidental circumstances.

Lastly, it may be mentioned that many beginners, believing that they will be able easily to ascertain the nature of the substance in the ordinary course of analysis, omit the preliminary examination altogether as a waste of time and trouble. As an example of the effect of this, the student who proceeds in this way may spend hours in testing for the different organic acids, and in the end find that none are present, as he would have learned at once if he had made a preliminary examination.

II. REMARKS ON THE SOLUTION, ETC., OF SUBSTANCES.

To §§ 179–181.

If the behaviour towards solvents of the substances in the different classes mentioned in § 179 is considered, they will, with the exception of the metals themselves, appear to be more sharply divided than they really are. This uncertainty, which often causes beginners to make mistakes, applies especially to the sparingly soluble substances, lying as they do on the border line between the soluble and insoluble; on this account, it is advisable to give some additional information on this subject.

It is a task of some difficulty to draw a sharp line between substances soluble in water and those which are insoluble, since the number of substances which are sparingly soluble in water is very considerable, and the transition from sparingly soluble to insoluble is very gradual. Sulphate of lime, which is soluble in about 500 parts of water, may perhaps be taken as the limit between the two classes, as it can be detected with the greatest certainty in aqueous solution by the delicate reagents which we possess for lime and sulphuric acid.

When an aqueous liquid is examined by evaporating a few drops of it upon platinum foil, to see whether it holds any solid substance in solution, a very minute residue sometimes remains, which leaves the analyst in doubt respecting the nature of the substance. In cases of the kind the reaction of the liquid is first tested with litmus-papers; a drop of solution of chloride of barium is then added to a portion of it; and lastly, to another portion some carbonate of soda. If the liquid is neutral, and no change is produced by the reagents, it is not necessary, as a rule, to examine further for bases or acids. The analyst may therefore feel assured that the substance of which the residue left on evaporation consists will be more readily detected in the class of compounds insoluble in water, as both the acids and bases which form sparingly soluble compounds are readily detected by the reagents just employed.

If water has dissolved any part of the substance under examination, it is as well to examine the solution both for acids and bases, as the nature of the compound present can be ascertained in this way more readily and with greater certainty—two advantages which will amply counterbalance the drawback of sometimes meeting with the same substance both in the aqueous and in the acid solution.

The following substances, with few exceptions, are insoluble in water, but soluble in hydrochloric acid or in nitric acid: the phosphates, arsenates, arsenites, borates, carbonates, and oxalates of the earths and metals; also several tartrates, citrates, malates, benzoates, salicylates, and succinates; the oxides and sulphides of the heavy metals; alumina, magnesia; many of the metallic iodides and cyanides, &c. Nearly the whole of these compounds are, indeed, decomposed, if not by dilute, by boiling concentrated hydrochloric acid;* but this gives rise to the formation of insoluble or sparingly soluble compounds, if oxide of silver, mercurous oxide, or lead is present. This does not occur with nitric acid, so that the latter often completely dissolves the substance

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* For the exceptions, see § 203.

where hydrochloric acid would leave a residue. On the other hand, however, nitric acid leaves undissolved not only the compounds insoluble in any simple acid, but also teroxide of antimony, stannic oxide, peroxide of manganese, binoxide of lead, &c., and dissolves many other substances less readily than hydrochloric acid—ferric oxide and alumina, for example.

Substances insoluble in water are therefore, briefly, to be treated as follows:—An attempt must be made to dissolve them in hydrochloric acid, dilute or concentrated, cold or boiling; if this fails or does not completely dissolve them, a fresh portion must be treated with nitric acid; if they are insoluble in this, the substance must be warmed with aqua regia, which is an excellent solvent, particularly for metallic sulphides. In most cases, it is neither necessary nor desirable to examine separately the solution in hydrochloric acid or in nitric acid, on the one hand, and that in nitro-hydrochloric acid on the other; neither is it advisable to prepare a solution in nitric acid or in aqua regia, if the nature of the substance does not absolutely demand it, as a solution in hydrochloric acid is much better suited for precipitation with sulphuretted hydrogen. It is unadvisable also to concentrate a solution in aqua regia by evaporation for the purpose of driving off the excess of acid, as volatile chlorides, such as mercuric chloride, may be volatilized, in part at all events; on this account it is always best to use no more of the acid mixture than is necessary to effect solution. Solutions prepared with hydrochloric acid generally contain the metallic oxides in the same state of oxidation as they were originally (except peroxides, and also mercurous oxide, since mercurous chloride by protracted boiling with hydrochloric acid is gradually decomposed into mercury and mercuric chloride). If, however, solutions are prepared with nitric acid or aqua regia, the metallic oxides frequently pass into a higher state of oxidation; thus, for instance, ferrous oxide, stannous oxide, and arsenious acid are converted into ferric oxide, stannic oxide, and arsenic acid.

With regard to the dissolution of metals and alloys, it is to be noted that, on boiling them with nitric acid, white precipitates will frequently form, even when neither tin nor antimony is present (45). The inexperienced student often confounds such precipitates with the oxides of these two metals, although their appearance is quite different; these precipitates are merely nitrates, sparingly soluble in nitric acid, but readily soluble in water. It is necessary, therefore, to ascertain whether these white precipitates are soluble in water or not, before it is inferred that they consist of tin or antimony.

III. ADDITIONAL REMARKS TO THE ACTUAL EXAMINATION.

To §§ 182–204.

A. General Review and Explanation of the Analytical Course.

a. Detection of the Bases.

The classification of the bases into six groups, and the methods which serve to detect and isolate them individually, have been fully explained in Part I., Section III. These groups are in general identical with those into which the bases are separated in the ordinary course of analysis; and the systematic course, from § 189 to § 198, is founded upon this classification into groups and the subsequent detection of the individual members of the group. It is, of course, necessary to give some practical details as to the method to be followed when an actual analysis is to be made. For this purpose, however, much will have to be considered which is not necessary for understanding the purely theoretical part of the process, and which would moreover interfere with the conciseness advisable in a summary; on this account, the principles of the methods employed for the separation of the bases into groups will be considered in the first place. With respect to the detection of the individual bases, the student is referred to the recapitulations and remarks in §§ 88–134.

The general reagents which are used in analysis to divide the bases into principal groups are—hydrochloric acid, sulphuretted hydrogen, sulphide of ammonium, and carbonate of ammonia: this is likewise the order in which they are successively applied. Sulphide of ammonium performs a double part; sulphide of sodium is sometimes substituted for it.

Suppose all the bases are in the solution, together with arsenious and arsenic acids, and also phosphate of lime (which may serve as a type of the salts of the alkaline earths soluble in acids and reprecipitated unaltered by ammonia), that is, all the substances to be tested for in the systematic examination for bases.

Chlorine forms insoluble compounds only with silver and mercury; chloride of lead is sparingly soluble in water. The insoluble mercurous chloride corresponds with mercurous oxide. If, therefore, we add to the solution:

1. **Hydrochloric Acid**, the metallic oxides of the first division of the fifth group will be removed, that is, the whole of the oxide of silver and the whole of the mercurous oxide. From concentrated solutions, a portion of the lead may likewise be precipitated as chloride, but this is immaterial, as a sufficient quantity of the lead remains in the solution to allow of its subsequent detection.

Sulphuretted hydrogen completely precipitates the oxides of the fifth and sixth groups from solutions containing a free mineral acid; none of the other bases, however, is precipitated under these circumstances, since the sulphides of the metals of the first and second groups are soluble in water, quite apart from the fact that their sulphides cannot possibly be formed in acid solutions; as regards those of the third group, sulphide of aluminium and sulphide of chromium cannot possibly be formed in the humid way; and those of the fourth group because, although insoluble in water, they cannot be formed in the presence of excess of a mineral acid.

If, therefore, after the oxide of silver and mercurous oxide have been removed by means of hydrochloric acid, we add to the solution, which still contains free hydrochloric acid,

2. **Sulphuretted Hydrogen**, the remainder of the oxides of the fifth and of the sixth group are removed, namely, the oxides of lead, mercury, copper, bismuth, and cadmium, also the oxides of gold and platinum, stannous and stannic oxides, oxide of antimony, arsenious acid, and arsenic acid. All the other oxides remain in solution, either unaltered, or

reduced to a lower degree of oxidation, for example, ferric oxide, chromic acid, &c.

The sulphides, or at all events the higher sulphides corresponding with the oxides of the sixth group, possess the property of combining with basic metallic sulphides (the sulphides of the alkali metals) to form sulphur salts soluble in water; the sulphides corresponding with the oxides of the fifth group, however, do not possess this property, or only to a limited extent.* If, therefore, the whole of the sulphides precipitated from an acid solution by sulphuretted hydrogen is treated with

3. **Sulphide of Ammonium** (or, it may be, **Sulphide of Sodium**), with addition, if necessary, of some sulphur or yellow sulphide of ammonium, the sulphides of mercury, lead, copper, bismuth, and cadmium remain undissolved, whilst the other sulphides dissolve as double compounds of sulphide of gold, platinum, antimony, tin, arsenic, with sulphide of ammonium (or sulphide of sodium), and on adding hydrochloric acid to this solution are precipitated again, either unaltered, or in a state of higher sulphuration (they take up sulphur from yellow sulphide of ammonium); the acid having decomposed the sulphur salt formed. The sulphur base (sulphide of ammonium or sulphide of sodium) is decomposed by the hydrochloric acid into chloride and sulphuretted hydrogen, whilst the liberated sulphur acid is precipitated; sulphur will be precipitated at the same time if the sulphide of ammonium contains an excess of that element. It should be noted that this sulphur makes the precipitated sulphides appear of a lighter colour.

The sulphides corresponding with the oxides which still remain in solution are in part—as those of the alkalies and alkaline earths—soluble in water; others—as those of alumina and sesquioxide of chromium—are decomposed by water into hydrated oxides and sulphuretted hydrogen; whilst the rest—as those of the fourth group—are insoluble in water: the latter would, therefore, have been precipitated by the sulphuretted hydrogen but for the free acid present. If, therefore, this free acid is removed, that is, if the solution is made alkaline, and then treated with more sulphuretted hydrogen, if required, or, what is the same thing, if

4. **Sulphide of Ammonium** is added to the solution,† the sulphides corresponding with the oxides of the fourth group will be thrown down, namely, the sulphides of iron, manganese, cobalt, nickel, and zinc. But in conjunction with them, hydrate of alumina, hydrated sesquioxide of chromium, and phosphate of lime are precipitated, because the acids which keep the alumina and the sesquioxide of chromium, and that which keeps the phosphate of lime, in solution are converted into salts of ammonia, and the sulphuretted hydrogen set free is incapable of entering into combination with the liberated oxides or with the phosphate of lime.

There remain now in solution only the alkaline earths and the

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* Sulphide of mercury combines with sulphide of potassium and sulphide of sodium, but not with sulphide of ammonium; sulphide of copper dissolves a little in sulphide of ammonium, but not in sulphide of potassium or sulphide of sodium.

† The free acid in this should be previously almost neutralized with ammonia, to prevent unnecessary evolution of sulphuretted hydrogen: and, if necessary, chloride of ammonium should also be added to prevent the precipitation of magnesia by ammonia.

alkalies. The neutral carbonates of the former are practically insoluble in water, whilst those of the latter are soluble. If, therefore, we now add

5. **Carbonate of Ammonia**, together with a little pure ammonia, to guard against the possible formation of bicarbonates, as in that case the whole of the alkaline earths would not be precipitated. This is, however, true only of baryta, strontia, and lime;[*] magnesia, owing to its tendency to form double compounds with ammonia salts, is only partly precipitated; whilst the presence of a salt of ammonia altogether prevents its precipitation, at least for a considerable time. In order to guard against any uncertainty arising from this cause, chloride of ammonium should be added before adding the carbonate of ammonia, and the mixture, after remaining for a short time at a gentle heat, is filtered, so that the precipitation of the magnesia may be entirely prevented.

Magnesia and the alkalies still remain in solution. The magnesia may be detected by means of phosphate of soda and ammonia; but as the presence of phosphoric acid would interfere with the further progress of the analysis, it has to be separated by a different method founded on the insolubility of hydrate of magnesia. The substance is first ignited in order to expel the salts of ammonia, chloride of barium is added to remove sulphuric acid and other acids forming insoluble baryta salts, as these would render the detection of the alkalies more difficult, and then the magnesia is thrown down by hydrate of baryta or milk of lime, the alkalies remaining in solution, together with the soluble salts of baryta or lime. On adding carbonate of ammonia, the compounds of baryta or lime are removed from the solution, which now only contains the fixed alkalies, the salts of ammonia formed, and the excess of carbonate added; if the salts of ammonia are expelled by ignition, the residue contains nothing but salts of fixed alkalies. As carbonate of baryta and carbonate of lime are not absolutely insoluble in salts of ammonia, however, and on evaporation with chloride of ammonium give carbonate of ammonia and chloride of barium or chloride of calcium, it is usually necessary, after the removal of the ammonia salts by ignition, to precipitate once more with a little carbonate of ammonia and a few drops of ammonia, in order to obtain a solution perfectly free from baryta or lime, in which the potassa and soda can be detected without difficulty.

Lastly, the ammonia must be tested for in a fresh portion of the substance.

b. Detection of the Acids.

Before passing on to the examination for acids and halogens, it is necessary to consider which of these may be expected to be present, judging from the nature of the bases found and the class to which the substance under examination belongs as regards its solubility, so as not

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[*] It has been already mentioned in § 99 that traces of these bases remain in solution partly because their carbonates are not absolutely insoluble in water, but chiefly because they are appreciably soluble in chloride of ammonium. On this account, it is necessary to test the filtrate from the carbonate of ammonia precipitate with sulphate and oxalate of ammonia (162). In the general explanation of the course given in the text, these traces of baryta, strontia, and lime are not taken into account.

to make unnecessary experiments. The table in Appendix IV. will be found useful for this purpose.

The general reagents used for the detection of the acids are, for the inorganic acids, chloride of barium and nitrate of silver, for the organic acids chloride of calcium and ferric chloride. First of all, therefore, it is necessary to ascertain whether the substance under examination contains inorganic acids only, or whether organic acids must also be looked for. The latter is invariably the case if the substance turns black and carbonizes when ignited. In the examination for bases, the general reagents serve to effect the actual separation of the several groups of bases from each other; but in the examination for acids they serve chiefly to demonstrate the presence or absence of the acids belonging to the different groups.

Suppose, as in the case of the bases, that the whole of the acids are present in aqueous solution—say, in combination with soda.

Baryta forms insoluble, or sparingly soluble, compounds with sulphuric acid, phosphoric acid, arsenious acid, arsenic acid, carbonic acid, silicic acid, boric acid, chromic acid, oxalic acid, tartaric acid, and citric acid; fluoride of barium also is insoluble, or at least only sparingly soluble; all these compounds are soluble in hydrochloric acid, with the exception of sulphate of baryta. If, therefore, to a portion of the neutral or, if necessary, neutralized solution

1. **Chloride of Barium** is added, the formation of a precipitate shows that at least one of these acids is present. If a residue is left undissolved on heating the precipitate with hydrochloric acid, it at once becomes evident whether sulphuric acid is present or not, as all the salts of baryta are soluble in this menstruum, with the exception of the sulphate. If sulphuric acid is present, the re-action with chloride of barium cannot be used for the detection of all the other acids above mentioned; for on filtering the hydrochloric solution of the precipitates and supersaturating the filtrate with ammonia, the borate, tartrate, citrate, &c., of baryta do not always fall down again, being kept in solution by the chloride of ammonium formed. For this reason, chloride of barium cannot be employed to separate the whole of the acids named, and, except as regards sulphuric acid, no value can be attached to it as a means of effecting their individual detection. It is, however, of great importance as a reagent; for if it gives no precipitate in the neutral solution a large number of acids are at once excluded.

The compounds of silver with sulphur, chlorine, iodine, bromine, cyanogen, ferrocyanogen and ferricyanogen, and of oxide of silver with phosphoric acid, arsenious acid, arsenic acid, boric acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid are insoluble or sparingly soluble in water. All these compounds are soluble in dilute nitric acid, except the chloride, iodide, bromide, cyanide, ferrocyanide, ferricyanide, and sulphide of silver. If, therefore, a precipitate is formed on adding

2. **Nitrate of Silver,** the solution, which, for the reason just now stated, must be quite neutral, this shows at once that one or more of the acids enumerated is present: chromic acid, arsenic acid, and several others, which form coloured salts with silver, may be individually

recognized with tolerable certainty by the colour of the precipitate. By treating the precipitate with nitric acid, the presence of sulphide of silver or of any of the haloïd compounds of silver can be at once recognized, as these remain undissolved, whilst all the oxide salts dissolve. Nitrate of silver cannot be used for the complete separation of those acids which form compounds with oxide of silver insoluble in water, from the same cause which renders the separation of acids by chloride of barium uncertain; the ammoniacal salt formed prevents the reprecipitation, by ammonia, of several of the salts of silver from the acid solution. Nitrate of silver is useful not only in the separation of chlorine, iodine, bromine, cyanogen, &c., and in indicating the presence of chromic acid, &c., but also, like chloride of barium, to prove the absence of many acids, when it produces no precipitate in neutral solutions.

The behaviour of the solution with these two reagents, therefore, indicates at once the further course of the investigation. Thus, for instance, if chloride of barium gives a precipitate, and nitrate of silver does not, it is unnecessary to test for phosphoric acid, chromic acid, boric acid, silicic acid, arsenious acid, arsenic acid, oxalic acid, tartaric acid, and citric acid, provided always the solution was sufficiently concentrated, and did not already contain salts of ammonia. The same is the case if we obtain a precipitate with nitrate of silver, but none with chloride of barium. It is evident, therefore, how many special tests are rendered unnecessary by this simple combination.

Returning to the former supposition that the whole of the acids are present, these reactions would prove the presence of sulphuric acid, and lead to the application of special tests for chlorine, bromine, iodine, cyanogen, ferrocyanogen, ferricyanogen, and sulphur;* there would be grounds also for testing for all the other acids precipitable by the two reagents. The detection of these acids is based upon the results of a series of special experiments, which have already been fully described and explained: the same remark applies to the rest of the inorganic acids, including nitric acid and chloric acid.

Of the organic acids, oxalic acid, (racemic acid,) and tartaric acid are precipitated by chloride of calcium in the cold, in presence of chloride of ammonium; the two former immediately, the latter often only after some time; the precipitation of citrate of lime, however, is prevented by the presence of salts of ammonia, and takes place only on ebullition or on adding alcohol to the solution. Alcohol may also be used to throw down malate and succinate of lime from aqueous solutions. If, therefore, we add to the solution

3. **Chloride of Calcium in excess** and Chloride of Ammonium, oxalic acid, (racemic acid,) and tartaric acid are precipitated, but the lime salts of several inorganic acids, which have not yet been separated—phosphate of lime, for instance—are precipitated at the same time. For the individual detection of the precipitated organic acids, therefore, it is necessary to employ such reactions only as preclude the possibility of confounding the organic acids with the inorganic acids which are thrown down along with them. Accordingly, for the detection of oxalic acid, solution of sulphate of lime, with acetic acid is used (§ 145, 5); for the detection of tartaric acid (and racemic acid), the

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* For the separation and special detection of these substances, see § 157.

precipitate produced by chloride of calcium is treated with solution of soda, since the lime salts of these two acids only are soluble in this menstruum in the cold, but become insoluble upon ebullition.

Of the organic acids, there are still in solution citric acid and malic acid, succinic acid, salicylic acid, and benzoic acid, acetic acid and formic acid. Citric acid, malic acid, and succinic acid are thrown down on adding alcohol to the filtrate from the oxalate, tartrate, &c., of lime, which still contains excess of chloride of calcium. Sulphate and borate of lime are invariably precipitated along with the malate, citrate, and succinate of lime, if sulphuric acid or boric acid happens to be present; care must be taken, therefore, not to mistake the lime precipitates of these acids for those of citric acid, malic acid, and succinic acid. The alcohol is now removed by evaporation, and

4. **Ferric Chloride** added to the perfectly neutral solution. This reagent precipitates the benzoic acid and the rest of the succinic acid in combination with ferric oxide; salicylic acid is recognized by the violet colour it imparts to the liquid, and the formic acid and acetic acid remain in solution. The methods which serve to effect the separation of the several groups from each other, and the reactions on which the individual detection of the various acids is based, need not be repeated here, as they have been fully described and explained in the former part of this work.

B. SPECIAL REMARKS AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

Attention is here directed to several matters which were necessarily passed over in the description of the ordinary course of analysis, and at the same time a short account will be given of the modifications of the ordinary course of analyses which have to be adopted for the detection of the rare metals.

To § 189.

At the commencement of § 189, directions are given to add hydrochloric acid to the neutral or acid aqueous solution; this should be done drop by drop. If no precipitate is formed, a few drops are sufficient, since the only object in that case is to acidify the solution, so as to prevent the subsequent precipitation of the metals of the iron group by sulphuretted hydrogen. If a precipitate is formed, it is sometimes recommended to take a fresh portion of the solution and acidify it with nitric acid; but quite apart from the fact that nitric acid also produces precipitates in many cases—in a solution of tartrate of antimony and potassa, for instance—the use of hydrochloric acid is preferable, that is, the complete precipitation of all that is precipitable by it, on three grounds: 1. Metals are more readily precipitated by sulphuretted hydrogen from solutions acidified with hydrochloric acid than from those acidified with nitric acid; 2. If the solution contains silver, mercurous oxide, or lead, the total or partial precipitation of these three metals in the form of chlorides greatly facilitates future operations; and 3. This is the best form for the individual detection of these three metals when present in the same solution. Moreover, if hydrochloric acid is used, it is not necessary to make a special test to ascertain whether the mercury, detected with the other metals of the fifth group, was present as oxide or suboxide. That the lead, if present in large proportion, is obtained partly as chloride, and partly in the precipitate produced by treating the acid solution with sulphuretted hydrogen, can scarcely be considered as an objection to this method, for the removal of the larger portion of the lead from the solution in this manner facilitates the examination for other metals of the fifth and sixth groups.

As already mentioned, a basic salt of teroxide of antimony may separate from tartar emetic, or from some other analogous compound, and be precipitated along with the two insoluble chlorides, and the sparingly soluble chloride of lead; the same is true of chloride of bismuth, metastannic chloride, and also of benzoic and salicylic acids. As, however, both oxychloride of antimony and oxychloride of bismuth are readily soluble in excess of hydrochloric acid, they dissolve at once on adding more of the acid. It is neither necessary nor advisable to warm the solution mixed with excess of hydrochloric acid, since it might cause the conversion of a little of the precipitated mercurous chloride into mercuric chloride.

If bismuth, antimony, lead, or metastannic acid be present, the addition of the washings of the precipitate produced by hydrochloric acid to the first filtrate will cause turbidity; this is occasioned, in the case of bismuth and antimony, by the free hydrochloric acid present being insufficient to prevent the separation of basic salt, in the case of chloride of lead and metastannic acid, by the metastannic chloride and chloride of lead which have been precipitated, re-dissolving in the wash water, and then being re-precipitated by the excess of hydrochloric acid in the filtrate. This turbidity, however, has no influence on the further process, for these finely divided precipitates are converted into sulphides by sulphuretted hydrogen as if the metals were in solution.

If the precipitate which has been obtained by excess of hydrochloric acid, and subsequently washed with cold water, contains benzoic or salicylic acid, these will dissolve along with the chloride of lead when the precipitate is treated with boiling water, but will not in any way interfere with the detection of the lead in this solution.

In the case of alkaline solutions, hydrochloric acid must be added until the solution is strongly acid; the compound which causes the alkaline reaction combines with the hydrochloric acid, and the substances dissolved or combined with it are thrown down. Thus, if the alkali is present in the free state, oxide of zinc, for instance, or alumina, &c., may be precipitated; but these oxides will re-dissolve in the excess of hydrochloric acid, whereas chloride of silver or silicic acid will not re-dissolve, and chloride of lead only with difficulty. If a metallic sulphur salt is the cause of the alkaline reaction, the sulphur acid—sulphide of antimony, for example—is precipitated on adding hydrochloric acid; whilst the sulphur base—sulphide of sodium, for example—forms chloride of sodium and sulphuretted hydrogen with the components of the hydrochloric acid. If an alkaline carbonate, a cyanide, or the sulphide of an alkali metal is the cause of the alkaline reaction, carbonic acid, or hydrocyanic acid, or sulphuretted hydrogen escapes. All these phenomena should be carefully noted, since they not only indicate the presence of certain compounds, but also demonstrate the absence of entire groups.

Precipitates are produced also by hydrochloric acid in solutions containing thallium, alkali salts of antimonic acid, tantalic acid, niobic acid, molybdic acid, and tungstic acid.* The antimonic, tantalic, and molybdic precipitates dissolve (the tantalic acid precipitate to an opalescent liquid), whilst the chloride of thallium, niobic acid, and tungstic acid do not dissolve in excess of hydrochloric acid, or only slightly; the latter therefore remain with the precipitate, which may also contain chloride of silver, mercurous chloride, chloride of lead, and silicic acid. If, on addition of hydrochloric acid, sulphur begins to separate after some time, accompanied by the odour of sulphurous acid, this indicates hyposulphurous acid. If rare metals are to be tested for in the hydrochloric acid precipitate, it should be exhausted with boiling water, and the filtrate examined for thallium by iodide of potassium (confirming by the spectroscope). On exhausting the washed precipitate with ammonia, the chloride of silver dissolves wholly or in part, together with some tungstic acid; from this solution sulphide of ammonium throws down the silver as sulphide, and on adding dilute hydrochloric acid to the filtrate sulphide of tungsten is precipitated. The mercurous chloride is converted into mercurosamide mercurous chloride by treatment with ammonia, which may retain chloride of silver (J. Barnes). The residue is then warmed with hydrochloric acid and a little nitric acid; this leaves the niobic acid with any chloride of silver that may be present, and, under some circumstances, silicic acid. After heating it with hydrochloric acid, the niobic acid may be dissolved by water.

To §§ 190 and 191.

In order to complete an analysis in as short a time as possible, several of the operations should be carried on simultaneously; for instance, after throwing the sulphuretted hydrogen precipitate on to the filter, it is quite unnecessary to wait until the precipitate is collected and thoroughly washed; the first drops of the filtrate may be tested with sulphide of ammonium to see if there is any metal of that group present, and if this is not the case, whether carbonate of ammonia does not give a precipitate. In this way it is possible, while washing the sulphuretted hydrogen precipitate, to throw down the filtrate with the proper group test. In like manner while the first precipitate is being treated with sulphide of ammonium, the second precipitate may be washed. If the work is carried out methodically in this way, an analysis may be completed in half the time.

In cases where we have to deal merely with metallic oxides of the sixth group, oxide of antimony for example, and of the fourth or fifth group, such as iron or bismuth, it is not necessary to precipitate the acidified solution with sulphuretted hydrogen, but, after neutralization, sulphide of ammonium in excess may be at once added. The sulphide of iron, &c., will in that case be precipitated, while the antimony, &c., will remain in solution, and, on the addition of an acid, will be at once thrown down as sulphide of antimony, &c. This method has the advantage that the solution is diluted less than when sulphuretted hydrogen water is used; and the operation is performed more quickly and conveniently than when the gas is passed into the liquid. The beginner is often apt to make mistakes through using spoilt sulphuretted hydrogen water, or by adding too little good sulphuretted hydrogen water to effect complete precipitation, or through passing the gas into a solution containing *too great an excess* of hydrochloric or nitric acid. Imagine a very acid solution containing iron and bismuth; if sulphuretted hydrogen

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* The hydrate of tungstic acid is not thrown down on adding hydrochloric acid to a solution of a metatungstate, unless the solution is boiled for a long time.

is passed through it, or if only a few drops of sulphuretted hydrogen water is added, there will be no precipitate, as the presence of a large excess of acid entirely prevents its formation; and if, in the idea that no metal of the sulphuretted hydrogen group is present, sulphide of ammonium is then added, a precipitate will be formed containing the sulphides of iron and bismuth. On treating this with dilute hydrochloric acid, a black residue will be left, which in the ordinary course indicates nickel or cobalt. If a mistake of this kind is once made, it is exceedingly difficult, almost impossible in fact, for the beginner to proceed successfully with the analysis. The use of gaseous sulphuretted hydrogen with very acid solutions without previously diluting them with water is the rock on which the beginner is more likely to be shipwrecked than any other. Arsenic acid also may be overlooked if the action of the sulphuretted hydrogen is not facilitated by warming the solution. This source of error may be avoided by taking a small portion of the clear filtrate from the precipitate obtained with sulphuretted hydrogen, and, before adding ammonia and sulphide of ammonium, adding to it about four times its volume of good sulphuretted hydrogen water, and observing whether any further precipitate is formed in the cold or on warming.

Just as, on the one hand, if the solution is too concentrated or contains too large an excess of hydrochloric acid, the complete precipitation by sulphuretted hydrogen is prevented, especially with the gas, so, on the other, the addition of too small an amount of hydrochloric acid, and this is especially the case if alkaline acetates are present, may cause the sulphuretted hydrogen to precipitate metals of the fourth group, particularly sulphide of zinc, along with the metals of the fifth and sixth groups. Sometimes this cannot be prevented by increasing the amount of hydrochloric acid added, and it must be remembered, therefore, in the examination of the metallic sulphides of the fifth group, that it is possible that metals of the fourth group, and especially zinc, may also be present.

If the precipitate obtained with sulphuretted hydrogen in the hydrochloric acid solution is incompletely washed, many sources of error are introduced. These are due, in the first place, to the fact that mercuric sulphide is insoluble in hot nitric acid only when no hydrochloric acid is present. Secondly, unnecessary confusion is caused on treating the incompletely washed precipitate of sulphides with ammonium sulphide to ascertain whether it is completely, partially, or not at all soluble in this solvent. It is manifest that it is impossible to decide this important point if the precipitate still contains iron or nickel salts, &c.

It happens occasionally that on treating acid solutions with sulphuretted hydrogen, or on decomposing by hydrochloric acid the sulphide of ammonium used for dissolving the sulphides of the sixth group that may be present, a precipitate is obtained which looks almost like pure sulphur, leaving a doubt as to whether it is really requisite to examine it for metals. In such cases the precipitate may be washed and dried, and then treated with bisulphide of carbon to remove the sulphur; this will show whether or not there is any sulphide mixed with the sulphur.

Very frequently, however, especially with precipitates very rich in sulphur, it is more advantageous to treat the washed and still moist precipitate with a solution of bromine in hydrochloric acid, or with hydrochloric acid and some chlorate of potassa, then to dilute, filter, and, after driving off the free bromine or chlorine by heat, to again treat the solution with sulphuretted hydrogen to ascertain if any metals of the fifth or sixth group are present.

The following sulphides of the rarer elements are found in the precipitate produced by sulphuretted hydrogen in the acid solution: the sulphides of palladium, rhodium, osmium, ruthenium, iridium,* molybdenum, tellurium, selenium, and possibly of thallium.†

The following rare compounds cause separation of sulphur, by decomposing the sulphuretted hydrogen: the higher oxides and chlorides of manganese and cobalt, vanadic acid (with blue coloration of the solution), nitrous acid, sulphurous acid, hyposulphurous acid, hypochlorous and chlorous acids, bromic acid, and iodic acid.

On treating the precipitate with sulphide of ammonium (sulphide of sodium), the sulphides of iridium, molybdenum, tellurium, and selenium dissolve, whilst the sulphides of palladium, rhodium, osmium, and ruthenium, also that of thallium, remain undissolved.

To § 192.

In § 192 two methods for the separation of the metals of the sixth group are given—one to be employed when there is reason to believe gold and platinum to be absent, and the second if these metals are to be sought for. The latter method, according to which the metallic sulphides are first heated with a mixture of ammonic chloride and nitrate, must also be employed if iridium is present; this remains with the gold and platinum, whilst all the other elements pass into the sublimate, and may be precipitated from the solution by sulphuretted hydrogen.

If the precipitate thus obtained, containing the metallic sulphides of the remaining members of the sixth group and also the sulphides of tin, antimony, arsenic, tellurium, selenium, and molybdenum, is fused with carbonate and nitrate of soda as described in § 192, and the melt treated with cold water, telluric, selenic, and molybdic acids are dissolved out with the arsenic acid, whilst stannic oxide and sodium antimoniate remain undissolved.

The method by which the rare elements in the solution and the iridium in the sublimation residue may be detected is given under § 135.

To § 193.

The separation of the metallic sulphides of the fifth group from those of the sixth by means of sulphide of ammonium or sodium, especially if only treated once, is not always complete, and some of the metallic sulphides of the sixth group may under certain circumstances be found along with the sulphides of the fifth group: platinum and gold sulphides are especially liable to remain undissolved; this fact must therefore be carefully taken into consideration when proceeding to § 193. As the solution of nitrate of platinum—which is

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* The metals of the platinum ores are precipitated with difficulty by sulphuretted hydrogen; for that purpose, the gas must be passed into the solution for a long time, heat being applied.

† Tungsten and vanadium are not found in the precipitate thrown down from an acid solution by sulphuretted hydrogen; they are present only when the solution has been mixed first with sulphide of ammonium, then with acid in excess; in that case, the sulphides of nickel and cobalt will also be found with those of the fifth and sixth groups. Thallium, although it is not precipitated from acid solutions by sulphuretted hydrogen under ordinary circumstances, may be thrown down along with sulphide of arsenic.

obtained when sulphide of platinum is precipitated in the cold—is brown, the presence of platinum among the bases of the fifth group may sometimes be detected by the brown colour of the solution obtained by heating the metallic sulphides with nitric acid. On evaporating this brown solution, igniting, and again heating with nitric acid, the platinum remains as metal, whilst the other oxides are dissolved.

Besides the methods for the separation of lead, copper, bismuth, and cadmium given in the systematic course, the following is also very accurate. Carbonate of soda is added to the nitric acid solution as long as any precipitate forms, then solution of cyanide of potassium in excess, and the mixture is gently heated; in this way the lead and bismuth are completely separated as carbonates, whilst copper and cadmium remain in solution in the form of cyanide of copper and potassium, and cyanide of cadmium and potassium. The lead and bismuth may be readily separated from one another by means of sulphuric acid, and the copper and cadmium by adding sulphuretted hydrogen in excess to the solution of their cyanides in cyanide of potassium, heating gently, and then adding some more cyanide of potassium to re-dissolve the sulphide of copper which may have been precipitated along with the sulphide of cadmium; an insoluble yellow precipitate of sulphide of cadmium indicates the presence of cadmium. Hydrochloric acid is added to the filtrate from this precipitate, when the formation of a black precipitate of sulphide of copper indicates copper; as hydrocyanic acid is liberated on acidifying, the operation must be carried on in a draught.

If there is reason to suppose that the precipitate containing the sulphides of the fifth group contains also the sulphides of palladium, rhodium, osmium, ruthenium, or thallium along with the sulphides of copper, bismuth, &c., a portion is first tested for thallium by the spectroscope, and the bulk of the precipitate treated as follows:—

The precipitate is fused with hydrate of potassa and chlorate of potassa, ultimately heating to redness; it is then allowed to cool, and the melt treated with water. The solution contains osmate and ruthenate of potassa, being coloured deep yellow by the latter. If the solution is cautiously neutralized with nitric acid, black hydrated sesquioxide of ruthenium separates; if more nitric acid is added to the filtrate, and it is then distilled, osmic acid passes over. If the residue left on extracting the fused mass with water is gently ignited in a current of hydrogen,* and then cautiously treated with dilute nitric acid, the copper, lead, &c., are dissolved, whilst the rhodium and palladium are left. The palladium may then be dissolved out of the residue by means of aqua regia, leaving the rhodium. The further examination of the isolated metals is described in § 124. A separate portion of the precipitate of sulphides must be examined for mercury, in the event of the above process being adopted.

To § 194.

Assuming all the elements not yet precipitated to be present in the filtrate from the precipitate produced by sulphuretted hydrogen in the acid solution, the precipitate thrown down on adding chloride of ammonium to this filtrate, neutralizing with ammonia, and adding sulphide of ammonium in excess, will contain the following elements:

a. As sulphides: cobalt, nickel, manganese, iron, zinc, uranium, thallium, and indium;

b. In the form of oxides: aluminium, beryllium, thorium, zirconium,

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* Cadmium may escape in this operation.

yttrium, cerium, lanthanium, didymium, chromium, titanium, tantalum, and niobium.*

It will be found to be an exceedingly difficult task to elaborate any method for the separation of all the elements in this precipitate, based on the difference in their behaviour towards reagents, for many of the metallic oxides when in solution together behave towards the same reagent differently from what they do when in solution by themselves. As, however, it would never actually be the case that all the members of the third and fourth groups would be present in the precipitate obtained with ammonia and sulphide of ammonium, no method is given for detecting all these elements, but merely the most important processes for separating the elements in question into smaller or larger groups, so as to facilitate their further examination.

1. For the separation of tantalic, niobic, and titanic acids the following method may be employed :—The precipitate obtained with ammonia and sulphide of ammonium is roasted, the residue fused for some time with **acid sulphate of potassa**, and the cooled mass is treated with cold water, digested for some time without heating, and the solution filtered off from the residue. The residue, which contains the acids of tantalum and niobium, and possibly silicic acid and a little undissolved ferric and chromic oxides, is fused with **hydrate of soda** and some **chlorate of potassa**, when a mass is obtained from which dilute soda solution will dissolve chromate and silicate of potassa, leaving undissolved the ferric oxide and tantalate and niobate of soda (which are insoluble in solution of soda). The niobic and tantalic acids are most conveniently separated by converting them into the potassio-fluorides (p. 117). For the further examination, compare § 104, 9 and 10.

The acid solution, which contains the titanic acid, or at all events the greater portion of it, along with the bases of the third and fourth groups, is treated with sulphuretted hydrogen to reduce the ferric oxide, diluted considerably, heated to boiling, and carbonic acid passed into the boiling solution for some time; the titanic acid is thus thrown down as a white precipitate, which may possibly contain a little zirconia also.

The filtrate obtained after the separation of the tantalic, niobic, and titanic acids, or the solution from which these acids are absent, is boiled with nitric acid to oxidize any ferrous oxide which may be present, chloride of ammonium added, and then **ammonia**; the precipitate is collected, washed, re-dissolved in hydrochloric acid, and precipitated again with ammonia; almost the whole of the zinc, manganese, nickel, cobalt, and gallium remain in solution, whilst the earths remain undissolved along with the oxides of iron, indium, uranium, and chromium.

3. Gallium may be separated from zinc, manganese, nickel, and cobalt by digesting the hydrochloric acid solution of these metals with **carbonate of baryta** in the cold. By this means, the oxide of gallium is precipitated whilst the other metals remain in solution.

4. For the separation of alumina and beryllia, as also oxide of chromium, from iron, indium, and uranium oxides, as also from the other bases of the third group, their hydrochloric acid solution is treated with *concentrated* **potash** in the cold. This will leave in solution the sesquioxide of chromium, the alumina, and the beryllia whilst precipitating the other earths with the oxides of iron, indium, and uranium. The alkaline solution is diluted, filtered, and boiled for some time; this will throw down the beryllia, and the oxide of chromium, leaving the alumina in solution; the latter can then be precipitated by chloride of ammonium. By fusing the precipitate of beryllia and sesquioxide of chromium with carbonate of soda and chlorate of potassa, the two can be separated in the same way as alumina and oxide of chromium (§ 103).

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* Of niobic acid only the traces re-dissolved on precipitating by hydrochloric acid and washing the precipitate can be present here.

5. K. F. Föhr* states that the following method is particularly adapted for the separation of ferric oxide and any residue of alumina (which under certain circumstances, as, for instance, when yttrium and cerium oxides are present, is not completely dissolved by the potash solution) from cerium, lanthanium, didymium, thorium, zirconium, yttrium, and uranium oxides:—The precipitate insoluble in aqueous potash obtained according to 4 is, while still moist, digested with excess of cold concentrated solution of **carbonate of ammonia** for about twelve hours; the solution is then poured off on to a filter, and the residue digested once more with carbonate of ammonia. A residue of insoluble hydrated ferric oxide and some hydrate of alumina is thus separated, whilst the uranium, cerium, lanthanium, didymium, thorium, zirconium, and yttrium oxides are dissolved. On heating this solution to boiling, thorium, zirconium, and yttrium oxides are precipitated, and may be separated from one another by means of **sulphate of potassa** (vide 7); the oxides of cerium, lanthanium, and didymium may be thrown down by the addition of a concentrated solution of **oxalic acid.** Uranium oxide now remains in solution, and may be precipitated by the addition of **potash.** (In the separation of cerium oxide, &c., from uranium oxide, the solution must not stand for any time, as otherwise oxalate of uranium is also precipitated.)

6. The separation of the bases contained in the ammonia precipitate from 2, that is, ferric oxide, alumina, and beryllia, the oxides of chromium, uranium, cerium, lanthanium, and didymium, also thoria, yttria, and zirconia, may be easily effected by treating the washed moist precipitate with a concentrated solution of **oxalic acid**; this dissolves the ferric oxide, alumina, beryllia, and the oxides of chromium and uranium, leaving the other bases as insoluble oxalates (K. F. Föhr*).

7. Zirconia and thoria (and also members of the cerite group) may be separated from yttria (and also from beryllia and alumina) by means of sulphate of potassa; crystals of neutral **sulphate of potassa** are added to the neutral or faintly acid solution, the solution is boiled, allowed to stand for twelve hours, filtered, and the precipitate, which consists of the double sulphates of potassa and zirconia and thoria (as also of members of the cerite group), is washed with a solution of sulphate of potassa. On adding ammonia to the filtrate, yttria, oxide of beryllium, and alumina are precipitated; the latter may be separated from the yttria by means of oxalic acid (see 6). On repeatedly boiling the precipitated potassa double sulphates with water and a little hydrochloric acid, the thoria and members of the cerite group pass into solution, and may be re-precipitated by ammonia; but the double sulphate of potassa and zirconia remains undissolved.

8. Barium carbonate is best adapted for the separation of indium from zinc and iron. The hydrochloric acid solution is first heated with sulphurous acid in order to convert the ferric into ferrous chloride, and, when cold, freshly precipitated **carbonate of baryta** is added, air being carefully excluded. If much iron is present, the operation must be repeated. The precipitate containing the indium oxide is dissolved in hydrochloric acid, and the baryta precipitated by sulphuric acid. On adding ammonia to the filtrate, hydrated oxide of indium is precipitated.

9. To detect thallium in the precipitate produced by ammonia and sulphide of ammonium, a portion of it is dissolved in boiling dilute hydrochloric acid, the solution treated with sulphurous acid until the ferric oxide is reduced, then nearly neutralized with ammonia, and tested with iodide of potassium. The precipitate must, under all circumstances, be further examined in the spectroscope.

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* Written communication of September 2, 1881, in part founded on the methods given in Will's tables for qualitative analysis.

To §§ 195–198.

The filtrate from the precipitate produced by sulphide of ammonium may contain not only the alkaline earths and the alkalies, but some **nickel**, also **vanadic acid** and that portion of the **tungstic acid** which has been left unprecipitated by hydrochloric acid. The nickel, the vanadic acid, and the tungstic acid are present as sulphides dissolved in the excess of sulphide of ammonium, and are thrown down as such on acidifying the solution with hydrochloric acid. The precipitate is collected, washed, dried, and fused with carbonate of soda and nitrate of potassa; on treating the fused mass with water, the vanadate and tungstate of potassa dissolve, leaving the oxide of nickel undissolved. The vanadic acid may be separated from this solution by means of solid chloride of ammonium, the tungstic acid by evaporating with hydrochloric acid and treating the residue with water. The two acids may then be examined as directed § 113, *e*, and § 135, *c*.

The detection of **lithium**, **cæsium**, and **rubidium**, is described pp. 92 and 93, and in the analysis of mineral waters (**259** and **260**).

To § 201 and § 203.

In order to avoid unnecessary complication, the detection of small quantities of silica in the presence of a large amount of calcium fluoride or other metallic fluoride was not considered in § 201 and § 203. Should such a case, however, occur, as not unfrequently happens in the analysis of mineral fluorides, and if the method given in § 201, 2 (**194**), or § 203, 4 (**208**), be employed, the silica present may be completely overlooked, being volatilized as silicic fluoride on evaporating with hydrochloric acid the alkaline solution obtained from the fusion. In order, therefore, to separate the silica in the analysis of substances containing fluorine, the alkaline solution of the fused mass obtained according to **194** or **208** must be heated with carbonate of ammonia, the carbonate of ammonia lost by evaporation being replaced; the solution is then filtered, and, in order to separate the silica, the filtrate is treated with a solution of zinc oxide in ammonia, evaporated until all the ammonia is driven off, and filtered. The silica contained in the precipitate produced by the carbonate of ammonia is then separated by evaporating it with hydrochloric acid; it is better, however, to add nitric acid to the precipitate obtained with ammonia and zinc oxide, and evaporate.

If the rare elements also are taken into account, the substances which may remain undissolved on treating a substance with water, hydrochloric acid, nitric acid, and aqua regia are far more numerous. The following substances, more especially, are insoluble or slowly and sparingly soluble in acids, either ordinarily, or in the ignited state, or in certain combinations:

Beryllia, thoria, and zirconia, oxide of cerium, titanic acid, tantalic acid, niobic acid, molybdic acid, tungstic acid, rhodium, iridium, osmium, ruthenium.

In the systematic course of analysis, having arrived at **208**, the substance, free from silver, lead, and sulphur, is fused with carbonate of soda and some nitrate of potassa, the fused mass extracted repeatedly with hot water, and, if a residue is left, this is fused for some time in a silver crucible, with hydrate of potassa and nitrate of potassa, and the fused mass is again treated repeatedly with water. The alkaline solutions, which may be examined separately or together, may contain beryllia, a portion of the titanic acid, tantalic acid, niobic acid, molybdic acid, tungstic acid, osmic and ruthenic acids, and a portion of the iridium.

If the residue left undissolved in the preceding operation is fused with acid sulphate of potassa, and the fused mass treated with water, the thoria, zirconia, oxide of cerium, the remainder of the titanic acid, and the rhodium will dissolve; if any residue is left, it may consist of platinum-ore metals, and had best be mixed with chloride of sodium, and ignited in a stream of chlorine.

With regard to the separation and detection of the several elements that have passed into the different solutions, the requisite directions and instructions have been given in the third section of Part I., and in the additional remarks to §§ 189–198.

To § 204.

The analysis of cyanogen compounds is not very easy in certain cases, and it is even sometimes a difficult task to ascertain whether we have really a cyanide present or not. However, if the reactions of the substance when ignited (8) be carefully observed, and also whether there is any odour of hydrocyanic acid (33 and 37) when it is boiled with hydrochloric acid, the presence of a cyanide will not usually remain a matter of doubt.

Above all it must be borne in mind that the insoluble cyanogen compounds occurring in pharmacy, &c., belong to two distinct classes, namely, either simple cyanides, or compounds of metals with ferrocyanogen or some other analogous compound radicle.

All the simple cyanides are decomposed by boiling with concentrated hydrochloric acid yielding metallic chlorides and hydrocyanic acid; their analysis is therefore never difficult. The ferrocyanides, &c., however, to which indeed the method described in § 204 exclusively refers, undergo such complicated decompositions when treated with acids, that their analysis cannot be easily effected in this manner. Their decomposition by potassa or soda is far more simple. The alkali separates the metal combined with the ferrocyanogen, or other similar radicle, as oxide, whilst the alkali metal itself combines with the radicle to form a soluble ferrocyanide, cobalticyanide, &c. Several oxides, however, such as oxide of lead, oxide of zinc, &c., are soluble in an excess of potassa or soda. If, therefore, the double ferrocyanide of zinc and potassium, for instance, is boiled with solution of caustic potassa, it dissolves completely, and we may assume that the solution contains ferrocyanide of potassium and oxide of zinc dissolved in potassa. If an acid were added to this solution, the original precipitate of the double ferrocyanide of zinc and potassium would of course be again thrown down, and the experiment would be unsuccessful. To prevent this, sulphuretted hydrogen is passed into the solution in potassa, but only until the precipitable oxides are completely thrown down, and not until the solution smells of sulphuretted hydrogen; by this means all the heavy metals which the potassa holds in solution as oxides are converted into sulphides. Those sulphides which are insoluble in potassa, such as sulphide of lead, sulphide of zinc, &c., are precipitated, whilst those which are soluble in alkaline sulphides, as well as the sulphides of the sixth group and a little mercuric sulphide if present, remain in solution. In order not to overlook these, the filtrate is acidified, and, if necessary, more sulphuretted hydrogen is passed into it.

Those metals which form compound radicles with cyanogen will be in the filtrate from the oxides and sulphides, and also alumina, which was dissolved in the original treatment with potash, and has not been separated. Finally also the other acids must be tested for here. The solution, therefore, should be divided into two parts, the one tested for acids, and the other for alumina and those metals which form compound radicles with cyanogen. On heating this second part with concentrated sulphuric acid, all the cyanogen compounds are decomposed, and the metals remain in the residue as sulphates (H. Rose*).

If it is merely wished to test for bases in simple or compound cyanides, and for that purpose to destroy the cyanogen compound, it is only necessary to heat the powdered substance in a platinum dish with concentrated sulphuric acid diluted with a little water, until almost all the free acid is driven off; the residue, consisting of sulphates, should be dissolved in hydrochloric acid and water.

The reason why ferrocyanides and similar compounds which have been carefully washed with water have to be tested for alkalies is because alkaline ferrocyanides, &c., are often precipitated along with insoluble ferrocyanides, &c., and cannot be removed by washing; there are many such insoluble compounds which contain both heavy metals and the alkali metals in combination with ferrocyanogen, &c.

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* Zeit. anal. Chem., **1**, 194.

APPENDIX.

I.

Behaviour of the more important Alkaloïds with Reagents, and a Systematic Method of Detecting them.

§ 229.

The detection and separation of the alkaloïds is far more difficult than the detection and separation of the inorganic bases. In many cases, the combination in which an alkaloïd can be separated from others is not sufficiently insoluble to allow of a sharp separation, in others we only know the external characteristics of a reaction and not its cause, so that we are ignorant of the conditions which may modify its action; again, many alkaloïds may be said to have no characteristic reaction whatever. These difficulties are still greater when the alkaloïds are not quite pure, as frequently happens when they have been separated from articles of food, organs of the body, &c.

In the following pages, the methods of detecting the more important and commonly occurring alkaloïds will be given, including nicotine, conine, morphine, narcotine, quinine, cinchonine, strychnine, brucine, veratrine, and atropine.

If the student is thoroughly acquainted with these, and can separate them, it will be comparatively easy for him to widen the sphere of his knowledge in this special subject.

This appendix will be divided into the following sections:

A. General reagents for the alkaloïds.

B. Properties and reactions of the individual alkaloïds, arranged in groups.

C. Properties and reactions of certain non-nitrogenous compounds which are allied to the alkaloïds as poisons or are employed in their adulteration, namely, salicin, digitalin, and picrotoxin.

D. Systematic course for the detection of the alkaloïds above mentioned—

a. When only one is present.
b. When several or all of them may be present.
c. In the presence of other organic substances.

A. GENERAL REAGENTS FOR THE ALKALOÏDS.

§ 230.

General reagents for the alkaloïds are those which give precipitates with all or nearly all of them; they are therefore well suited to test for the presence of an alkaloïd, and may serve to separate alkaloïds from their solutions, but they will not serve to distinguish individual alkaloïds except in a subordinate degree.

These reagents are as follows:—Chloride of platinum, a solution of iodine in iodide of potassium (Wagner[*]), potassium mercury iodide (v. Planta[†]), potassium cadmium iodide (Marmé[‡]), potassium bismuth iodide (Dragendorff[||]), phosphomolybdic acid (de Vrij, Sonnenschein[¶]), phosphoantimonic acid (F. Schulze[**]), phosphotungstic acid (Scheibler[††]), picric acid (H. Hager[‡‡]).

Chloride of platinum forms with the hydrochlorides of the alkaloïds compounds analogous to the platinochloride of ammonium. Some of these compounds are sparingly soluble in water, some are rather easily soluble. These double salts are best obtained and most completely separated by adding a sufficient quantity of chloride of platinum to the solution, evaporating nearly to dryness, and treating with alcohol; the compounds are yellow of various shades, some are crystalline, some flocculent, and they are usually more soluble in hydrochloric acid than in water.

A solution of iodine in iodide of potassium (containing 12·7 grams of free iodine per litre) precipitates the solutions of the salts of all alkaloïds; the precipitates are brown and flocculent. Their formation and separation are assisted by acidifying with sulphuric acid. By washing the precipitate, dissolving it in solution of sulphurous acid, and evaporating on the water-bath to remove the excess of sulphurous acid and the hydriodic acid, the alkaloïd will remain in combination with sulphuric acid. If the precipitate was thrown down from a solution containing much organic matter, it should be dissolved in a dilute solution of hyposulphite of soda, filtered, the filtrate re-precipitated with the iodine solution, and the precipitate treated in the manner described above.[||||]

Potassium mercury iodide precipitates solutions of the salts of all the alkaloïds. The precipitates are white or yellowish white, insoluble in water and in dilute hydrochloric acid.

Potassium cadmium iodide[¶¶] gives precipitates with solutions of salts of the alkaloïds which have been acidified with sulphuric acid, even when they are very dilute; these precipitates are at first flocculent and white, but some of them become crystalline after a short time. They are insoluble in ether, readily soluble in alcohol, less soluble in water, readily soluble in excess of the precipitant. They have a tendency to decompose by long standing. The alkaloïd may be obtained from the undecomposed precipitate by mixing it with an alkaline carbonate or hydrate and water, and then shaking it with some solvent

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[*] Zeit. anal. Chem., **4**, 387.

[†] *Verhalten der wichtigsten Alkaloide gegen Reagentien* (Heidelberg, 1846).

[‡] Zeit. anal. Chem., **6**, 123.

[||] *Ibid.*, **5**, 406.

[¶] Ann. Chem. Pharm., **104**, 47.

[**] *Ibid.*, **109**, 179.

[††] Jour. pr. Chem., **80**, 211.

[‡‡] Pharm. Centralhalle, 10r Jahrg., 131.

[||||] If the brownish-red precipitate produced on mixing the iodine solution with a salt of strychnine is dissolved in alcohol containing sulphuric acid and evaporated, prismatic crystals, which act strongly on polarized light, are obtained (de Vrij and van der Burg, "Jahresber. von Liebig u. Kopp," 1857, 602). As regards the sulphate of iodoquinine, comp. § 235, 7.

[¶¶] Prepared by saturating a boiling concentrated solution of iodide of potassium with iodide of cadmium, and adding an equal volume of a cold saturated solution of iodide of potassium. The concentrated solution keeps well, but not the dilute.

which is immiscible with water, such as benzene, amylic alcohol, ether, or the like.

Potassium bismuth iodide* added drop by drop to solutions containing a salt of the alkaloïd acidified with sulphuric acid (10 c.c. of the alkaloïd solution and 5 drops of concentrated sulphuric acid) produces a flocculent orange precipitate almost immediately if nicotine, conine, morphine, narcotine, quinine, cinchonine, strychnine, brucine, atropine, and most other alkaloïds are present; veratrine, on the other hand, gives only a faint turbidity. The precipitate formed with any of the first-named alkaloïds agglutinates together to some extent when heated, dissolves on long-continued boiling, and separates again for the most part on cooling. None of the precipitates is crystalline. The alkaloïds may be separated from the precipitate in the manner described in the preceding paragraph.

Phosphomolybdic acid† is precipitated by the solutions of all alkaloïds, even when their quantity is very minute. The precipitates are light yellow, ochreous or brownish yellow, insoluble or sparingly soluble at the ordinary temperature in water, alcohol, ether, and dilute mineral acids, with the exception of phosphoric acid; they are most insoluble in dilute nitric acid, especially when it contains some of the reagent; acetic acid also is almost without action in the cold, but has a solvent action if hot. The precipitates dissolve in the hydrates and carbonates of the alkalies, generally with ease and with separation of the alkaloïds; the alkaline earths, the oxides of silver and lead and their carbonates also slowly decompose the precipitates with liberation of the alkaloïd. The latter may be removed by shaking with ether, amylic alcohol, benzene, or the like.

Phosphoantimonic acid, obtained by dropping perchloride of antimony into aqueous phosphoric acid, like phosphomolybdic acid gives precipitates with ammonia and with most of the alkaloïds (but not with caffeïne). The reactions are delicate, but generally less so than with the reagent last mentioned, especially in the case of nicotine and conine; this reagent is, however, a more delicate test for atropine than phosphomolybdic acid. The precipitates are mostly flocculent and whitish; the

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* To prepare this reagent, Dragendorff recommends that 32 parts of sulphide of bismuth should be heated in a combustion tube sealed at one end with 41·5 parts of iodine, the iodide of bismuth collected in a receiver, purified by re-sublimation, and heated with solution of iodide of potassium; this is filtered hot, and an equal volume of a cold saturated solution of iodide of potassium added to the filtrate. The concentrated orange-coloured solution keeps well, but not the dilute. No turbidity should be produced on mixing 10 c.c. water with 5 drops of concentrated sulphuric acid and adding 1 or 2 drops of the reagent. Fron (Chem. Centralbl., 1875, 263) prepares the solution by mixing 1·5 gram of freshly precipitated basic nitrate of bismuth (without washing it) with 20 c.c. of water, heating to boiling, adding 7 grams of iodide of potassium, and then 20 drops of hydrochloric acid. Before using this reagent to precipitate the solution containing the alkaloïd, a few drops of hydrochloric acid must be added to the latter, otherwise the reagent will be decomposed by the water.

† Prepared as follows:—The nitric acid solution of molybdate of ammonia is precipitated with ordinary phosphate of soda, the precipitate well washed, suspended in water, and warmed with a solution of carbonate of soda until it is completely dissolved. The solution is evaporated to dryness, the residue ignited, and, if reduction has taken place, it is moistened with nitric acid and ignited again. The product is warmed with water, and dissolved by adding nitric acid in considerable excess. One part of the residue should make 10 parts of solution. The golden yellow solution must be protected from ammoniacal fumes.

brucine precipitate, however, is rose-coloured; on heating, this dissolves, but on cooling it separates again, leaving the solution of an intense carmine colour.

Phosphotungstic acid precipitates the solutions of all the alkaloïds; the precipitates are white and flocculent. This reaction is extremely delicate; acid solutions containing 1 : 200,000 of strychnine or 1 : 10,000 of quinine are rendered distinctly turbid; if the precipitate settles at the bottom of the vessel after the lapse of twenty-four hours, it may be collected on a filter, and washed with acidulated water without passing through the filter. The precipitate is decomposed by lime or baryta with formation of an insoluble phosphotungstate and separation of the alkaloïd.

Picric acid precipitates almost all the alkaloïds, even from solutions containing a large excess of sulphuric acid. The precipitates, which are yellow and crystalline or soon become crystalline, are insoluble in excess of the precipitant; they are usually formed even in very dilute solutions; the exceptions will be considered under the individual alkaloïds.

B. PROPERTIES AND REACTIONS OF THE INDIVIDUAL ALKALOÏDS.

I. Volatile Alkaloïds.

The volatile alkaloïds are liquid at the ordinary temperature, and may be volatilized in the pure state as well as with water vapour; they pass over, therefore, with the distillate when their salts are distilled with strong fixed bases and water. Their vapours, when brought in contact with those of volatile acids, form a white cloud.

1. Nicotine, $C_{20}H_{14}N_2$ [$C_{10}H_{14}N_2$].

§ 231.

1. Nicotine occurs in the leaves and seed of tobacco, and in its pure state forms a colourless, oily liquid, which becomes yellowish or brownish on exposure to the air. Its sp. gr. (compared with water at 4°) is 1·01837 at 10·2° and 1·01101 at 20° (Landolt). In an atmosphere of hydrogen it boils at 247° without decomposition (Landolt), but when heated to boiling in contact with air it is partly decomposed.

It mixes with water in all proportions, but on adding hydrate of potassa or soda it separates from the solution. It is easily soluble in alcohol, ether, amyl alcohol, and light petroleum.

Nicotine has a peculiar, disagreeable, somewhat ethereal odour, recalling that of tobacco. When heated, it emits a very powerful odour of tobacco. It has a pungent burning taste, and is very poisonous. When dropped on paper, it leaves a transparent spot, which slowly disappears; it turns turmeric-paper brown and litmus-paper blue. These reactions are more distinct with a concentrated aqueous solution of nicotine than with the pure alkaloïd.

2. Nicotine is a tolerably strong base; it precipitates metallic oxides from their solutions, and forms salts with acids; these are not volatile or scarcely volatile, and freely soluble in water and alcohol,

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* This reagent is prepared by adding some phosphoric acid to a solution of ordinary tungstate of soda.

insoluble in ether with the exception of the acetate, and insoluble in amylic alcohol, chloroform, benzene, and light petroleum; they are inodorous, but taste strongly of tobacco; some of them are crystallizable. Their solutions may be evaporated at a gentle heat without loss of nicotine, but when distilled with solution of potassa they give a distillate containing nicotine. By neutralizing this with oxalic acid, and evaporating, oxalate of nicotine is obtained, which may be freed from any admixture of oxalate of ammonia by treatment with spirit, in which the former is soluble, the latter insoluble.

3. If an aqueous solution of nicotine, or a solution of a salt of nicotine mixed with solution of soda or potassa, is shaken with **ether** or **light petroleum**, the nicotine is taken up by the solvent; if the latter is then allowed to evaporate on a watch-glass at 20° or 30°, the nicotine remains behind in drops and streaks; on warming the watch-glass, it volatilizes, forming white fumes of strong odour. If an ethereal solution of hydrochloric acid is added to the evaporating liquid, a yellowish amorphous residue of hydrochloride of nicotine is left, which becomes crystalline if kept for a considerable time.

4. **Chloride of platinum** produces a yellowish-white flocculent precipitate in aqueous solutions of nicotine or its salts if not too dilute. On heating the liquid in which the precipitate is suspended, it dissolves, but, on continuing to heat, it very speedily separates again as an orange-yellow, crystalline, heavy powder, which, under the microscope, appears to be composed of roundish crystalline grains. If chloride of platinum is added to a rather dilute solution of nicotine supersaturated with hydrochloric acid, it remains clear at first, but after a time the double salt separates in small crystals (oblique, four-sided prisms), clearly discernible with the naked eye. An alcoholic solution, containing some free hydrochloric acid, gives a yellow precipitate immediately on the addition of hydrochloric acid; the platinochloride separates as a sandy powder.

5. **Chloride of gold** added in excess to aqueous solutions of the alkaloïd or its salts throws down a reddish-yellow flocculent precipitate, sparingly soluble in hydrochloric acid.

6. The solution of **iodine in iodide of potassium**, when added in small quantity to an aqueous solution of nicotine, produces a yellow precipitate, which disappears after a time; on adding more iodine solution, a copious kermes-coloured precipitate separates; but this also disappears again after a time.

7. Solution of **tannic acid** gives a copious white precipitate with aqueous solution of nicotine; this re-dissolves on adding hydrochloric acid or dilute sulphuric acid.

8. If an aqueous solution of nicotine is added to excess of solution of **mercuric chloride**, an abundant, flocculent, white precipitate is formed, soluble in hydrochloric acid and in chloride of ammonium solution. A *neutral* solution of hydrochloride of nicotine is also precipitated by mercuric chloride, but not if it contains excess of acid.

9. Cold *concentrated* **sulphuric acid** and **nitric acid** of 1·2 sp. gr. dissolve nicotine without any coloration. Cold **nitric acid** of 1·4 sp. gr. dissolves it, forming a red solution.

10. By gently warming 1 drop of nicotine with 3 or 4 drops of **hydrochloric acid** of 1·12 sp. gr., a pale brownish-red solution is obtained, and if after cooling a drop of nitric acid, sp. gr. = 1·4, be added, the solution will become violet-red, gradually changing to red.

11. If an **ethereal solution of iodine** is added to solution of 1 part of nicotine in about 100 parts of ether, a brownish-red resinous oil is precipitated, which gradually solidifies to a crystalline mass. The clear pale brownish-yellow solution after some time yields long transparent, ruby-red, acicular crystals, which exhibit a dark blue lustre by reflected light. (Roussin's crystals.)

12. On adding an excess of **picric acid** to an aqueous solution of nicotine, or to a solution of a nicotine salt, a yellow precipitate is formed; this is soluble in hydrochloric acid.

13. **Chlorine water** forms a white turbidity or slight precipitate in an aqueous solution of nicotine, which, however, immediately disappears on the addition of hydrochloric acid.

14. According to Dragendorff and Zalewsky, the **general reagents** for alkaloïds added to 0·1 c.c. of a neutral solution of nicotine hydrochloride give reactions when the following amounts of nicotine are present:—For platinic chloride, 1 part in 5000; auric chloride, 1 part in 10,000; phosphomolybdic acid, 1 part in 40,000; potassium bismuth iodide, 1 part in 40,000; potassium mercuric iodide, 1 part in 15,000; mercuric chloride, 1 part in 1000; tannic acid, 1 part in 500; solution of iodized iodide of potassium, 1 part in 1000.

2. Conine, $C_{16}H_{17}N$ [$C_8H_{17}N$].

§ 232.

1. Conine occurs in the seeds of the hemlock (*C. maculatum*), especially if unripe, and also in other parts of the plant; it is a colourless oily liquid, of 0·886 sp. gr., which becomes brown on exposure to air. In the pure state, it boils at 168·5°, and distils unaltered in a current of hydrogen; but if distilled in vessels containing air, it turns brown and is decomposed in part; it passes over freely with aqueous vapour. It is only sparingly soluble in water, 90 parts of water dissolving 1 part of conine at the ordinary temperature; the solution becomes turbid on warming, and clear again on cooling. Conine is miscible in all proportions with alcohol, and is easily soluble in ether, light petroleum, and the volatile and fatty oils; somewhat less soluble in chloroform. The aqueous and alcoholic solutions have a strongly alkaline reaction. Conine is volatile to a considerable extent at the ordinary temperature; it has a very strong, pungent, repulsive odour resembling that of mouse urine;* the fumes affect the head, and it is very poisonous.

2. Conine is a strong base, precipitating metallic oxides from their solutions in a way similar to ammonia, and forming salts with acids; these are soluble in water and in spirit, insoluble in light petroleum, and insoluble or but little soluble in ether. With the volatile acids, conine forms thick white fumes. Hydrochloride of conine crystallizes readily; the smallest quantity of the base brought in contact with a trace of hydrochloric acid yields almost immediately a corresponding quantity of non-deliquescent rhombic crystals (T. Wertheim). Sulphate of conine separates from its solution at first in needles, later on in large plates (Dragendorff). The dry salts do not smell of the alkaloïd,

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* According to Zalewsky, when it is quite pure the odour is different.

and, when moistened, they smell but feebly of it; on adding soda solution, however, they at once emit a strong odour, and, on distilling, conine passes over with the distillate. On neutralizing this with oxalic acid, evaporating to dryness, and treating the residue with spirit, the oxalate of conine is dissolved, whilst any oxalate of ammonia that may be present remains undissolved.

As conine is only sparingly soluble in water, and dissolves with still greater difficulty in solution of the alkalies, a concentrated solution of a salt of conine turns milky on addition of soda solution. The minute drops which separate gradually unite and collect on the surface.

3. If an aqueous solution of a salt of conine is shaken with solution of **soda** and **ether** or **light petroleum**, the conine is taken up by the solvent. If the latter is then allowed to evaporate on a watch-glass at 20° or 30°, the conine is left in yellowish oily drops.

4. In solutions of the alkaloïd or its salts, **chloride of gold** produces a yellowish-white precipitate, insoluble in hydrochloric acid.

5. **Mercuric chloride** gives with conine a copious white precipitate, soluble in hydrochloric acid.

6. **Chloride of platinum** does not precipitate solutions of hydrochloride of conine even if they are concentrated; moreover, no precipitate is formed on the addition of alcohol (distinction from nicotine).

7. If **chlorine water** is added to conine mixed with water, an abundant white precipitate is formed, easily soluble in hydrochloric acid.

8. If a little water and then a concentrated solution of **picric acid** is added to conine, a yellow precipitate is thrown down; a somewhat dilute solution is not precipitated.

9. With solution of **iodine in iodide of potassium**, and with **tannic acid**, conine behaves like nicotine.

10. Conine dissolves without any coloration in cold concentrated **sulphuric acid** and in cold **nitric acid** of 1·4 sp. gr.

11. According to Dragendorff and Zalewsky, the usual alkaloïd reagents added to 0·1 c.c. of a neutral solution of sulphate of conine give reactions when present in the following proportions:—Phosphomolybdic acid, 1 in 6000; potassium bismuth iodide, 1 in 6000; potassium mercuric iodide, 1 in 1000; tannic acid, 1 in 100; iodized iodide of potassium, 1 in 10,000.

As the volatile alkaloïds are most easily recognized when pure, the chief aim of the analyst must be to obtain them in that state. The way of effecting this is the same for nicotine and conine, and has already been given in the foregoing paragraphs. The solution is distilled with addition of solution of soda, the distillate neutralized with oxalic acid, evaporated, and the residue dissolved in alcohol, and evaporated. The product is then treated with water, solution of soda added, the mixture shaken with ether or light petroleum, and the solvent containing the alkaloïd allowed to evaporate spontaneously at 20°. Conine is distinguished from nicotine chiefly by its odour, its sparing solubility in water, the behaviour of its aqueous solution when heated, the rapid crystallization, crystalline form, and optical properties of its hydrochloride, and also by its behaviour with chloride of platinum and with picric acid. The behaviour of nicotine is characteristic on heating it with hydrochloric acid, and then adding nitric acid, and more particularly the reaction with ethereal solution of iodine. Lastly, it should be remembered that the general reagents for alkaloïds throw down nicotine from far more dilute solutions than they do conine.*

II. NON-VOLATILE ALKALOÏDS.

The non-volatile alkaloïds are solid, and cannot be distilled over with water.

First Group.

Non-volatile Alkaloïds which are precipitated by Potassa or Soda from the Solutions of their Salts, and re-dissolve readily in an excess of the precipitant.

Of the alkaloïds treated of here, only one belongs to this group, namely :—

Morphine or Morphia, $C_{34}H_{19}NO_6$ [$C_{17}H_{19}NO_3$].

§ 233.

1. Morphine occurs with the alkaloïds codeïne, thebaïne, papaverine, narcotine, narceïne, &c., and with meconic acid and the indifferent non-nitrogenous compounds, meconin and meconoisin, in opium, the dried milky juice of the green capsules of the poppy (*Papaver somniferum*). Crystallized morphine, $C_{34}H_{19}NO_6 + 2aq$ [$C_{17}H_{19}NO_3, H_2O$], usually forms colourless, brilliant, transparent needles, rhombic prisms, or, when obtained by precipitation, a white crystalline powder. It has a bitter taste, and dissolves in 1000 parts of cold and 400 parts of boiling water; cold absolute alcohol dissolves $\frac{1}{50}$th and boiling alcohol $\frac{1}{13}$th of its weight, whilst spirit of 90 per cent. in the cold dissolves $\frac{1}{100}$th, and when boiling $\frac{1}{36}$th. The solutions of morphine in alcohol or in hot water are distinctly alkaline, and have a bitter taste. Morphine is almost insoluble in ether, especially when crystallized, but dissolves in amylic alcohol, especially when hot; it is insoluble in benzene (Rodgers), and very sparingly soluble in chloroform (Pettenkofer, v. d. Burg). Crystallized morphine loses its water of crystallization at 120° (C. Tausch† gives 100°); when cautiously heated, morphine melts, and may be sublimed without decomposition.‡

2. Morphine neutralizes acids completely, and forms with them the salts of morphine. Most of these are crystalline, easily soluble in water and also in spirit of wine (the sulphate, however, requires 700 parts of cold and 144 parts of boiling alcohol of sp. gr. 0·82), insoluble in ether, chloroform, and amylic alcohol; their taste is disagreeably bitter. Morphine and its salts are poisonous.

3. **Potassa, soda,** and **ammonia** throw down from the solutions of salts of morphine—generally only after some time—a white crystalline

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* For the detection of conine in presence of nicotine by means of platino-iodide of potassium, see Selmi, Ber. deut. chem. Ges., **9**, 195.

† Zeit. anal. Chem., **19**, 505.

‡ For the best way of subliming morphine and other alkaloïds, and for the value of the sublimate in microscopic diagnosis, see Helwig (Zeit. anal. Chem., **3**, 43). In "*Das Mikroscop in der Toxikologie*" by Dr. A. Helwig (V. v. Zabern, Mainz, 1864) the subject is treated more completely, and illustrated by photographs of the microscopic preparations. For this interesting experiment to succeed, it is necessary that the alkaloïd should be perfectly pure and free from all extraneous organic matter.

powder, consisting of morphine containing water of crystallization. Stirring and rubbing the sides of the glass vessel under the liquid promote the separation of the precipitate, which re-dissolves with great readiness in excess of potassa or soda, but more sparingly in ammonia. It is also soluble in chloride of ammonium and, though with difficulty only, in carbonate of ammonia. On shaking a solution of morphine in potassa or soda with ether, very little of the alkaloïd passes into the ether; on shaking it with warm amylic alcohol, however, the whole of the alkaloïd is taken up by the latter.

4. **Carbonate of potassa** or **carbonate of soda** produces the same precipitate as potassa, soda, or ammonia, but does not re-dissolve it when in excess. Consequently, if a fixed alkaline bicarbonate is added to a solution of morphine in potassa or soda, or if carbonic acid is passed into the solution, morphine with water of crystallization separates—especially after ebullition—as a crystalline powder. On careful inspection, particularly with a lens, it is seen that this powder consists of small acicular crystals; magnified 100 times, these crystals present the form of rhombic prisms.

5. **Bicarbonate of soda** or **potassa** throws down hydrated morphine from solutions of neutral salts of morphine as a crystalline powder. The precipitate is insoluble in excess of the precipitants. Acidified solutions of salts of morphine are not precipitated in the cold by these reagents.

6. The action of strong **nitric acid** on morphine or one of its salts, in the solid state or in concentrated solutions, produces a yellowish-red colour; on adding **stannous chloride** there is no violet coloration, as in the case of brucine. When nitric acid is added to dilute solutions, there is no change in colour in the cold, but on heating they acquire a yellow tint.

7. *Concentrated* **sulphuric acid** dissolves morphine in the cold, forming a colourless solution. If a trace of **nitrate of potassa** is added to the freshly prepared solution, it sometimes becomes reddish for an instant where the two are in contact, but this quickly changes to brown; sometimes a brown colour alone is produced. If, however, the solution of morphine in concentrated sulphuric acid is allowed to remain for twelve to fifteen hours, and is then heated at 100° for half an hour or for a moment to 150°, an essential alteration takes place. This is apparent from the appearance of a feeble, dirty-violet coloration, but is especially manifest when the cooled solution is treated with a trace of nitrate of potassa, or a drop of nitric acid, sp. gr. = 1·2, on a porcelain plate; a magnificent coloration is produced, which according to the author's observation is sometimes violet at first, and then turns a blood-red, or is sometimes of a blood-red at once, with a slightly brownish tinge; with extremely small quantities it is only of a rose tint (A. Husemann[*]). The reaction is very characteristic and also very delicate, although perhaps not quite so delicate at Fröhde's (vide 8). Kauzmann and Dragendorff[†] were enabled by this means to detect from 0·00001 to 0·00002 gram of dry morphine sulphate.

8. If a solution of **molybdic acid** or of the **molybdate of an alkali** in concentrated **sulphuric acid** is mixed with morphine or a dry salt of morphine, a very characteristic coloration is produced, even with the

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[*] Zeit. anal. Chem., 3, 149, and 15, 103.

[†] Dragendorff, "*Beiträge zur gerichtlichen Chemie einzelner organischer Gifte*" (St. Petersburg: Schmitzdorff, 1872), p. 124.

smallest particle of morphine (Fröhde[*]); this colour varies somewhat with the amount of molybdic acid dissolved in the sulphuric acid. Fröhde employed a solution containing 0·005 gram of molybdate of soda in 1 c.c. The author, however, agrees with Buckingham[†] in giving the preference, at least for the examination of solutions of morphine salts,[‡] to a concentrated solution containing 0·1 gram of molybdate of ammonia in 1 c.c. sulphuric acid. If a few drops of the solution be placed upon a porcelain plate and a very minute crystal of morphine added and crushed with a glass rod, a deep violet colour is at once produced. This gradually changes to an olive-green, whilst the edges of the sulphuric acid become blue. On stirring, the solution becomes brownish-green, gradually changing to a beautiful deep blue. On adding a drop of a dilute solution of a morphine salt to the solution of molybdate of ammonia in concentrated sulphuric acid, a deep blue ring is at once formed, the edge of which is sometimes violet; the centre of the drop and by degrees the whole of the liquid gradually becomes of a magnificent blue colour. The reaction is extremely delicate. Kauzmann and Dragendorff[||] were able to detect the presence of 0·000005 gram of dry morphine sulphate by this method; the reaction, however, is not characteristic, as other organic substances, such as phloridzin, salicin, digitalin, &c., yield similar colorations. It is to be noted that the reaction should take place at once, for the solution always becomes blue if exposed to the air for some time, owing to the action of atmospheric dust. On adding water to the blue liquid, it becomes pale yellow, in fact almost colourless (distinction from salicin, which under these circumstances yields a reddish-coloured solution).

9. If 1 part of morphine is intimately mixed with 6 to 8 parts of white **sugar** on a porcelain plate, and a few drops of *concentrated* **sulphuric acid** added, a rose-red to purple-red solution is obtained, the intensity of the colour depending on the amount of morphine present; the colour remains unchanged for a considerable time. On adding water, the colour gradually changes through a bluish-violet to a dirty bluish-green, and finally turns to dirty brownish-yellow.

This reaction is perfectly distinct with 0·0001 to 0·00001 gram of morphine. In examining dilute solutions of morphine salts by this method, a drop of the solution is placed on a porcelain plate, as much sugar added as the liquid will dissolve, a drop of concentrated sulphuric acid is placed near it, and the two mixed by inclining the plate (R. Schneider[¶]). The addition of 1 to at most 3 drops of **bromine water** still further increases the delicacy of the reaction (Weppen[**]).

10. If a small quantity of morphine is dissolved in about 1 to 1·5 c.c. of concentrated **hydrochloric acid**, a drop of concentrated **sulphuric acid** added, and the mixture heated in the oil-bath at from 100° to 120° (heating on the water-bath will also answer) until all the hydrochloric acid is driven off, a purplish-red residue is obtained. If to this residue a small quantity of hydrochloric acid is again added, then a cold saturated solution of **bicarbonate of soda** until the mixture is neutral or only faintly alkaline, and lastly, a drop of an alcoholic **solution of iodine**, the liquid becomes emerald-green. On shaking this solution

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[*] Zeit. anal. Chem., **5**, 214.

[†] *Ibid.*, **13**, 234.

[‡] Fröhde's reagent must be employed when freshly prepared, as it gradually decomposes.

[||] *Loc. cit.*, p. 124.

[¶] Zeit. anal. Chem., **12**, 218.

[**] *Ibid.*, **13**, 455.

with ether, the substance which produces the green coloration (apomorphine) is dissolved by the ether forming a layer of a beautiful violet-red colour (Pellagri[*]). Codeïne gives the same reaction.

11. The addition of **neutral ferric chloride** to *concentrated* solutions of morphine salts produces a beautiful dark-blue coloration, which disappears on adding an acid. Excess of ferric chloride also is prejudicial to the delicacy of the reaction; 0·2 c.c. of a 5 per cent. solution of ferric chloride is sufficient to show the presence of morphine in a solution of 0·01 gram of hydrochloride of morphine in 100 to 200 c.c. of water. With these proportions, Dragendorff[†] obtained the reaction with solutions of 1 part of a morphine salt in 1000 to 1500 parts of water. If the solution of the morphine salt contains vegetable or animal extractive matters or acetates, the colour is not pure and is less marked.

12. If **iodic acid** or iodate of soda and sulphuric acid is added to a solution of morphine or of a salt of morphine, iodine separates. In concentrated aqueous solutions, the separated iodine appears as a kermes-brown precipitate, but alcoholic and dilute aqueous solutions are merely coloured a brown or yellowish-brown by it. The addition of starch paste to the solution, either before or after adding the iodic acid, considerably increases the delicacy of the reaction, since the blue tint of the iodide of starch, which in exceedingly dilute solutions often does not appear until after the lapse of some time, is far more easily detected than the brown colour of the iodine. The reaction is most delicate when the iodic acid solution is mixed with starch paste, and the dry morphia salt is added to the mixture. It need scarcely be mentioned that the delicacy of the reaction may also be increased by shaking with bisulphide of carbon, which dissolves the liberated iodine and acquires a purple tint. As other nitrogenous bodies such as albumin, caseïn, fibrin, &c., likewise reduce iodic acid, this reaction has only a relative value; if, however, **ammonia** is added after the iodic acid, the liquid becomes colourless if the separation of iodine has been caused by other substances, whilst the coloration becomes much more intense if it is due to morphine (Lefort[‡]).

13. **Tannic acid** throws down a white precipitate from aqueous solutions of salts of morphine if they are not too dilute; this is readily soluble in acids.

14. **Picric acid** throws down yellow picrate of morphine from concentrated solutions of morphine salts; it dissolves on adding water.

15. The most delicate **general reagents** for morphine are phosphomolybdic acid, potassium bismuth iodide, iodized iodide of potassium, and potassiomercuric iodide.[||]

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[*] Zeit anal. Chem., **17**, 373.

[†] *Loc. cit.*, p. 125.

[‡] Lefort, Zeit. anal. Chem., **1**, 134. The reducing power of morphine, renders the following reactions available for its detection: nitrate of silver, Horsley, *ibid.*, **7**, 485), ferricyanide of potassium and ferric chloride, Kieffer, Kalbrunner, *ibid.*, **12**, 444; and ammoniacal oxide of copper; Nadler, *ibid.*, **13**, 235.

[||] For other reactions for the detection of morphine, see Pelletier, Flückiger, Zeit. anal. Chem., **11**, 319; Nadler, *ibid.*, **13**, 236; Grove, Siebold, *ibid.*, **13**, 236; Flückiger, *ibid.*, **19**, 120; Lindo, *ibid.*, **19**, 359; Tatersall, *ibid.*, **20**, 119; Vitali, *ibid.*, **21**, 581; Jorissen, *ibid.*, **20**, 422; Palm, *ibid.*, **22**, 224; Grimaux, *ibid.*, **22**, 267; Mandelin, *ibid.*, **23**, 235.

Second Group.

Non-volatile Alkaloïds which are precipitated by Potassa from the Solutions of their Salts, but do not re-dissolve to any perceptible extent in Excess of the Precipitant, and are precipitated by Bicarbonate of Soda even from Acid Solutions, if the latter are not diluted in a larger proportion than 1 : 100; Narcotine, Quinine, Cinchonine.

1. Narcotine, $C_{44}H_{23}NO_{14}$ [$C_{22}H_{23}NO_{7}$].

§ 234.

1. Narcotine accompanies morphine in opium (p. 418). Crystallized narcotine usually forms colourless, brilliant, right rhombic prisms, or, when precipitated by alkalies, a white, loose, crystalline powder. It is insoluble in cold water, and only very slightly soluble in hot; alcohol and ether dissolve it but sparingly in the cold, somewhat more readily on heating. It dissolves very easily in chloroform, sparingly in amyl alcohol, more readily in benzene, whilst it is almost insoluble in light petroleum. Solid narcotine is tasteless, but the alcoholic and ethereal solutions are intensely bitter. Narcotine does not alter vegetable colours. It melts at 176°.

2. Narcotine dissolves readily in acids, forming salts with them; these invariably have an acid reaction. The salts with weak acids are decomposed by a large amount of water, and, if the acid is volatile, even on evaporation. Most of the salts of narcotine are uncrystallizable, and soluble in water, alcohol, and ether; they have a bitter taste. Narcotine does not dissolve in water acidified with acetic acid; and when a solution of a narcotine salt is shaken with chloroform, the narcotine is taken up by the chloroform even when the solution contains free acid (Dragendorff). Benzene, amyl alcohol, and light petroleum do not take up any narcotine if the solution is acid.

3. **The alkalies** and **alkaline carbonates** and **bicarbonates** immediately throw down narcotine from solutions of its salts in the form of a white powder, which, magnified 100 times, is seen to be an aggregate of small crystalline needles; the precipitate is insoluble in an excess of the precipitant. When a solution of a salt of narcotine is mixed with ammonia, and ether added in sufficient quantity, the precipitate re-dissolves in the ether, two distinct layers being formed; if, now, a drop of the ethereal solution is evaporated on a watch-glass, the residue, when magnified 100 times, is seen to consist of small, distinct, elongated, and lance-shaped crystals.

4. *Concentrated* **nitric acid** of sp. gr. 1·4 dissolves narcotine, on warming, with evolution of nitrous fumes, and forms a reddish-yellow solution; on heating strongly, more nitrous fumes are evolved, and the liquid becomes yellow.

5. *Concentrated* **sulphuric acid** dissolves narcotine, with a pale greenish-yellow coloration, but this soon changes to a pure yellow. On carefully heating it in a porcelain dish, the solution becomes orange-red at first, changing to a bluish violet at the edge, or purplish-blue stripes are seen proceeding from the edge, and finally, at a temperature when the sulphuric acid begins to evaporate, it becomes of a dirty reddish-violet

colour; if the heating is stopped before this, the solution slowly becomes cherry red in the cold. If the sulphuric acid contains but very little narcotine, a delicate crimson colour is produced instead of the blue (A. Husemann). The red coloration passing into violet is particularly well exhibited when narcotine is dissolved in dilute sulphuric acid (1 : 5), the colourless solution evaporated over a small flame, and the residue very cautiously heated (Dragendorff).

6. If to a solution of narcotine in strong **sulphuric acid** prepared in the cold, 10 to 20 drops of sulphuric acid containing a minute quantity of **nitric acid** is added, the liquid is at first brownish, but quickly becomes of a deeper and deeper red (Couerbe). According to Dragendorff, the delicacy of this reaction may be increased by allowing the solution of narcotine in sulphuric acid to remain for one or two hours before adding the nitric acid. The same reaction may be obtained by dissolving narcotine in **Erdmann's reagent**[*] (sulphuric acid containing nitric acid). Hypochlorite of soda changes the yellow sulphuric acid solution prepared in the cold first of all crimson, then to yellowish-red (A. Husemann).

7. If a solution of narcotine in concentrated **sulphuric acid** is heated (at *about* 150°) until the reddish coloration appears, and, after cooling, some **ferric chloride** is added, the portions of the liquid which are immediately in contact with the ferric chloride solution become red with more or less brilliant violet edges; after ten to fifteen minutes, however, a tolerably permanent, cherry-red coloration is produced (A. Husemann[†]).

8. **Fröhde's reagent** (0·005 gram of molybdate of soda dissolved in 1 c.c. of sulphuric acid) dissolves narcotine, forming a green solution. If the solution, however, contains 0·01 gram of molybdate of soda in each 1 c.c. of sulphuric acid, the green colour soon changes to a magnificent cherry-red (Dragendorff).

9. **Chlorine water** added to a solution of narcotine gives a yellow colour, slightly inclining to green; on adding ammonia, a yellowish red and much more intense colour is produced.

10. If narcotine or a salt of narcotine is dissolved in excess of dilute **sulphuric acid**, some finely powdered **binoxide of manganese** added, and the mixture boiled for some minutes, the alkaloïd is oxidized and converted into opianic acid, cotarnine (a base soluble in water), and carbonic acid. On filtering and adding ammonia to the filtrate, no precipitate will be obtained.

11. **Tannic acid** does not produce any precipitate in solutions of salts of narcotine, but it is formed at once on adding a drop of hydrochloric acid. This precipitate dissolves on warming, but comes down again as the solution cools; it is only very slightly soluble in hydrochloric acid.

12. Of the **general reagents**, the most delicate tests for narcotine are potassium mercuric iodide, phosphomolybdic acid, and potassium bismuth iodide (Dragendorff[‡]).

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[*] This is prepared in the following way: 6 drops of nitric acid of 1·25 sp. gr. are mixed with 100 c.c. of water, and 10 drops of this solution are added to 20 grams of pure concentrated sulphuric acid.

[†] Zeit. anal. Chem., **3**, 152.

[‡] For other reactions of narcotine, see Palm, Zeit. anal. Chem., **22**, 226, and Mandelin, *ibid.*, **23**, 238.

2. Quinine, $C_{40}H_{24}N_2O_4$ [$C_{20}H_{24}N_2O_2$].

§ 235.

1. Quinine occurs in cinchona bark, along with cinchonine and other bases. Crystallized quinine, $C_{40}H_{24}N_2O_4 + 6aq$ [$C_{20}H_{24}N_2O_2, 3H_2O$], forms either slender silky lustrous needles, which effloresce on exposure to the air, and are frequently aggregated into tufts, or a loose white powder. Anhydrous quinine may also be obtained crystallized in silky needles. Quinine is sparingly soluble in cold, but somewhat more readily in hot water. It dissolves more or less easily in alcohol, ether, chloroform, and bisulphide of carbon. Its taste is intensely bitter; its solutions have an alkaline reaction. Crystallized quinine melts at 57°, but becomes solid again when the water of crystallization has been given off; it loses all its water of crystallization at 100°, and the anhydrous base melts at 177°.

2. Quinine neutralizes acids completely. The neutral salts are intensely bitter; most of them are crystallizable, sparingly soluble in cold, more easily in hot water and in spirit. The acid salts dissolve very freely in water; the solutions, which contain an oxygen acid, especially sulphuric acid, have a bluish fluorescence. If a cone of light is projected into the solution by means of a lens either horizontally or vertically, a blue cone of light is seen even in highly dilute solutions (A. Flückiger). A solution of sulphate of quinine acidified with sulphuric acid turns the polarized ray strongly to the left (distinction from cinchonine).

3. **Potassa, soda, ammonia**, and the neutral **carbonates of the alkalies** throw down from solutions of salts of quinine, if they are not too dilute, a white, loose, pulverulent precipitate of hydrated quinine, which immediately after precipitation appears opaque and amorphous under the microscope, but, after the lapse of some time, assumes the appearance of an aggregate of crystalline needles. The precipitate is but little soluble in excess of potassa (less than in water), and still less soluble in soda solution (F. Sestini); more easily in ammonia. It is only very slightly soluble in fixed alkaline carbonates. Chloride of ammonium increases its solubility in water. If a solution of a quinine salt is mixed with ammonia, ether (containing 2 per cent. alcohol) added, and the mixture shaken, the precipitated quinine re-dissolves in the ether, and the clear liquid forms two distinct layers. (In this respect quinine differs essentially from cinchonine, which by this means may be readily detected in presence of the former and separated from it.)

4. **Bicarbonate of soda** also produces a white precipitate both in neutral and acid solutions of salts of quinine. In acidified solutions containing 1 part of quinine to 100 parts of acid and water, the precipitate forms immediately. If the proportion is 1 : 150, the precipitate separates after an hour or two, in the form of distinct needles, aggregated into groups. If the proportion is 1 : 200, the mixture remains clear, and it is only after from twelve to twenty-four hours that a slight precipitate makes its appearance. As the precipitate is not altogether insoluble in the precipitant, the separation is the more complete the less the excess of the precipitant; the precipitate contains carbonic acid.

5. *Concentrated* **nitric acid** dissolves quinine to a colourless solution, turning yellowish on application of heat.

6. The addition of strong **chlorine water** (about one-fifth its volume) to a solution of a quinine salt does not colour the solution, or, at all events, imparts to it only a very faint tint; but if ammonia is now added until it is in excess, an intense emerald-green colour is produced. This characteristic reaction, the thalleïoquinine reaction, takes place in solutions as dilute as 1 : 2500. According to Flückiger, 1 part in 4000 or 5000 may be detected if to the solution about one-tenth of its volume of chlorine water be added without shaking, and then a drop or two of ammonia; on gently shaking the test-tube the colour will appear.* If, after the addition of the chlorine water, some solution of **ferrocyanide of potassium** is added, and then a few drops of **ammonia** or some other alkali, the liquid acquires a beautiful deep-red tint, which, however, speedily changes to a dirty brown. On adding an acid † to the red liquid, the colour vanishes, but reappears again on the cautious addition of ammonia. (O. Livonius, A. Vogel.) Morphine interferes with the thalleïoquinine reaction (Stuart‡).

7. If quinine sulphate is dissolved in a little acetic acid, alcohol added, and then sufficient alcoholic **solution of iodine** to colour the liquid brownish-yellow, iodoquinine sulphate (Herapathite) separates out after a short time as a black crystalline powder, or in the form of plates, which are beautifully dichroic, and polarize light strongly (Herapath‖). This is a very characteristic and, if the microscope be employed, a very delicate reaction.

8. *Concentrated* **sulphuric acid** dissolves pure quinine and pure salts of quinine, forming a colourless or very faintly yellowish solution; if gently heated, the liquid turns yellow, and at higher temperature brown. Sulphuric acid containing nitric acid dissolves quinine to a colourless or very faintly yellowish solution.

9. **Tannic acid** produces a white precipitate in aqueous solutions of salts of quinine, even when they are rather dilute. The precipitate is curdy, and agglutinates on warming; it is soluble in acetic acid, also in a little hydrochloric acid, but is thrown down again on adding more hydrochloric acid.

3. Cinchonine, $C_{38}H_{22}N_2O_2$ [$C_{19}H_{22}N_2O$].

§ 236.

1. Cinchonine occurs in cinchona bark accompanying quinine and other bases. It forms either transparent, brilliant, rhombic prisms, or fine white needles, or, if precipitated from concentrated solutions, a loose white powder. At first it is tasteless, but after some time a bitter taste of bark becomes perceptible. It is almost insoluble in cold water, and dissolves with extreme difficulty in hot water; it is but little soluble in dilute spirit, somewhat more freely in absolute alcohol. Hot alcohol dissolves it more easily than cold, and on cooling deposits the greater

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* The reaction is even more delicate if bromine be used instead of chlorine, but either excess or deficiency of bromine interferes with it more than excess or deficiency of chlorine (Flückiger, Zeit. anal. Chem., **11**, 318).

† Acetic acid answers the purpose best.

‡ Pharm. Centralhalle, **23**, 312.

‖ Phil. Mag., VI. 171; Jour. pr. Chem., **61**, 87.

portion of the dissolved cinchonine in a crystalline state. Solutions of cinchonine taste bitter, and have an alkaline reaction. Cinchonine is but little soluble in ether or chloroform, but chloroform mixed with one-fourth to one-third of its bulk of alcohol dissolves it very readily (Oudemans, Junr.*). It is almost insoluble in light petroleum.

2. Cinchonine neutralizes acids completely. The salts have the bitter taste of cinchona bark: most of them are crystallizable, and they are generally more readily soluble in water, spirit, and chloroform than the corresponding quinine compounds. Ether does not dissolve them. The solutions of its salts do not exhibit fluorescence, and they turn the polarized ray to the right (distinction from quinine salts).

3. When cinchonine is heated cautiously, it melts and then gives off white fumes, which, like benzoic acid, condense upon cold surfaces, in the form of small brilliant needles, or as a loose sublimate, a peculiar aromatic odour being exhaled at the same time. If the operation is conducted in a current of hydrogen, long brilliant prisms are obtained (Hlasiwetz).

4. **Potassa, soda, ammonia**, and the **neutral carbonates of the alkalies** throw down a white loose precipitate of cinchonine from solutions of its salts insoluble in excess of the precipitants. If the solution is concentrated, the precipitate does not exhibit a distinctly crystalline appearance, even when magnified 200 times; but if the solution is so dilute that the precipitate is not formed until after some time, it appears under the microscope as stellate groups of needles.

5. **Bicarbonate of soda** and **bicarbonate of potassa** precipitate cinchonine in the same form as in 4, both from neutral and acidified solutions of cinchonine salts, but not so completely as the monocarbonates of the alkalies. Even in solutions containing 1 part of cinchonine in 200 of water and acid, the precipitate forms immediately; it increases in quantity, however, after a time.

6. *Concentrated* **sulphuric acid** dissolves cinchonine, forming a colourless liquid, which on warming becomes brown, and finally black. On adding **nitric acid** the solution is also colourless in the cold, but on warming it becomes yellowish-brown, then brown, and finally black.

7. The addition of **chlorine water** to a solution of a salt of cinchonine causes no change of colour, but, on adding ammonia, a yellowish-white precipitate is formed.

8. If a solution of a cinchonine salt containing little or no free acid is mixed with **ferrocyanide of potassium**, a flocculent precipitate of ferrocyanide of cinchonine is formed. If an excess of the precipitant is added, and the solution gently and slowly heated, the precipitate dissolves, but separates again on cooling, in brilliant gold-yellow scales, or in long needles, often aggregated in the shape of a fan. With the aid of the microscope, this reaction is as delicate as it is characteristic (C. Dollfus, Bill, Seligsohn).

9. **Tannic acid** throws down from aqueous solutions of salts of cinchonine a white flocculent precipitate; this is soluble in a small quantity of hydrochloric acid, but is re-precipitated on adding more hydrochloric acid.

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* Zeit. anal. Chem., 11, 287.

Recapitulation and Remarks.

§ 237.

Narcotine may be separated from quinine and cinchonine by repeatedly shaking up the acidified solution with chloroform; the chloroform which contains the narcotine is then separated, and ammonia and ether containing 2 per cent. of alcohol are added to the acid aqueous solution, when the cinchonine separates out and the quinine dissolves in the ether. The narcotine is obtained by evaporating the chloroform solution, and the quinine in the same way from the ethereal solution.* The alkaloïds separated in this way may then be readily tested by the reactions given above.

Third Group.

Non-volatile Alkaloïds which are precipitated on adding Potassa to Solutions of their Salts, and do not re-dissolve to a perceptible extent in Excess of the Precipitant;† but are not thrown down from (even somewhat concentrated) Acid Solutions by the Bicarbonates of the Fixed Alkalies: Strychnine, Brucine, Veratrine, Atropine.

1. Strychnine, $C_{42}H_{22}N_2O_4$ [$C_{21}H_{22}N_2O_2$].

§ 238.

1. Strychnine is found along with brucine in various kinds of strychnos, especially in the fruit of *Strychnos nux vomica* and *Strychnos ignatii*. It forms either white brilliant rhombic prisms, or, when obtained by precipitation or rapid evaporation, a white powder. It has an alkaline reaction and is exceedingly bitter. It is almost insoluble in cold water, and but very little more soluble in hot; the aqueous solution even when diluted with 100 times its volume of water is distinctly bitter. It is insoluble in absolute alcohol or ether, and only sparingly soluble in cold dilute spirit, somewhat more so if hot; ordinary ether containing water and spirit dissolves it slightly. Strychnine dissolves with the greatest ease in chloroform but only sparingly in amyl alcohol or in benzene, and scarcely at all in light petroleum. It cannot be melted without decomposition, but by cautious heating small quantities may be sublimed unaltered (Helwig), see foot-note ‡, p. 418.‡

2. Strychnine neutralizes acids completely. The salts of strychnine are, for the most part, crystallizable; they are also mostly soluble in

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* If it is necessary to separate the quinine from the other bases present in cinchona bark (quinidine, cinchonidine, &c.), this method of testing with ammonia and ether is insufficient. For methods for separating and detecting these alkaloïds, see G. Kerner, Zeit. anal. Chem., **1**, 150, and **20**, 150; Mann, *ibid.*, **3**, 382; Schwarzer, *ibid.*, **4**, 129; de Vrij, *ibid.*, **4**, 202, and **13**, 320; Van der Burg, *ibid.*, **4**, 273, **9**, 179 and 305; Hager, *ibid.*, **8**, 477, and Pharm. Centralhalle, **21**, 411; Hesse, Zeit. anal. Chem., **11**, 328; Godeffroy, Zeit. des oesterr. Apothekervereins, 1878, No. 1; Glenard, Zeit. anal. Chem., **18**, 629; C. H. Wolff, Arch. Pharm., **219**, 1; Hielbig, Zeit. anal. Chem., **20**, 144; Molnár, *ibid.*, **20**, 152; Rozsnyay, *ibid.*, **23**, 589.

† Regarding atropine, see § 241, 4.

‡ According to Schützenberger strychnine is not a homogeneous compound, but a mixture of three alkaloïds. Compare Hager, Pharm. Centralhalle, 1884, p. 181.

water and spirit, but insoluble in ether, chloroform, amyl alcohol, and benzene. All the salts have an intolerably bitter taste, and, like the pure alkaloïd, are poisonous in the highest degree. On adding a small quantity of acid to their concentrated aqueous solutions, a part of the salt is precipitated, but this re-dissolves on adding more acid (Hanriot and Blarez).

3. **Potassa, soda,** and **carbonate of soda** throw down white precipitate of strychnine from solutions of its salts; it is insoluble in an excess of the precipitant. Magnified 100 times, the precipitate appears as an aggregate of small needle-shaped crystals. From dilute solutions, it separates only after the lapse of some time, in the form of needles, distinctly visible to the naked eye.

4. **Ammonia** produces the same precipitate as potassa; the precipitate re-dissolves in excess of ammonia; after a short time, however—or, if the solution is highly dilute, after a longer time—the strychnine crystallizes from the ammoniacal solution in the form of needles, distinctly visible to the naked eye.

5. If **bicarbonate of soda** is added to a neutral solution of a salt of strychnine, strychnine separates after a short time in the form of fine needles, insoluble in excess of the precipitant. But, on adding a drop of acid (so as to leave the solution still alkaline), the precipitate dissolves readily in the liberated carbonic acid. The addition of bicarbonate of soda to an acid solution of strychnine produces no precipitate, and it is only after the lapse of twenty-four hours, or even longer, that strychnine crystallizes out in well-formed prisms, as the free carbonic acid gradually escapes. If a solution of a salt of strychnine supersaturated with bicarbonate of soda is boiled, a precipitate forms at once if the solution is concentrated, but if dilute the precipitate separates only after concentration.

6. **Sulphocyanate of potassium** immediately produces a precipitate in a concentrated solution of a strychnine salt, whilst in dilute solutions a white crystalline precipitate separates after the lapse of some time; this appears under the microscope as an aggregate of flat needles, truncated or pointed at an acute angle, and is but little soluble in an excess of the precipitant.

7. **Mercuric chloride** throws down a white precipitate from solutions of salts of strychnine; this changes after some time to stellate clusters of needles, distinctly visible through a lens. On heating the solution, these crystals re-dissolve, but on cooling the double salt is again deposited in larger needles.

8. If a few drops of pure *concentrated* **sulphuric acid** are added to a little strychnine in a porcelain dish, it dissolves, without coloration; if now a small quantity of an oxidizing agent (chromate of potassa, permanganate of potassa, ferricyanide of potassium, peroxide of lead, or binoxide of manganese) be added—best in the solid form, as dilution is prejudicial to the reaction—the liquid will become of a magnificent blue-violet colour, which, after some time, changes to wine-red, then to reddish-yellow. With **chromate of potassa** and **permanganate of potassa** the reaction is immediate; on inclining the dish, blue-violet streaks are seen to flow from the fragment of salt, and by moving the latter about, the whole of the liquid soon becomes coloured. With **ferricyanide of potassium** the reaction is less rapid, and it is slowest with the peroxides. The more speedy the manifestation of the reaction, the more rapid also

is the change of colour. Chromate of potassa, as recommended by Otto, is to be preferred. The reaction is particularly delicate if traces of strychnine on a watch-glass are treated with a dilute solution of dichromate of potassa; in this way the strychnine is gradually converted into the chromate, the liquid is poured off, the strychnine chromate rinsed with a little water, the water poured off, and the last traces removed with filter-paper; concentrated sulphuric acid is then poured on to the chromate of strychnine when the blue or bluish-violet streaks appear. Strychnine may also be directly precipitated from its solutions as strychnine chromate by the addition of dichromate of potassa (R. Otto). The most delicate method of testing, however, is to use the bright green solution of 1 part of potassium permanganate in 2000 parts of sulphuric acid, first proposed by Guy. Wenzell[*] states that by means of this test he has been able to detect 0·0005 mgram. of strychnine with certainty. As, however, other organic substances yield colours with a solution of potassium permanganate in sulphuric acid, which are very similar to that produced by strychnine, it is not advisable to employ this reagent in testing a substance for strychnine if other organic compounds are present. Under these circumstances, it is better to use dichromate of potassa (Sedgwick[†]). Metallic chlorides or somewhat large quantities of nitrates, also large quantities of organic substances, prevent the reaction or impair its delicacy. It is therefore always advisable to free the strychnine, as far as possible, from all foreign matters before testing it in this way. If the solution coloured red (by binoxide of manganese) is mixed with from 4 to 6 times its volume of water, heating being avoided, and ammonia is then added until the reaction is *nearly* neutral, the liquid acquires a magnificent violet-purple tint; on adding more ammonia, it changes to yellowish-green or yellow (J. Erdmann). The author has found, however, that this reaction is seen only when relatively large, though still very minute, quantities of strychnine are present. Morphine, if present, interferes with this reaction.[‡] In order to remove the morphine, ferricyanide of potassium (Neubauer) or neutral chromate of potassa (Horsley) is added to the concentrated aqueous neutral solution of the substance; the morphine remains in solution, and the precipitate, consisting of ferricyanide or chromate of strychnine, is washed a little, dried, and a portion of it mixed in a watch-glass with strong sulphuric acid; the blue-violet colour is immediately produced. It should be borne in mind that the strychnine precipitates are not insoluble in water, but merely sparingly soluble.[||] For the detection of strychnine in the presence of brucine by means of this reaction, see § 242.

Lastly, it should be noted that curarine gives the same reaction as strychnine with sulphuric acid and chromate of potassa. They differ, however, in this, that curarine is coloured red by sulphuric acid alone, and it gives much more permanent colorations with chromate of potassa than strychnine does (Dragendorff).

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[*] Pharm. Centralhalle, 1871, p. 234.

[†] Zeit. anal. Chem., **20**, 421.

[‡] Reese, Zeit. anal. Chem., 1, 399. Horsley, *ibid.*, 1, 515. Thomas, *ibid.*, 1, 517.

[||] Rodgers (Zeit. anal. Chem., **5**, 406) recommends to separate strychnine from morphine by benzene or chloroform, in which the former alone is soluble. Thomas recommends to render the solution of the acetates alkaline with potash, and to shake with chloroform; the morphine remains in the alkaline solution, while the strychnine dissolves in the chloroform.

9. If **cerosoceric oxide** is added to a solution of strychnine in concentrated sulphuric acid, a magnificent blue colour is developed, which slowly changes to violet, and finally becomes red (Sonnenschein[*] and also Djurberg[†]).

10. If a few drops of a solution of 1 part of **vanadate of ammonia** in 100 to 200 parts of *concentrated* **sulphuric acid** be added to a little strychnine on a watch-glass, and allowed to remain for a few moments until the mixture becomes darker in colour, and the watch-glass then slightly inclined, a magnificent blue colour will be seen at the moment the vanadium sulphate solution runs off the residue; this colour soon turns to violet, and lastly to vermilion or reddish-yellow. If **potash** or **soda** solution is added as soon as the red colour appears, a permanent rose, or purplish-red, solution is obtained, the colour becoming still more brilliant on diluting with water. The blue colour is distinctly visible with 0·001 mgm. of strychnine. This reaction is moreover distinguished by the fact that the presence of other alkaloïds either does not affect it at all, or to a much less extent than is the case with the reaction described in 8 (Mandelin[‡]).

11. Strong **chlorine water** added to a solution of a strychnine salt produces a white precipitate, soluble in ammonia to a colourless liquid.

12. Strong **nitric acid** dissolves strychnine or its salts, yielding a colourless solution, which turns yellow when heated.

13. **Tannic acid** produces in solutions of strychnine salts a heavy white precipitate, insoluble in hydrochloric acid.

14. The most delicate **general reagents** for strychnine are potassium mercuric iodide, potassium bismuth iodide, iodized potassium iodide, and picric acid.

2. Brucine, $C_{46}H_{26}N_2O_8$ [$C_{23}H_{26}N_2O_4$].

§ 239.

1. Brucine occurs along with strychnine in different kinds of strychnos (see p. 427). Crystallized brucine, $C_{46}H_{26}N_2O_8 + 8aq$ [$C_2H_{26}N_2O_4,4H_2O$], forms either transparent right rhombic prisms, or stellate clusters of needles, or a white powder composed of minute crystalline scales. Brucine is sparingly soluble in cold, but somewhat more readily in hot water. It dissolves freely in alcohol, both absolute and dilute, also in cold, but more readily still in hot, amyl alcohol; it is also easily soluble in chloroform, far less so in benzene, somewhat soluble in ordinary, but almost insoluble in absolute ether. Its taste is intensely bitter. When heated, it fuses with loss of its water of crystallization; by careful heating, it may be sublimed unchanged (see foot-note ‡, p. 418). Brucine in alcoholic solution turns the polarized ray to the left.

2. Brucine neutralizes acids completely; its salts are readily soluble in water, and of an intensely bitter taste; most of them are crystallizable. Both the alkaloïd and its salts are poisonous.

3. **Potassa, soda,** or **carbonate of soda** added to a solution of a salt of brucine throws down a white precipitate of brucine insoluble in excess of the precipitant. Viewed under the microscope, immediately after

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[*] Zeit. anal. Chem., **9**, 495. [†] *Ibid.*, **11**, 440. [‡] *Ibid.*, **23**, 240.

[‖] For other reactions of strychnine, see Godeffroy, Zeit. anal. Chem., **16**, 244; Selmi, *ibid.*, **18**, 292; Fraude, *ibid.*, **19**, 87; Jorissen, *ibid.*, **19**, 358; Palm, *ibid.*, **22**, 226; Arnold, *ibid.*, **23**, 231 and 234.

precipitation, it appears to consist of very minute grains; but on closer inspection these grains are seen to suddenly form into needles (water being absorbed), and these subsequently arrange themselves without exception into concentric groups. These successive changes of the precipitate may be traced distinctly even with the naked eye.

4. **Ammonia** produces a whitish precipitate in solutions of salts of brucine; this appears at first like a number of minute drops of oil, but gradually changes (with absorption of water) to small needles. Immediately after it has been formed, the precipitate will re-dissolve very readily in excess of the precipitant; and after a very short time—or, in dilute solutions, after a somewhat longer time—the brucine crystallizes from the ammoniacal liquid in small concentrically grouped needles, containing water of crystallization; these do not re-dissolve on adding more ammonia.

5. **Bicarbonate of soda** added to a neutral solution of a salt of brucine produces, after a short time, a precipitate of brucine containing water of crystallization; this precipitate consists of concentrically grouped silky needles, which are insoluble in excess of the precipitant, but dissolve in free carbonic acid (compare Strychnine). Bicarbonate of soda gives no precipitate in acid solutions of salts of brucine; and it is only after the lapse of a considerable time, and with the escape of the carbonic acid, that the alkaloïd separates from the solution in regular and comparatively large crystals.

6. *Concentrated* **nitric acid** dissolves brucine and its salts, yielding intensely red solutions, which subsequently acquire a yellowish-red tint, and turn yellow when warmed. On adding **stannous chloride** or colourless **sulphide of ammonium** to the solution heated until it has become yellow, no matter whether concentrated or diluted with water, the pale yellow colour changes to a most intense violet; from concentrated solutions a violet precipitate separates. If **hydrosulphide of sodium** is used instead of the above-mentioned reducing agents, the violet colour which is formed at first changes to green (St. Cotton*).

7. If a little brucine is treated with from 4 to 6 drops of pure *concentrated* **sulphuric acid**, a pale rose-coloured solution is obtained, which afterwards turns yellow. If it be treated with a small quantity of **sulphuric acid containing nitric acid** (Erdmann's mixture of acids†), a transient-red colour is produced, which finally changes to yellow. This reaction is very delicate.

8. On mixing a solution of a brucine salt with a solution of **mercurous nitrate** containing as little free acid as possible, a colourless solution is obtained; on gently heating the mixture on the water-bath, however, a beautiful carmine colour gradually appears, and slowly increases in intensity; this coloration is very stable. Strychnine under the same circumstances yields no colour. 1 part of brucine may be readily recognized in the presence of 20 parts of strychnine in this way (Flückiger‡).

9. On treating brucine with a solution of **vanadate of ammonia** in concentrated sulphuric acid (1 : 200), the solution is coloured yellowish-red, changing to a reddish orange, but soon becomes colourless (Mandelin||).

10. On adding **dichromate of potassa** to a solution of a brucine

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* Zeit. anal. Chem., 9, 111.

† For its preparation, see p. 423, note *.

‡ Zeit. anal. Chem., 15, 342.

|| *Ibid.*, 23, 236.

salt, it at first remains clear, but after some time small yellowish-red crystals are deposited; these dissolve in concentrated sulphuric acid with a brownish-red coloration.

11. On adding **chlorine water** to a solution of a salt of brucine, it becomes bright red; ammonia changes this to yellowish-brown.

12. **Sulphocyanate of potassium** added to a solution of a brucine salt produces a granular crystalline precipitate immediately if it is concentrated, but in more dilute solutions it does not appear until after some time; under the microscope, this precipitate is seen to be composed of variously aggregated polyhedral crystalline grains. Rubbing the sides of the vessel promotes the separation of the precipitate.

13. **Mercuric chloride** also produces a white granular precipitate, which, under the microscope, is seen to be composed of small roundish crystalline grains.

14. **Tannic acid** throws down a heavy dirty white precipitate from solutions of salts of brucine; this is soluble in acetic acid, insoluble in hydrochloric acid.

15. The most delicate tests for brucine among the **general reagents** are iodized iodide of potassium, potassium mercuric iodide, phosphomolybdic acid, and potassium bismuth iodide.*

3. Veratrine.†

§ 240.

1. Veratrine occurs in various species of veratrum, especially in the seeds of *Veratrum sabadilla*, and in small quantity in the rhizomes of *V. album* and *V. lobelianum*. It forms a white, loose, odourless powder of a sharp burning taste, but not bitter; it is exceedingly poisonous. It has a most irritating action on the membranes of the nose, even the most minute quantity of the powder exciting the most violent sneezing. It is only slightly soluble in water, but more readily when freshly precipitated than after drying. The solution has a burning taste and a slightly alkaline reaction. The cold saturated solution becomes turbid when heated, but becomes clear again on cooling if the heating has not been continued for any length of time. Veratrine is soluble in 2 parts of chloroform and in 4 parts of alcohol, and is somewhat less soluble in ether, amyl alcohol, and benzene, and still less so in light petroleum. At 115°, it melts like wax, and, on cooling, solidifies to a transparent yellow mass. If cautiously heated, it may be sublimed unchanged (see foot-note ‡, p. 418).

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* For other reactions of brucine see Hager, Zeit. anal. Chem., **11**, 201; Buckingham, *ibid.*, **13**, 235; Dragendorff, *ibid.*, **18**, 108; Fraude, *ibid.*, **19**, 87; Palm, *ibid.*, **22**, 226; Arnold, *ibid.*, **23**, 229 and 232.

† Officinal veratrine, which is usually understood by the name veratrine, is a mixture of two isomeric alkaloïds, having the composition $C_{64}H_{49}NO_{18}$ [$C_{32}H_{49}NO_9$]. One of these alkaloïds—crystalline veratrine, or cevadine—is almost insoluble in water; the other—veratridine—is not crystallizable, and is soluble in water. They cannot, however, be separated from one another by this means, as the presence of a small quantity of cevadine renders the veratridine insoluble in water, and on the other hand the presence of a small admixture of veratridine deprives cevadine of its property of crystallizing (Bosetti). The account of the properties of veratrine given above refer to the "officinal veratrine." For the method of separating the mixed alkaloïds, see E. Schmidt and R. Köppen (Annalen, **185**, 224) and Bosetti (Pharm. Centralhalle, 1885, p. 117).

2. Veratrine neutralizes acids completely; some of its salts crystallize with difficulty, but most of them dry up to a gummy mass. They are in part soluble in water, and have a sharp burning taste.

3. **Potassa, soda, ammonia,** and the **monocarbonates of the alkalies** added to solutions of salts of veratrine throw down a white flocculent precipitate, which, immediately after precipitation, does not appear crystalline under the microscope. After the lapse of a few minutes, however, it alters its appearance, and small scattered clusters of short prismatic crystals may be observed here and there, instead of the original coagulated flakes. The precipitate is insoluble in excess of potassa or soda, or of carbonate of potassa. It dissolves slightly in cold ammonia, but separates again on heating.

4. With **bicarbonate of soda** and **bicarbonate of potassa,** the salts of veratrine behave like those of strychnine and brucine. Veratrine, however, separates readily on boiling, even from dilute solutions.

5. When *concentrated* **nitric acid** is poured on veratrine, the latter agglutinates in small resinous lumps, which afterwards dissolve slowly in the acid. If the veratrine is pure, the solution is colourless.

6. If veratrine is treated with *concentrated* **sulphuric acid,** it also agglutinates at first into small resinous lumps: but these dissolve with great readiness, forming a pale yellow solution, which at first has a greenish yellow fluorescence; the solution gradually becomes deeper in colour, changing to a reddish-yellow, then to an intense blood-red, and finally to purple-red. The colour lasts two or three hours, and then gradually disappears. If the yellow solution is warmed, it at once changes to red. If a little powdered **sugar** be sprinkled on a thin layer of the yellow solution of veratrine in concentrated sulphuric acid, water is taken up and a dark-green colour is produced, which gradually turns to an intense blue, and then slowly disappears (Weppen*). The appearance of the green colour is accelerated by breathing on the solution. This reaction also takes place very readily if about 1 part of veratrine and 6 parts of sugar (Beckurts)—this proportion is the best (R. Otto)—are rubbed up together, and then mixed with not too much concentrated sulphuric acid.

7. If veratrine is dissolved in *strong* **hydrochloric acid,** a colourless solution is obtained, which on long boiling becomes intensely red; the colour being permanent, the reaction is very delicate (Trapp).

8. **Sulphocyanate of potassium** produces a flocculent, gelatinous precipitate in concentrated solutions only of salts of veratrine.

9. If sufficient **chlorine water** is added to a solution of a salt of veratrine, the solution becomes intensely yellow; ammonia does not perceptibly alter the colour.

10. The most delicate tests for veratrine amongst the **general reagents** are phosphomolybdic acid, iodized iodide of potassa, potassium mercuric iodide, and tannic acid.†

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* Zeit. anal. Chem., **13**, 454.

† For other reactions of veratrine, see Buckingham, Zeit. anal. Chem., **13**, 235; Godeffroy, *ibid.*, **16**, 244; Jorissen, *ibid.*, **19**, 359; Rossbach (action on infusoria), *ibid.*, **21**, 482; Arnold, *ibid.*, **23**, 231 and 234.

§ 241.

4. Atropine, $C_{34}H_{23}NO_6$ [$C_{17}H_{23}NO_3$].

1. Atropine occurs along with hyoscyamine in all parts of the deadly nightshade (*Atropa belladonna*) and of the thorn-apple (*Datura stramonium*) (Ladenburg, E. Schmidt). It forms small brilliant prisms and needles; when pure, it is without odour and has a nauseous, persistently bitter taste. It melts at 115°–115·5° to a colourless liquid which solidifies to a crystalline mass on cooling; at 140°, it volatilizes with partial decomposition. When heated between watch-glasses, it volatilizes without blackening. Atropine is only sparingly soluble in cold water, but somewhat more easily in boiling water. The solution has an alkaline reaction, and on boiling it some of the atropine volatilizes with the steam. It is very soluble in alcohol; the solution is optically active (Poehl). It is very soluble in chloroform and in amyl alcohol, more sparingly in ether and benzene, and almost insoluble in light petroleum.

2. Atropine combines with acids, forming salts, some of which, particularly the acid salts, do not crystallize, or only with difficulty. The salts dissolve easily in water and alcohol, scarcely at all in ether, benzene, or amyl alcohol. The aqueous solutions of the salts acquire a dark colour by long heating.

3. Atropine and its salts are active narcotic poisons; applied to the eye, they dilate the pupil for a considerable time. Hyoscyamine has the same action; but the dilatation in this case is rather slower in making its appearance, and more lasting.

4. **Potassa, soda,** and **monocarbonates of the fixed alkalies** added to concentrated aqueous solutions of salts of atropine throw down a portion of the alkaloïd. The precipitate, which is at first pulverulent, does not dissolve in excess of the precipitant more readily than in water; by long standing it becomes crystalline. **Ammonia** likewise produces a precipitate, soluble in excess. Atropine is decomposed in contact with fixed alkalies or with baryta water, forming atropic acid and tropine; this action takes place slowly in the cold, rapidly on heating.

5. **Carbonate of ammonia** and **bicarbonates of the alkalies** do not precipitate solutions of salts of atropine.

6. **Chloride of gold** added to aqueous solutions of salts of atropine throws down a compound of hydrochloride of atropine with chloride of gold as a yellow precipitate which gradually becomes crystalline; it forms small lustreless plates which melt at 135°–137° (Ladenburg).

7. **Tannic acid** added to an aqueous solution of a salt of atropine throws down a white curdy precipitate, soluble in ammonia and in hydrochloric acid.

8. If atropine is warmed with concentrated **sulphuric acid** until the solution is slightly brown, and a few drops of water are then added to it, it evolves an agreeable odour, recalling that of the sloe blossom. If a fragment of dichromate of potassa is added to the hot solution, the odour developed recalls that of the flowers of *Spirea ulmaria*, and on continued heating resembles that of essence of bitter almonds (Guglielmo, Pfeiffer).

This odour of flowers so characteristic of atropine is also produced when some crystals of *chromic acid* are gently warmed with atropine until the chromic acid turns green from incipient reduction (Brunner).

9. If atropine or an atropine salt is treated with a little fuming *nitric acid*, evaporated to dryness on the water-bath, and, after cooling, a few drops of an alcoholic solution of potash are added to the residue, a violet coloration appears, which soon passes into red; this is characteristic of atropine (Vitali).

10. If atropine is mixed with *concentrated* **sulphuric acid** on a white porcelain tile, and a crystal of nitrite of potassa stirred into the mixture, it becomes deep yellow or orange-coloured. If now a few drops of an alcoholic solution of potassa are added, the mixture turns a magnificent reddish-violet, which quickly changes to a pale rose colour (Arnold).

11. **Picric acid** does not behave in the same way with all samples of commercial atropine. A solution of English atropine sulphate becomes turbid from the formation of small amorphous drops. On warming the solution until it becomes clear, and then allowing it to cool, beautiful rectangular crystalline plates separate. German atropine sulphate, however, on the addition of picric acid, yields an immediate crystalline precipitate, and only very rarely an amorphous turbidity. The crystals are also small rectangular plates (Hager[*]).

12. Phosphomolybdic acid and iodized potassium iodide are the most delicate of the **general reagents** for the detection of atropine.[†]

§ 242.

Recapitulation and Remarks.

Strychnine may be separated from brucine, veratrine, and atropine by means of cold absolute alcohol, since it is insoluble in this solvent, whilst the other alkaloïds dissolve readily in it. Brucine may be separated from strychnine by means of chromate of potassa; for this purpose, chromate of potassa is added to a very concentrated solution of the alkaloïds in weak acetic acid; almost the whole of the strychnine then separates as chromate, whilst the brucine remains in solution (R. Otto). Strychnine is most conveniently identified by the reaction with sulphuric acid and the above-mentioned oxidizing agents;[‡] also by its crystalline form when thrown down by alkalies (viewed under the microscope); and lastly, by the form of the precipitates produced by sulphocyanate of potassium and by mercuric chloride. Brucine and veratrine may be separated from atropine by making the solution alkaline and shaking

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[*] From this reaction, and also from the behaviour of different samples of atropine sulphate with a solution of iodized potassium iodide, Hager considers that the officinal atropine consists of two different alkaloïds (Hager's commentary on the German Pharmacopœia, 1, 422). According to Pöhl, picric acid has no action on pure atropine salts (Zeit. anal. Chem., **18**, 629).

[†] For other atropine reactions, *vide* Godeffroy, Zeit. anal. Chem., **16**, 244; Rossbach, Action on Infusoria, *ibid.*, **21**, 482; Vitali, *ibid.*, **21**, 581; Palm, *ibid.*, **22**, 226.

[‡] The only substance besides curarine (see above) which shows somewhat analogous reactions in this respect is aniline. A. Guy has, however, called attention to the fact that aniline, treated with sulphuric acid and oxidizing agents, acquires a pale green tint at first, which gradually deepens, and only then changes to a magnificent blue, which remains for some time, but finally turns black. Brucine does not interfere with the colour reaction which strychnine gives with concentrated sulphuric acid and chromate of potassa, if some nitric acid is first added to the solution of the alkaloïds in sulphuric acid and the colour reaction produced by brucine allowed to fade away before adding the dichromate of potassa.

with light petroleum (Dragendorff); this takes up the brucine and veratrine, but not the atropine. By separating the aqueous liquid from the light petroleum and shaking it with ether, the atropine may be obtained in ethereal solution. Brucine and veratrine are not readily separated from one another, but may be detected in presence of each other; for this purpose, the best tests for brucine are the reactions with nitric acid and stannous chloride or sulphide of ammonium, or it may be recognized by the crystalline form of the precipitate thrown down by ammonia from solutions of salts of brucine. Veratrine is distinguished from brucine and the other alkaloïds treated of, by its characteristeric behaviour when gently heated, and also by the crystalline form of the precipitate produced by alkalies in solutions of its salts. To distinguish veratrine in presence of brucine, the reaction with concentrated sulphuric acid or with hydrochloric acid should be selected.

C. PROPERTIES AND REACTIONS OF CERTAIN NON-NITROGENOUS COMPOUNDS ALLIED TO THE ALKALOÏDS.

These compounds, Salicin, Digitalin, and Picrotoxin, will be considered here, although they are not alkaloïds.

§ 243.

1. Salicin, $C_{26}H_{18}O_{14}$ [$C_{13}H_{18}O_7$].

1. Salicin exists in the bark and leaves of most kinds of willow and some kinds of poplar. It forms either white crystalline needles and scales of silky lustre, or, where the crystals are very small, as a silky powder. It has a bitter taste, is somewhat sparingly soluble in water and cold alcohol, but more easily when boiling; it is insoluble in ether, but soluble in potassa and in glacial acetic acid. It melts at 198°, and is decomposed at a higher temperature.

2. Salicin is not thrown down by any reagent, with the exception of acetate of lead, in such a state of combination that the salicin can be recovered from the precipitate; **acetate of lead**, however, with a hot concentrated aqueous solution of salicin, yields a precipitate which is a compound of salicin with lead oxide.

3. If salicin is treated with *concentrated* **sulphuric acid,** it agglutinates into a resinous lump, and acquires an intense blood-red colour, the sulphuric acid remaining unaltered at first. Solution, however, slowly takes place, and the acid gradually becomes red in proportion as the substance dissolves.

4. If **hydrochloric acid** or dilute **sulphuric acid** is added to an aqueous solution of salicin and the mixture boiled for a short time, it suddenly becomes turbid, sugar is formed, and a white flocculent agglutinating precipitate (saliretin) is deposited. If 1 or 2 drops of a solution of chromate of potassa be added to the liquid containing the precipitate, and the whole boiled, the saliretin will acquire a bright rose colour, the characteristic odour of salicylic aldehyde being emitted at the same time. If the solution is distilled with dilute sulphuric acid and dichromate of potassa in a small retort, the receiver of which contains a little water, the salicylic aldehyde in the distillate may be readily detected by the addition of a drop of neutral ferric chloride; this produces an intense violet coloration (Parrot).

5. **Ferric chloride** colours solutions of salicin a pale brown, but, on boiling, the solution becomes colourless, whilst a dull yellow precipitate is formed.

6. On heating a solution of salicin with **nitrate of silver** solution to which excess of ammonia and either potassa or soda has been added, the silver is reduced, and a brilliant mirror of metallic silver is formed. Other glucosides, mannitol, cane sugar, and grape sugar, yield the same reaction (E. Salkowski).

7. On moistening a little salicin with a few drops of a solution of pure **chloride of zinc** in dilute hydrochloric acid (0·1 gram of fused zinc chloride, 3 c.c. of fuming hydrochloric acid, and 3 c.c. of water), and evaporating to dryness on the water-bath, an intensely violet-red residue is obtained (A. Jorissen).

8. Salicin does not neutralize acids, nor does it combine with them.

§ 244.

2. Digitalin.

1. The preparations met with in commerce under the name of digitalin differ greatly in their properties. They consist of mixtures of the active principles of *Digitalis purpurea* with their decomposition products. Schmeideberg states that the following occur:—Digitoxin (very poisonous), digitalin and digitaleïn (both poisonous), and digitonin, which has a feeble action.[*] Other investigators, however, have arrived at quite different results; so that the investigation of the active principles of the digitalis cannot yet be regarded as complete. The constituents of commercial digitalin vary greatly in different specimens; they contain no nitrogen, but belong to the glucosides or bitter principles.

2. For practical purposes, two varieties of commercial digitalin have to be considered, namely, the German, which is soluble in water, and the French, which dissolves but sparingly; both, however, have the same physiological action. German digitalin is, according to most accounts, an amorphous powder, although R. Otto states that it is crystalline when seen under the microscope; it dissolves in cold water, forming a neutral, turbid, bitter solution, which froths strongly when shaken. Ethyl and amyl alcohol dissolve it completely, but it is only partially soluble in ether, benzene, or chloroform, and not at all in light petroleum. French (Nativelle's) digitalin occurs in the form of loose tufts of slender needles, and has a neutral reaction. It is only very sparingly soluble in water, and its bitter taste does not become apparent until after some time; it is insoluble in ether and benzene, but dissolves readily in chloroform and in alcohol. Homolle's French digitalin exhibits somewhat different properties. It forms white or yellowish-white granules or scales, is but sparingly soluble in water, has a neutral reaction, and very bitter taste; it dissolves readily in 90 per cent. alcohol, but is only very sparingly soluble in ether. All digitalins may be dissolved by saturating them with glacial acetic acid and then adding water (Dragendorff[†]).

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[*] N. Rep. Pharm., 24, 89; Chem. Centralbl., 1875, 262, which may be consulted for the details of the properties of the separate constituents.

[†] See his "*Gerichtlich-chem. Ermittelung von Giften,*" second edition (St. Petersburg: Schmitzdorff, 1876), p. 274.

3. If a solution of commercial digitalin prepared with glacial acetic acid is shaken up with **chloroform** at 35°, the whole, or at least the greater part, of the active principles are extracted by the chloroform, and may be separated by washing the chloroform with water, filtering,[*] and evaporating to dryness at 30°.

4. On treating commercial digitalin, or the residue obtained from the evaporation of the chloroform in 3, with *concentrated* **sulphuric acid** or with the di- or tri-hydrate of sulphuric acid—the latter being preferable if foreign organic substances are present—(Dragendorff), and then adding, by means of a glass rod, 1 or 2 drops of a solution of bromine and stirring, a characteristic[†] purple colour, more or less pure, is produced.[‡] Instead of the bromine solution, Dragendorff recommends a solution of 1 part of potassa dissolved in 5 parts of water to which bromine has been added until a permanent yellow colour is produced.

This reaction, which was first mentioned by Grandeau, and subsequently confirmed by J. Otto (who employed bromine water), Dragendorff, and others, is very delicate, and, according to Dragendorff, takes place very distinctly with 0·0002 gram of commercial digitalin.

5. Besides the reaction described in 4, the *physiological action* of the residue from the evaporation of the chloroform solution in 3 must be ascertained (Dragendorff[‖]).

§ 245.

3. Picrotoxin, $C_{30}H_{16}O_{12}$ [$C_{15}H_{16}O_6$[¶]].

1. Picrotoxin, the poisonous principle of cocculus indicus, the fruit of *Menispermum cocculus*, forms white brilliant four-sided prisms or needles. It is without odour, very bitter, a narcotic poison, melts at 199°–200°, and gives off empyreumatic vapours.

2. Picrotoxin is neutral. It is only sparingly soluble in cold, more easily in boiling water, and crystallizes from the solution in needles on cooling or evaporation. Hot alcohol dissolves it very readily: the concentrated solution, when cold, solidifies to a silky mass; more dilute solutions give silky needles on evaporation. Picrotoxin is only sparingly soluble in ether, but dissolves easily in chloroform, amyl alcohol, and glacial acetic acid. It may be removed from its acidified solution by shaking it up with ether, chloroform, or amyl alcohol (but not with benzene or light petroleum). Mere traces, however, are taken up by

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[*] If the chloroform solution appears mucilaginous, a few drops of absolute alcohol should be added before filtering.

[†] Delphinin exhibits a similar reaction. On shaking up an acid solution of delphinin, however, with chloroform, only a mere trace passes into the chloroform.

[‡] Flückiger has, however, observed that Nativelle's crystallized digitalin behaves in a different manner (Pharm. Centralhalle, 1873, 275).

[‖] Dragendorff's "*Beiträge zur gerichtlichen Chemie einzelner organischer Gifte*" (St. Petersburg: H. Schmitzdorff), 1872, p. 34.

[¶] v. Barth and Kretschy (Zeit. anal. Chem., **19**, 360, and **21**, 582) have isolated from commercial picrotoxin two other compounds—*picrotin* and *anamirtin*. Both the correctness of the formula given above and also the presence of the two last-named compounds in commercial picrotoxin have been contested by Paternò, and Oglialoro, and also by E. Schmidt and Löwenhardt (*ibid.*, **21**, 581).

ether, chloroform, or amyl alcohol from the alkaline solutions. The ethereal solution when evaporated leaves the picrotoxin in the form of a powder or crystalline scales.

3. **Acids** do not neutralize picrotoxin, and, with the exception of acetic acid, do not increase its solubility in water.

4. **Ammonia, potassa,** and **soda** dissolve picrotoxin freely; acids, even carbonic acid, precipitate it again from the concentrated solution. Picrotoxin therefore possesses the character of an acid rather than of a base. On heating the solutions of picrotoxin in potassa or soda they become yellow or yellowish-red.

5. When picrotoxin is treated with *concentrated* **sulphuric acid**, it dissolves, forming a saffron-yellow solution, and on adding a trace of dichromate of potassa, the colour becomes violet-red, and ultimately changes to apple-green (Köhler).

6. If dry commercial picrotoxin is rubbed up with three times the quantity of **nitrate of potassa,** moistened with **sulphuric acid,** and excess of strong aqueous soda added, the mixture becomes brick-red; the colour gradually disappears (Langley). Dragendorff has modified this reaction by moistening the picrotoxin with a little concentrated nitric acid, warming on the water-bath until the residue is dry, then moistening with the smallest possible amount of sulphuric acid, and finally adding excess of a strong aqueous solution of soda. In this way, a pale red colour is obtained even with 0·1 mgrm. of substance.

It is uncertain whether *pure* picrotoxin as prepared by Barth and Kretschy exhibits this reaction. A specimen prepared by Langley did not yield it.

7. If a solution of picrotoxin containing potassa or soda is mixed with a solution of **tartrate of copper and potassa** (Fehling's solution) and warmed gently, cuprous oxide separates.

8. **Iodized iodide of potassium, picric acid, tannic acid, gold chloride,** and **platinum chloride** do not give a precipitate with solutions of picrotoxin; lead acetate, however, precipitates its ammoniacal solution (Palm*).

D. SYSTEMATIC COURSE FOR THE DETECTION OF THE ALKALOÏDS AND ALSO OF SALICIN, DIGITALIN, AND PICROTOXIN.

In the methods to be described under *a* and *b*, it is presupposed that the *non-volatile* alkaloïds, &c., are, in concentrated aqueous solution, dissolved by means of an acid, and free from any substances which would obscure or modify the reactions. When the method to be employed under these circumstances has been considered, other methods will be described under *c* which are convenient if colouring or extractive matters are present, and in which the detection of *volatile* alkaloïds will be included.

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* For the detection of picrotoxin by means of physiological experiments, see Dragendorff, p. 49 of "*Beiträge zur gerichtl. Chem.*" (St. Petersburg: Wienecke, 1884).

a. Detection of the Non-volatile Alkaloïds, &c., in an Aqueous Solution containing only one of these Substances.

§ 246.

1. A drop of dilute sulphuric acid is added to a portion of the solution, and then some solution of iodine in iodide of potassium or of phosphomolybdic acid.

a. No precipitate is formed: absence of all alkaloïds; possible presence of salicin, digitalin, picrotoxin. Pass on to 5.

b. A precipitate is formed. There is cause to suspect the presence of an alkaloïd. Pass on to 2.

2. To a portion of the aqueous solution, dilute potassa or soda is added drop by drop, until the liquid acquires a scarcely perceptible alkaline reaction; it is then stirred, and allowed to remain for some time.

a. No precipitate is formed: this is a proof, if the solution is concentrated, of the absence of all alkaloïds; if the solution is dilute, however, there is a possibility that atropine may be present. In this case, other portions of the solution are tested for atropine with chloride of gold, by heating with sulphuric acid, by treatment with fuming nitric acid, &c., as described in § 241, 6, 8, and 9.

b. A precipitate is formed. Potassa or soda is added drop by drop until the solution is strongly alkaline, and, if it does not become clear, some water is also added.

a. The precipitate disappears: morphine or atropine. Test a fresh portion of the solution with iodic acid (§ 233, 12).

aa. There is separation of iodine: morphine. Confirm by § 233, 7, 8, and 9.

bb. There is no separation of iodine: atropine. Confirm as in *a.*

β. The precipitate does not disappear: presence of an alkaloïd of the second or third group (atropine excepted). Pass on to 3.

3. To another portion of the original solution, 2 or 3 drops of dilute sulphuric acid is added, and then a saturated solution of bicarbonate of soda, until the acid reaction just vanishes; the mixture is then stirred actively with a glass rod, rubbing the sides of the vessel, and allowed to remain half an hour.

a. No precipitate is formed: absence of narcotine and cinchonine. Pass on to 4.

b. A precipitate is formed: narcotine, cinchonine, perhaps also quinine (since its precipitation by bicarbonate of soda is entirely dependent on the amount of water present). Ammonia in excess is added to a portion of the original solution, then a sufficient quantity of ether containing 2 per cent. alcohol, and the whole is shaken.

α. *The precipitate re-dissolves in the ether, the clear liquid separating into two distinct layers:* narcotine or quinine. To distinguish between them, a fresh portion of the original solution is tested with chlorine water and ammonia. If the solution turns green, quinine is present; if yellowish-red, narcotine. As a confirmatory test for narcotine, employ the reaction with sulphuric acid containing nitric acid (§ 234, 6).

β. *The precipitate does not re-dissolve in the ether:* cinchonine. Confirm by its behaviour on heating (§ 236, 3) or with ferrocyanide of potassium (§ 236, 8).

4. A portion of the original substance, or of the residue obtained by evaporating the original solution to dryness, is put into a watch-glass, and concentrated sulphuric acid added.

a. A *rose-coloured solution* is obtained, which becomes intensely red on addition of nitric acid: brucine. Confirm by nitric acid and stannous chloride (§ 239, 6).

b. A *yellow solution* is obtained, which gradually turns yellowish-red, blood-red, and crimson: veratrine.

c. A *yellow solution* is obtained, which remains colourless even on standing. A fragment of chromate of potassa is added: a deep blue coloration indicates strychnine; no change indicates quinine. Confirm by chlorine water and ammonia.

5. To determine whether the solution contains salicin, digitalin, or picrotoxin, a portion of the original dry substance, or the residue obtained on evaporating the solution, is treated with concentrated sulphuric acid.

a. The substance becomes at once *blood-red*, and then slowly dissolves, forming a red solution: salicin. Confirm by heating a small portion of the solution with dilute sulphuric or hydrochloric acid (§ 243, 4).

b. The substance dissolves with a *saffron-yellow* colour, and, on adding a trace of dichromate of potassa, a violet-red coloration is produced, finally changing to apple-green: picrotoxin. Confirm by nitric acid and soda (§ 245, 6).

c. The substance dissolves to a *reddish-brown* solution, which, on the addition of a drop of bromine water, changes to a more or less pure purple (§ 244, 4): digitalin.

b. Detection of the Non-volatile Alkaloïds, &c., in Aqueous Solutions which may contain several or all of these Substances.

§ 247.

1. The solution is acidified with hydrochloric acid, shaken with pure ether free from alcohol, and the ethereal layer allowed to evaporate in a glass dish.

a. There is no residue: absence of digitalin (German*) and picrotoxin. Pass on to 2.

b. There is a residue: digitalin and picrotoxin may be suspected, and it must also be remembered that other substances may pass into ethereal solution under these circumstances, such as oxalic acid, tartaric acid, lactic acid (J. Otto). The aqueous residue is again shaken up with fresh ether, in order to remove whatever is soluble in ether as completely as possible, and the ethereal layer allowed to evaporate. The exhausted aqueous residue is examined according to 2, whilst the residue left on evaporating the ethereal solution, which may contain traces of atropine, is treated as follows:—

α. A portion is dissolved in alcohol, and the solution allowed to evaporate slowly: long silky needles radiating from a point indicate picrotoxin. Confirm according to § 245.

β. A portion is dissolved in concentrated sulphuric acid, and bromine water added: a more or less pure purple colour indicates digitalin.

γ. Traces of atropine can only be recognized by the property which the aqueous solution of the residue possesses of dilating the pupil.

2. A solution of iodine in iodide of potassium is added to a portion of the aqueous solution, and to another portion some phosphomolybdic acid.

a. A precipitate is produced in both cases: alkaloïds are indicated. Pass on to 3.

b. No precipitate is produced in either case: alkaloïds are absent. Pass on to test for salicin according to § 243.

3. To a small portion of the aqueous solution, potassa or soda is added until it is just alkaline; observe whether a precipitate is produced or not, then add potassa or soda in good excess, and dilute with water.

a. No precipitate is produced by potassa or soda, or the precipitate produced has re-dissolved: presence of atropine or morphine, absence of all other alkaloïds. Another larger portion of the aqueous solution is mixed with bicarbonate of potassa or soda in excess, stirred, and allowed to remain for some time.

α. *No precipitate is produced:* absence of morphine. Soda is added to the solution, it is shaken with ether, and the ether separated and allowed to evaporate; the residue is tested for atropine according to § 241, 6, 8, and 9.

β. *A precipitate is produced:* morphine. The precipitate is collected and tested for morphine according to § 233, 7, 8, and 9, whilst the filtrate is tested for atropine according to *α.*

b. A precipitate is produced by potassa or soda, which does not re-dissolve in excess of the precipitant

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* The French must be dissolved by chloroform, which also takes up any narcotine which may be present.

or by moderate dilution: a larger portion of the acidified aqueous solution is treated in the same way as the small sample 3, and filtered. The precipitate is examined according to 4, whilst the alkaline filtrate is shaken with ether, allowed to remain for an hour in order that the morphine which has at first dissolved in the ether may separate again as completely as possible, and the ethereal layer separated from the aqueous solution. The ether is allowed to evaporate, and the residue tested for atropine according to § 241, 6, 8, and 9, whilst the morphine is thrown down from the alkaline aqueous solution by carbonic acid (§ 233, 4) and tested according to § 233, 7, 8, and 9.

4. The precipitate obtained in 3, *b*, is washed with cold water, dissolved in a slight excess of dilute sulphuric acid, and solution of bicarbonate of soda added until the acid reaction has disappeared; it is then stirred actively, rubbing the sides of the vessel, allowing it to remain for an hour.

a. No precipitate is formed: absence of narcotine and cinchonine. The solution is boiled down nearly to dryness, and the residue taken up with cold water. If nothing insoluble remains, pass on to 6; if there is a residue, it must be examined according to 5 for quinine (of which a small amount may be present), strychnine, brucine, and veratrine.

b. A precipitate is formed. (This may contain narcotine, cinchonine, and quinine; compare § 246, 3, *b.*) The precipitate is collected and the filtrate examined according to *a*; the precipitate is treated as follows:—It is washed with cold water, dissolved in a little hydrochloric acid, ammonia added in excess, and then a sufficient quantity of ether containing 2 per cent. of alcohol.

α. *The precipitate dissolves completely in the ether, and two clear layers are formed:* absence of cinchonine, presence of quinine or narcotine. The ethereal solution is evaporated, the residue taken up with a little hydrochloric acid, and enough water to make the dilution at least 1 : 200; bicarbonate of soda is then added until it is neutral, and the mixture allowed to remain for some time. A precipitate indicates narcotine: this should be confirmed by chlorine water and ammonia, also by sulphuric acid containing nitric acid (§ 234). The clear aqueous solution, or the filtrate from the narcotine, is evaporated to dryness, and the product treated with water. If a residue remains, it is washed, dissolved in hydrochloric acid, and chlorine water and ammonia added; a green coloration indicates quinine.

β. *The precipitate does not dissolve in the ether, or but incompletely:* cinchonine, perhaps also quinine or narcotine. The mixture is filtered, and the filtrate tested as in α for quinine and narcotine; the precipitate consists of cinchonine, and may be further tested according to § 236, 3 and 8.

5. The insoluble residue of 4, *a*—left on evaporating the solution to which bicarbonate of soda has been added—is washed with water and examined for quinine (of which a small quantity may be present),

strychnine, brucine, and veratrine as follows:—It is dried in a water-bath, and digested with absolute alcohol.

a. It dissolves completely: absence of strychnine, presence of (quinine,) brucine, or veratrine. The alcoholic solution is evaporated to dryness on the water-bath, and, if quinine has already been detected, the residue is divided into two portions, one being tested for brucine with nitric acid and stannous chloride (§ 239, 6), the other for veratrine by means of concentrated sulphuric acid (§ 240, 6). If, on the other hand, no quinine has as yet been detected, the residue is divided into three portions, *a*, *b*, *c*; *a* and *b* are examined for brucine and veratrine in the manner just stated, and *c* for quinine with chlorine water and ammonia. If brucine is present, however, *c* must be treated with absolute ether, the ethereal solution evaporated, and the residue examined for quinine.

b. It does not dissolve, or at least not entirely: presence of strychnine, perhaps also of (quinine,) brucine, and veratrine. It is filtered and the filtrate examined for (quinine,) brucine, and veratrine as directed in 5, *a*. The precipitate is shown to be strychnine by the reaction with sulphuric acid and chromate of potassa (§ 238, 8).

6. Salicin has still to be tested for: for this purpose, more hydrochloric acid is added to the rest of the acidified aqueous solution which has been exhausted with ether, and the whole boiled for some time. If no precipitate is formed, salicin is absent, but if there is a precipitate the presence of salicin is indicated; this is confirmed by adding chromate of potassa to the precipitated liquid, and boiling (§ 243, 4), and also by testing the original substance with concentrated sulphuric acid (§ 243, 3).

c. Detection of the Alkaloïds and of Digitalin and Picrotoxin in Presence of Extractive and Colouring Matters, Vegetable or Animal.

The presence of mucilaginous, extractive, and colouring matters renders the detection of the alkaloïds incomparably more difficult. These matters obscure the reactions so much that we are not able even to ascertain, by a preliminary experiment, whether the substance under examination contains alkaloïds or not. Several methods will be given in the following sections by means of which the separation of the alkaloïds from such extraneous matters may be effected, and their detection made practicable. One or other of these methods must be chosen according to the particular circumstances of each case.

It must, however, be carefully noted that these methods have reference merely to the alkaloïds described in this work. This section, consequently, although well-adapted as an introduction to the practice of such work, is not sufficiently extended for actual chemical researches, not only for the reason given above, but also because the ptomaïnes (cadaveric alkaloïds) have not been included, as being inconsistent with the scope of this treatise. When parts of animal bodies have to be examined, the danger of mistaking ptomaïnes for vegetable alkaloïds, as has already frequently happened, must be very carefully guarded against. This mistake may easily arise if the presence of some one or other of the vegetable alkaloïds is inferred from a single reaction, as there are various kinds of ptomaïnes, and in particular some which give single reactions strikingly like those obtained with certain vegetable alkaloïds. For actual chemico-legal investigations, therefore, it is necessary to consult works which on the one hand treat of all or almost all the alkaloïds, &c., or at all events those which have poisonous properties, and on the other hand take the ptomaïnes into account.*

1. Stas's† Method for the Detection of Poisonous Alkaloïds (also Digitalin and Picrotoxin), modified by J. and R. Otto.‡

§ 248.

Stas's process depends on the following facts:—

α. The acid salts of the alkaloïds are soluble in water and alcohol.

β. The neutral and acid salts of the alkaloïds are mostly insoluble in ether. On the one hand, therefore, salts of the alkaloïds do not usually pass into ethereal solution when the neutral or acid solution is shaken with ether, whilst, on the other, the alkaloïds pass into aqueous solution as acid sulphates when the ethereal solution of the pure alkaloïd is shaken with dilute sulphuric acid.

γ. If an aqueous solution containing neutral or acid salts of alkaloïds is mixed with caustic, carbonated, or bicarbonated alkalies, the alkaloïds are liberated, and, on shaking the alkaline solution with ether or amyl alcohol, the pure alkaloïds are taken up by the ether or amyl alcohol.

It will be seen, however, from the following, that there are certain exceptions to these general rules.

a. If the alkaloïd has to be sought for in the contents of a stomach or intestines, in food, or generally in pappy matters, the substance is mixed with twice its weight of strong pure alcohol || and just enough tartaric acid to produce a decidedly acid reaction, and is then heated with a reflux condenser at 70° or 75°. When quite cold, it is filtered, and washed with strong pure alcohol.

If the heart, liver, lungs, or similar organs have to be operated on, they should be cut up small, digested with the acidified alcohol

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* Such are F. J. Otto's "*Anleitung zur Ausmittelung der Gifte*," sixth edition (Brunswick: Vieweg, 1884) (also treats of ptomaïnes in detail); Dragendorff's "*Beiträge zur gerichtlichen Chemie einzelner organischer Gifte*" (St. Petersburg: Schmitzdorff, 1872), also his "*Die gerichtlich-chemische Ermittelung von Giften*," second edition (*ibid.*, 1876), and his "*Beiträge zur gerichtlichen Chemie*" (St. Petersburg: Wienecke, 1884); Sonnenschein's "*Handbuch der gerichtlichen Chemie*," second edition, edited by Classen (Berlin: Hirschwald, 1881). Numerous papers on the ptomaïnes have also appeared: see Zeit. anal. Chem.

† Bull. de l'Académie de Médecine de la Belgique, **9**, 304. Jahrb. pr. Pharm., **24**, 313. Jahresb. von Liebig u. Kopp, 1851, 640.

‡ Ann. Chem. Pharm., **100**, 44. F. J. Otto's "*Anleitung zur Ausmittelung der Gifte*," sixth edition, edited by R. Otto, p. 105.

|| In order to remove any alkaloïdal substances which may be present, the alcohol should be rectified after adding to it a little tartaric acid (R. Otto).

in the manner described above, squeezed, the treatment repeated until the substance is exhausted; when quite cold, the alcoholic extracts obtained are mixed and filtered.

b. The alcoholic solution is evaporated at a rather low temperature; this may be done in a porcelain evaporating basin on a water-bath, keeping the water at about 80°. The temperature of the solution under these circumstances will not rise higher than 40° or 50°; if this is considered too high, the evaporation may be hastened by blowing air across the surface of the solution. Stas considers that the temperature should not exceed 35°; he therefore evaporates under a bell glass over sulphuric acid, with or without the aid of an air pump, or in a retort with a current of air passing through it. Such extreme caution, however, is very rarely necessary; at all events, the greater bulk of the liquid may always be evaporated off on a gently heated water-bath.

If insoluble substances, fat, &c., separate on evaporation, as indeed is usually the case, the now aqueous liquid is filtered through a moistened filter, and the filtrate and washings evaporated to the consistence of an extract in the manner described. If no insoluble substances separate on evaporating the alcoholic solution, it may, of course, be at once evaporated to the consistence of an extract.

c. The residue left on evaporation is extracted as thoroughly as possible by gradually adding small portions of cold absolute alcohol, mixing intimately, and finally adding a large quantity of alcohol, in order to separate everything that can be precipitated by it. The alcoholic extract is filtered through a filter moistened with alcohol, the residue washed with cold alcohol, and the alcoholic solution evaporated at a low temperature (see above); the residue obtained in this way is now taken up with a little water, the greater part of the free acid neutralized with dilute soda, leaving the solution feebly but *distinctly acid*, and finally it is shaken up with pure ether free from alcohol and oil of wine. By means of a separating funnel, or an ordinary burette with a glass stop-cock, the ether is separated from the aqueous layer, and the latter washed by shaking it up again and again with fresh ether, until the ether is no longer coloured by it.

Besides colouring matters, the ether also takes up picrotoxin and digitalin (German, see note, p. 442), also traces of veratrine and atropine. It is advisable to keep the first strongly coloured ethereal extract apart from the ethereal washings subsequently obtained, in order that they may be examined separately (compare *h*).

d. The acid aqueous solution which has been separated from ether is gently warmed to drive off the dissolved ether, and solution of soda cautiously added until the liquid is distinctly alkaline to turmeric-paper. The alkaloïds are thus liberated, morphine dissolving in the excess of soda. The alkaline solution is shaken with pure ether (free from alcohol and oil of wine), and, after half an hour or an hour, the two layers of liquid are separated as in *c*. The ethereal extract now contains the whole of the alkaloïds, except the morphine, only a small part of which passes into the ethereal solution. The amount of morphine dissolved by the ether is smaller the more completely the acidified aqueous solution was freed from dissolved ether, and the longer the time which was allowed to elapse between the shaking with ether and the separation of the two layers of liquid. A portion of the ethereal extract is allowed to evaporate in a large watch-glass, which should be heated to about 25° or 30° (to prevent condensation of water). If there is no residue, no alkaloïd was dissolved in the ether; pass on to *g*. If a residue remains, its appearance will often give some idea of the nature of the alkaloïd: thus oily streaks which gradually collect to a drop, and when gently warmed give an unpleasant suffocating odour, would indicate a liquid volatile base; whilst a solid residue, or a turbid liquid containing solid particles in suspension, would indicate a non-volatile solid base. If the ethereal extract leaves a residue, the alkaline aqueous solution is treated with ether again and again until a portion of the last ethereal washings leaves no residue on evaporation. The mixed ethereal extracts are then allowed to evaporate in a small glass dish placed upon a bath containing water at about 30°, adding the solution in small quantities at a time as it evaporates.

The aqueous alkaline liquid separated from the ether contains the morphine, and is examined according to *g*.

e. If the acidified aqueous solution in *c* has been well and completely exhausted with ether, the alkaloïds left on the evaporation of the ethereal extract will remain in so pure a state that the tests may be applied at once to the residue. If this residue forms oily streaks or drops, the evaporation should be completed in a vacuum over sulphuric acid, in order to remove the remainder of the ether and ammonia; it is then tested for conine and nicotine according to p. 417. If the residue is crystalline, it should be examined under the microscope, and then tested according to § 246 or § 247, unless the appearance of the crystals should indicate a particular alkaloïd. If the residue consists of amorphous rings, it is dissolved in absolute alcohol with the aid of a gentle heat, the solution allowed to evaporate slowly, noticing whether any crystals are thus formed; the residue is then treated as directed.

f. If, on the contrary, the acidified aqueous solution in *c* has been insufficiently treated with ether, the residue obtained on the evaporation of the ethereal extract from the alkaline solution will not be pure enough to be tested at once. In this case, it must be dissolved in water slightly acidified with sulphuric acid, filtered if necessary, and the acid solution shaken repeatedly with ether (the ethereal solution thus obtained may contain the remainder of the picrotoxin and digitalin, and is to be treated like the ethereal solution obtained in *c*); the aqueous solution, after it has been freed from ether by gentle warming, is now mixed with potassa or soda in decided excess, and shaken repeatedly with ether, as prescribed in *d*, until the last ethereal extract no longer leaves a residue on evaporation. The ethereal extracts are allowed to evaporate, and the residue, thus purified, is examined as in *e*;* the aqueous solu-

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* As it appears that strychnine cannot be obtained pure in this way, F. Janssens recommends (Zeit. anal. Chem., **4**, 48) to mix the solution in dilute tartaric acid, which still contains foreign substances, with finely powdered bicarbonate of soda, so that the solution may be acid with free carbonic acid only. If any

tion, which may contain the remainder of the morphine, is added to the solution obtained in *d*.

g. The alkaline liquid obtained in *d*, or in *d* and *f*, which contains the whole or the greater part of the morphine, is freed from ether by gentle warming, acidified with hydrochloric acid, ammonia added in excess, then without delay pure amyl alcohol, and the mixture shaken.* As morphine is considerably more soluble in warm amyl alcohol than in cold, it is advisable to warm the flask by dipping it in warm water. After the amyl alcohol has been separated from the aqueous solution by means of a separating funnel, the extraction is repeated with a fresh quantity of amyl alcohol. The amyl alcohol extracts are united, freed entirely from water by subsidence and filtration, evaporated, and the residue, if any, is tested for morphine. If the residue is not pure enough, it is dissolved in water acidified with sulphuric acid, filtered, shaken with warm amyl alcohol, the aqueous solution separated, mixed with ammonia, and the alkaline liquid shaken with amyl alcohol. On evaporating this amylic extract after freeing it from water, the morphine will be left in a pure state, and may be tested as in § 233.

h. The ethereal extracts obtained in *c*, or in *c* and *f*, from the acidified aqueous solution have now to be tested for picrotoxin and digitalin. These extracts also contain colouring matters, which are principally present in the first portions extracted. It is therefore advisable to follow Otto's recommendation, and evaporate the first highly coloured portions apart from the latter slightly coloured portions, and examine the residues separately. These are next moistened with glacial acetic acid, warmed with water, and the solutions filtered from the resinous solid matter. The picrotoxin and digitalin present are then removed by shaking up the acid solution with chloroform. Any traces of atropine which may be present are obtained by adding excess of ammonia to the acid solution separated from the chloroform, and shaking it up with benzene (compare § 247, 1). On carefully evaporating the chloroform and benzene solutions, the compounds dissolved in them are obtained in a state fit for further examination.

2. DRAGENDORFF'S METHOD.†

§ 249.

The method elaborated by Dragendorff, which he has gradually rendered more and more complete, embraces a very large number

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precipitate is formed, this is filtered off as quickly as possible; the strychnine is dissolved in the carbonic acid, and will be precipitated on heating the filtrate and partially evaporating it. When the precipitate has been collected and washed, it is dissolved in a small quantity of dilute sulphuric acid (1 : 200), carbonate of potassa added in excess, and the liquid shaken repeatedly with six times its volume of ether, which is then poured off and allowed to evaporate. It is better to use chloroform instead of ether for extracting the alkaline solution.

* Stas recommends ether only for the extraction of alkaloïds, whilst L. v. Uslar and J. Erdmann (Ann. Chem. Pharm., **120**, 121, and **122**, 360) prefer to use amyl alcohol only; it is best, however, to employ the two solvents one after the other as directed in the text.

† "*Die gerichtlich-chemische Ermittelung von Giften*," second edition (St. Petersburg: Schmitzdorff, 1876), p. 141.

of the alkaloïds, and also includes many other organic compounds. An outline of the method is here given, and its application to the detection of the alkaloïds, &c., treated of in the preceding sections. In these operations, special care must be taken that the solvents shaken up with the liquid under examination are carefully separated from the aqueous portion before evaporating them to dryness, and this should be done at as low a temperature as possible; the separation of the aqueous portion is most conveniently effected by means of a burette fitted with a glass tap. The method includes the following operations:—

a. Extraction at 40° to 50° with water and sufficient sulphuric acid to render the extract distinctly acid.

b. Concentration of the aqueous extract to a syrupy consistence, digestion of the residue for twenty-four hours at 30° with 3 to 4 volumes of alcohol. The mixture is cooled, filtered, and the residue washed with 70 per cent. alcohol.

c. The alcohol is distilled off; the residue is cooled, diluted with water if necessary, and filtered.

d. The acid aqueous solution is shaken up with light petroleum (none of the alkaloïds treated of in this work pass into this petroleum extract).

e. The acid aqueous solution is then shaken up with benzene, and the benzene extract purified by shaking it up with water.

The benzene extract takes up some digitalin and traces of veratrine.

f. The acid aqueous solution is shaken up with chloroform: narcotine, cinchonine,* picrotoxin, digitaleïn, and traces of brucine and veratrine are dissolved.

g. The acid aqueous solution separated from the chloroform is shaken up with light petroleum to remove the last traces of chloroform.

h. Excess of ammonia is added to the aqueous solution, the cold ammoniacal solution is shaken up with light petroleum (rectified over oil), and the petroleum separated after the lapse of some time.

The petroleum extract contains the conine and nicotine, and also small quantities of strychnine, brucine, veratrine, and quinine.

i. The ammoniacal aqueous solution is shaken up with benzene. (If the benzene seems gelatinous, the aqueous solution must be separated, a few drops of absolute alcohol added to the benzene, and the solution filtered.)

The benzene extract contains strychnine, brucine, quinine, cinchonine, atropine, veratrine, and the remainder of the narcotine.

k. The ammoniacal aqueous solution is shaken up with chloroform.

In this way the remainder of the cinchonine and a small quantity of morphine are extracted.

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* In the author's own experiments he found that the cinchonine is not taken up by the chloroform.

l. The ammoniacal aqueous solution is shaken up with amyl alcohol. Morphine and salicin are dissolved.

m. The ammoniacal aqueous solution is evaporated to dryness with powdered glass, and the dry residue is extracted with chloroform.

This last operation is not required when dealing with the alkaloïds treated of here, as they have already been extracted.

It is evident that the methods based on the shaking up of solutions with various solvents may be modified in many ways, and that when a substance is to be examined for a definite alkaloïd, &c., as, for instance, in testing urine for morphine, or food for strychnine, the process may be greatly simplified. Numerous modifications of this kind have been described, for which the reader is referred to the "*Zeitschrift für analytische Chemie.*" A few methods will be described here based on totally different principles.

3. Sonnenschein's Method.*

§ 250.

The substance is extracted with water rendered strongly acid with hydrochloric acid, the extract evaporated at 30° to the consistence of a thin syrup, diluted with water, allowed to cool and remain for some time, then filtered, and the filtrate precipitated with phosphomolybdic acid. After a considerable time, the precipitate containing all the alkaloïds (but not digitalin, picrotoxin, or salicin) is collected, washed with water to which some phosphomolybdic acid and nitric acid have been added, and then rinsed into a flask; baryta water is then added to alkaline reaction, and the flask connected by means of a condenser with a receiver containing hydrochloric acid, to which a Peligot's tube is fitted. On boiling the contents of the flask for some time, the ammonia and volatile bases pass over and combine with the hydrochloric acid in the receiver. The excess of baryta is thrown down from the residue in the distillation flask by means of carbonic acid, the liquid evaporated to dryness, the residue treated with strong alcohol, filtered, and the filtrate allowed to evaporate. If the alkaloïds in the residue are not sufficiently pure, they may be purified by one of the methods given in § 248 or § 249. As gelatin is also precipitated by phosphomolybdic acid, it should, if present, be separated from the impure alkaloïds by dissolving them in a little dilute hydrochloric acid, and submitting the solution to dialysis (§ 251).

4. Separation by Dialysis.

§ 251.

The method of dialysis devised by Graham, and described in § 8, may also be advantageously employed to effect the separation of alkaloïds from the contents of the stomach, intestines, &c. The material is acidified with hydrochloric acid, and placed in the dialyser. The alkaloïds, being crystalloïds, pass through the membrane, and, after twenty-four hours, are found, for the greater part, in the outer liquid;

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* See his "*Handbuch der gerichtlichen Chemie,*" second edition, p. 312 (Berlin: Hirschwald, 1881).

this solution is concentrated by evaporation, and the alkaloïds may then, according to circumstances, be either at once precipitated, or they may be purified by one of the methods described above.

5. METHOD USED BY Graham and A. W. Hofmann* TO DETECT STRYCHNINE IN BEER.

§ 252.

This method, which is based on the known fact that a solution of a salt of strychnine, when shaken with animal charcoal, gives up its strychnine to the charcoal, will undoubtedly be found applicable also for the detection of other alkaloïds. The process is conducted as follows:—

The aqueous neutral or feebly acid liquid to be examined for strychnine is shaken with animal charcoal (Graham and Hofmann employed 30 grams of it to the litre), allowed to remain for twelve to twenty-four hours, with occasional shaking, the charcoal filtered off, washed twice with water, and then boiled for half an hour with spirit of wine of 80–90 per cent. (120 c.c.), avoiding loss of alcohol by the use of a reflux condenser. The spirit, filtered hot from the charcoal, is distilled down, and a few drops of solution of potassa added to the residual aqueous liquid; this is then shaken with ether (or, better still, with chloroform), and the supernatant ether separated from the aqueous liquid. The ethereal liquid, on spontaneous evaporation, leaves the strychnine in a state of sufficient purity to admit of its further examination by reagents (see § 238).

Macadam† employed the same method in his numerous experiments to detect strychnine in the bodies of dead animals. He treated the comminuted matters with a dilute aqueous solution of oxalic acid in the cold, filtered through muslin, washed with water, heated to boiling, filtered while still warm from the coagulated albuminous matters, shook with charcoal, and proceeded in the manner just described. According to his statements, the residue left by the evaporation of the alcoholic solution was generally at once fit to be tested for strychnine. Where it was not so, he treated the residue again with solution of oxalic acid, and repeated the process with animal charcoal.

II.

General Plan of the Order in which Substances should be Analysed for Practice.

§ 253.

When the student is familiar with the behaviour of substances with reagents, and has also learnt practically, not only how different groups of bases and acids, but also the members of the same group, may be detected or separated by the use of these reagents, it is time to pass on from learning qualitative analysis to actual investigations. It is not

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* Chem. Soc. Quart. Journ., **5**, 173, and Ann. Chem. Pharm. **83**, 39.

† Pharm. Journ. Trans., **16**, 120, 160.

a matter of indifference to the student, in choosing substances to analyse for the sake of practice, whether he proceeds without any rule or order, or whether, on the contrary, his investigations are carried on systematically. Many ways, indeed, may lead to the goal, but one of them is always the shortest. A course is therefore here laid down for the guidance of the student which experience has shown will lead safely and speedily to the attainment of the object in view.

As long as analyses are made for the sake of practice only, it is absolutely necessary to know with certainty whether the results obtained are correct or not; in no other way can a full belief in the trustworthiness of the methods and confidence in his own powers be instilled into the student, or the conviction that an accurate and systematic following of the process given will lead to the desired result.

If there is no opportunity for this, it is better to prepare one's own mixtures, so that their constituents may be known, rather than to examine substances whose composition is entirely unknown. Let a beginner, for instance, analyse a mixture the composition of which is not accurately known by the person who gives it him; he will, without doubt, find one or more substances, but what becomes of his trust in the methods employed and in his own skill when, in reference to his results, he is merely told "very possibly," "very likely," it is so, instead of the teacher being able to say definitely whether the results are correct or not.

According to the individual powers and previous knowledge of the student, a greater or smaller number of analyses must be undertaken before he has confidence in his work. The following scheme contains a hundred numbers, which the author is convinced is, on an average, sufficient for obtaining a thorough knowledge of qualitative analysis if the substances be carefully chosen.

A. *From* 1 *to* 20.

Aqueous solutions of simple salts: such as sulphate of soda, nitrate of lime, chloride of copper, &c.

These investigations will serve to teach the student the method of analysing substances soluble in water and containing one base only. It is merely necessary to ascertain what base is present in solution; neither the detection of the acid, nor the proof of the absence of all other bases, is required.

B. *From* 21 *to* 50.

Salts, &c., containing one base and one acid in the solid state (in form of powder): for example, carbonate of baryta, borate of soda, phosphate of lime, arsenious acid, chloride of sodium, bitartrate of potassa, acetate of copper, sulphate of baryta, chloride of lead, &c.

These investigations will serve to teach the manner in which the preliminary examination of a solid substance should be made by heating in a tube or before the blowpipe; how it may be obtained in a proper form for analysis, that is, how to dissolve or decompose it; how to detect *one* metallic oxide, even if the substance is *insoluble* in water; and how to demonstrate the presence of *one* acid. The detection of both the base and the acid is required, but it is not necessary to prove that no other substances are present.

This portion of the course will cultivate habits of careful observation and forethought; the indications afforded by the preliminary examination, and the behaviour of the substance towards solvents, taken along with a knowledge of the base present, leading the student to infer what acids should be tested for.

C. *From* 51 *to* 65.

Aqueous or acid solutions of several bases. These investigations will serve to teach the student the method of separating and distinguishing several metallic oxides. The proof is also required that no other bases are present besides those detected, The acids are not tested for.

D. *From* 66 *to* 80.

Dry mixtures of every description. Some of the salts should be organic, others inorganic; some soluble in water or hydrochloric acid, others insoluble; for example, mixtures containing chloride of sodium, carbonate of lime, and oxide of copper:—phosphate of magnesia and ammonia, and arsenious acid;—tartrate of lime, oxalate of lime, and sulphate of baryta;—phosphate of soda, nitrate of ammonia, and acetate of potassa, &c.

These will serve to teach the student how to make a preliminary examination of mixtures of different substances and how to treat them with solvents; how to detect several acids in presence of each other; how to detect the bases in presence of phosphates, oxalates, &c., of the alkaline earths;—and they will serve as a general introduction to scientific and practical analysis. All the component parts must be detected, and the nature of the substance ascertained.

E. *From* 81 *to* 100.

Native compounds, commercial products, &c. Mineral and other waters, minerals of all kinds, soils, ashes of plants, potash, soda, alloys, colours, &c.

III.

Arrangement of the Results of the Analyses Performed for Practice.

§ 254.

The way in which the results of an analytical investigation is arranged is not a matter of indifference, as although different arrangements may all serve the same purpose more or less, some are better than others, as showing at a glance the whole course of the analysis and the results obtained.

The following examples will serve to illustrate the method which the author has found to be the most suitable and convenient.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, NOS. 1–20.

Colourless solution of neutral reaction.

Hydrochloric Acid	Sulphuretted Hydrogen	Sulphide of Ammonium	Carbonate of Ammonia and Chloride of Ammonium
no precipitate, absent AgO ,, Hg_2O	*no precipitate,* absent PbO ,, HgO ,, CuO ,, BiO_3 ,, CdO ,, AsO_3 ,, AsO_5 ,, SbO_3 ,, SnO_2 ,, SnO ,, AuO_3 ,, PtO_2 ,, Fe_2O_3	*no precipitate,* absent FeO ,, MnO ,, NiO ,, CoO ,, ZnO ,, Al_2O_3 ,, Cr_2O_3	*a white precipitate,* consequently either BaO, SrO, or CaO. No precipitate by solution of sulphate of lime, consequently **lime.** Confirm by oxalic acid.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, NOS. 21–50.

White powder, melting in its water of crystallization when heated, no further alteration afterwards. Heated before the blowpipe on charcoal, it becomes incandescent; microcosmic bead not coloured, clear when cold. Soluble in water, solution neutral.

HCl	HS	NH_4S	NH_4O,CO_2, and NH_4Cl	$2NaO,HO,PO_5$ and NH_4O
no precipitate.	*no precipitate.*	*no precipitate.*	*no precipitate.*	*a white precipitate,* consequently **magnesia.**

As the base is magnesia, and the substance is soluble in water, the acid radicle can only be chlorine, iodine, bromine, sulphuric acid, nitric acid, acetic acid, &c. The preliminary examination has proved the absence of the organic acids and of nitric acid.

Chloride of barium produces a white precipitate insoluble in hydrochloric acid, indicating sulphuric acid.

PLAN OF ARRANGING THE RESULTS OF EXPERIMENTS, NOS. 51–100.

A white powder, which becomes permanently yellow when heated in the glass tube, and does not form a sublimate, or emit visible fumes marked by acid or alkaline reaction. Before the blowpipe, it gives a malleable metallic globule, and yellow incrustation, with white border on cooling. It is insoluble in water, effervesces with hydrochloric acid, is incompletely soluble in that acid, but readily soluble in nitric acid to a colourless solution.

<table>
<tr>
<td rowspan="2">Hydrochloric Acid.
White precipitate, insoluble in excess, completely soluble in hot water; sulphuric acid producing a white precipitate in the solution: **lead.**</td>
<td rowspan="2">Sulphuretted Hydrogen.
Black precipitate, insoluble in sulphide of ammonium, readily soluble in nitric acid. Sulphuric acid produces a white precipitate: **lead**. Examination for copper, bismuth, and cadmium gives negative results.</td>
<td colspan="2">Sulphide of Ammonium.
White precipitate; ammonia, by itself, gives no precipitate: the precipitate dissolved in hydrochloric acid remains clear on adding to it soda in excess.</td>
<td rowspan="2">Carbonate of Ammonia.
White precipitate, soluble in hydrochloric acid. This solution when evaporated to dryness, the residue dissolved in water, and sulphate of lime added to the liquid, gives a white precipitate after some time: **strontia.** Precipitation and boiling with sulphate of ammonia, filtrate tested for lime with oxalic acid: results negative.</td>
<td rowspan="2">No fixed residue on evaporation.</td>
<td rowspan="2">Heated with hydrate of lime, it gives off no ammonia.</td>
</tr>
<tr>
<td>NH_4Cl
no precipitate.</td>
<td>HS
white precipitate: **zinc.**</td>
</tr>
</table>

Of the acids **carbonic acid** has already been found. Of the remaining acids the following cannot be present:—

The preliminary examination has proved the absence of organic acids and nitric acid.

Chloric acid cannot be present, because the substance is quite insoluble in water.

Sulphur and sulphuric acid not present, because the substance dissolves readily in nitric acid, forming a clear solution.

Chromic acid not present, as it dissolves in nitric acid and the solution is colourless.

Phosphoric acid, silicic acid, hydrofluoric acid, and oxalic acid not present, because the solution filtered from the sulphide of lead gives no precipitate on adding ammonia alone.

Boric acid might be present in trifling quantity; but the test for it gave a negative result.

Cyanogen might be present as cyanide of zinc, and chlorine, iodine, and bromine as basic compounds of lead. However, nitrate of silver gives no precipitate in the nitric acid solution; so they cannot be present.

The substance contains, therefore, $\left\{\begin{array}{l}\text{bases: oxide of lead, oxide of zinc, strontia.}\\ \text{acids: carbonic acid.}\end{array}\right.$

IV.

TABLE

OF THE

MORE FREQUENTLY OCCURRING FORMS AND
COMBINATIONS OF THE SUBSTANCES TREATED OF IN THE
PRESENT WORK,

ARRANGED
WITH ESPECIAL REGARD TO THE CLASS TO WHICH THEY RESPECTIVELY BELONG
ACCORDING TO THEIR SOLUBILITY

IN WATER, IN HYDROCHLORIC ACID, IN NITRIC ACID,
OR IN NITROHYDROCHLORIC ACID.

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§ 255.

PRELIMINARY REMARKS.

The class to which the several compounds respectively belong according to their solubility in water or acids (see § 179) is expressed by figures in the table, pp. 458–459. Thus 1 or I means a substance soluble in water; 2 or II a substance insoluble in water, but soluble in hydrochloric acid, nitric acid, or nitrohydrochloric acid; 3 or III a substance insoluble in water, in hydrochloric acid, and in nitric acid. For those substances which stand as it were on the limits between the various classes, the figures of the two classes in question are both given: thus I–II or 1–2 signifies a substance sparingly soluble in water, but soluble in hydrochloric acid or nitric acid; I–III or 1–3 a substance sparingly soluble in water, and of which the solubility is not notably increased by the addition of acids; and II–III or 2–3 a substance insoluble in water, and sparingly soluble in acids. Wherever the behaviour of a substance with hydrochloric acid is materially different from that which it exhibits with nitric acid, the difference is given in the notes.

The haloïd salts and sulphur compounds, for the sake of clearness, are placed in the columns of the corresponding oxides. Thus, mercurous chloride comes in the column headed Hg_2O (mercurous oxide), mercuric chloride in the column HgO, stannous sulphide in the column headed SnO, and stannic sulphide in that headed SnO_2, &c.

The officinal compounds and those more commonly occurring are indicated by Roman figures: thus, baryta is I, sulphate of baryta III, carbonate of lime II, &c.; on the other hand, those which are not officinal or technical, or are but seldom met with, are indicated by Arabic numerals: thus, borate of baryta is 2, bromide of barium 1, &c.

The salts given are, as a general rule, the neutral salts; the basic, acid, and double salts, if officinal or technical, are mentioned in the notes; the small figures placed near the corresponding neutral or simple salts refer to these.

TABLE OF THE SOLUBIL

	KO	NaO	NH_4O	BaO	SrO	CaO	MgO	Al_2O_3	Cr_2O_3	ZnO	MnO	NiO	CoO
	I	I	I	I	1	I-II	II	II	II & III	II	2_{17}	II	II
CrO_3	I_1	1	1	2	1-2	1-2	1		2	1	1	2	2
SO_3	$\mathrm{I}_{13\cdot15}$	I	$\mathrm{I}_{14\cdot20\cdot30}$	III	III	I-III	I	$\mathrm{I}_{13\cdot14}$	I & II_{15}	I	I	I	I
PO_5	1	I_8	$1_{8\cdot12}$	2	2	II_{11}	2_{12}	2	2	2	2	2	2
BO_3	1_2	1_9	1	2	2	2	1-2	2	2	2	2	2	2
$\overline{O}$	I_3	I	I	2	2	II	2	2	1-2	2	1-2	2	2
F	1	1	I	2-3	2-3	II-III	2-3	1	1	1-2	2	1-2	1-2
CO_2	I_4	I_{10}	I	II	II	II	II			II	II	II	II
SiO_2	I	I		2	2	2	2	2-3	2	2	2	2	2
Cl	I_{37}	I_{35}	$\mathrm{I}_{21\cdot38}$	I	I	I	I	1	I & III	I	I	I	I
Br	I	I	1	1	1	1	1	1	1 & 3	1	1	1	1
I	I	1	I	1	1	1	1	1	1	1	1	1	1
Cy	I	1	1	1-2	1	1	1		2	II	2	2-3	2-3
Cfy	I	1	1	1-2	1	1	1			II-III	2	3	3
Cfdy	I	1	1			1	1			2	3	3	3
S	I	I	I	I	1	$\mathrm{I\text{-}II}_{45}$	2	2	2·3	II_{16}	II	2_{18}	2_{19}
NO_5	I	I	I	I	I	1	1	1	1	1	1	1	I
ClO_5	I	1	1	1	I	1	1	1	1	1	1	1	1
$\overline{T}$	$\mathrm{I}_{\substack{5\cdot6\cdot7\\22\cdot46}}$	I_7	1_6	2	2	II	1-2	1	1	2	1-2	2	1
$\overline{Ci}$	1	1	1	2	2	1-2	1	1	1	1-2	2	1	1
$\overline{Ma}$	1	1	1	1 & 2	1	$1\text{-}2_{47}$	1	1		1	1		
$\overline{Su}$	1	1	1	1-2	1-2	1-2	1	1-2		1-2	1	1	1-2
$\overline{Bz}$	1	1	1	1		1	1				1		
$\overline{Sa}$	1	I	I	1-2	1-2	1-2	1						
$\overline{A}$	I	I	I	I	1	I	1	I	1	I	1	1	1
$\overline{Fo}$	1	1	1	1	1	1	1	1	1	1	1	1	1
AsO_3	I	1	1	2	2	2	2				2	2	2
ASo_5	I	I	I	2	2	2	2	2	2	2	2	2	2
	K_2O	Na_2O	$(NH_4)_2O$	BaO	SrO	CaO	MgO	Al_2O_3	Cr_2O_3	ZnO	MnO	NiO	CoO

NOTES TO TABLE OF SOLUBILITY.

1. Dichromate of potassa I.
2. Tartarized borax I.
3. Binoxalate of potassa I.
4. Bicarbonate of potassa I.
5. Bitartrate of potassa I.
6. Tartrate of ammonia and potassa I.
7. Tartrate of soda and potassa I.
8. Phosphate of soda and ammonia I.

F COMPOUNDS.

e$_2$O$_3$	AgO	PbO	Hg$_2$O	HgO	CuO	BiO$_3$	CdO	AuO$_3$	PtO$_2$	SnO	SnO$_2$	SbO$_3$	
II	2	II$_{24}$	II	II	II	2	2		2	2	2 & 3	II$_{42}$	
1	2	II-III	2	1-2	1	2	2			2		2	CrO_3
1	I-II	II-III	1-2	1$_{27}$	I$_{20}$	1	I		1	1		2	SO_3
II	2	2	2	2	2	2	2			2	2	1-2	P_2O_5
2	2	2			2	2	1 2			2			B_2O_3
2	2	2	2	2	2	2	2		1	2	1	2	$\bar{\text{O}}$
1	1	2		1-2	2	1	1-2			1	1	1	F
	2	II	2	2	II	2	2						CO_2
2		2			2		2						SiO_2
I$_{21}$	III	I-III	II-III	I$_{28}$	I	I-II$_{33}$	I	I$_{35}$	I$_{37 \cdot 38}$	I	I$_{40}$	I-II$_{43}$	Cl
1	3	1-3	2-3	1	1	1-2	I	1	1			1-2	Br
1	3	I II	II	II	1	2	I	2	3	1	1	1-2	I
	III	2		1	2		2	I	1				Cy
III	3	2			3					3	3		Cfy
1	3	1-2								3			Cfdy
2	2$_{23}$	II	II	II$_{29}$	2$_{31}$	2	II	2$_{36}$	2$_{39}$	2$_{41}$	2$_{41}$	II$_{44 \cdot 45}$	S
1	I	I	I$_{26}$	I	I	I$_{34}$	1		1				N_2O_5
1	1	1	1	1	1	1	1			1			Cl_2O_5
I$_{22}$	2	2	1-2	2	1	2	1-2			2		2$_{46}$	$\bar{\text{T}}$
I	2	2	2	1-2	1		2						$\overline{\text{Ci}}$
I	1-2	1-2	2	1-2	1					1	1		$\overline{\text{Ma}}$
2	2	2	2	1-2	1-2		1						$\overline{\text{Su}}$
2	1-2	2	2	1-2	2		1						$\overline{\text{Bz}}$
	1-2	1-2			1								$\overline{\text{Sa}}$
I	1	I$_{25}$	1-2	1	I$_{32}$	1	1			1	1		$\bar{\text{A}}$
I	1	1-2	1	1	1	1	1			1			$\overline{\text{Fo}}$
2	2	2	2	2	II							2	As_2O_3
2	2	2	2	2	2	2					2	2	As_2O_5
e$_2$O$_3$	Ag_2O	PbO	Hg_2O	HgO	CuO	Bi_2O_3	CdO	Au_2O_3	PtO_2	SnO	SnO_2	Sb_2O_3	

9. Biborate of soda I.
10. Bicarbonate of soda I.
11. Basic phosphate of lime II.
12. Phosphate of ammonia and magnesia II.
13. Sulphate of alumina and potassa I.
14. Sulphate of alumina and ammonia I.
15. Sulphate of chromium and potassa I.
16. Sulphide of zinc, as blende, readily in nitric acid, rather difficultly in hydrochloric acid on heating.

[OVER.

17. Peroxide of manganese readily in hydrochloric acid, not in nitric acid.
18. Sulphide of nickel is decomposed rather readily by nitric acid, with great difficulty by hydrochloric acid.
19. Sulphide of cobalt like sulphide of nickel.
20. Sulphate of protoxide of iron and ammonia I.
21. Ammonium ferric chloride I.
22. Tartrate of sesquioxide of iron and potassa I.
23. Sulphide of silver in nitric acid only.
24. Minium is converted by hydrochloric acid into chloride of lead, by nitric acid into protoxide, which dissolves in excess of acid, and into brown peroxide, which is insoluble in nitric acid.
25. Triacetate of lead I.
26. *Mercurious solubilis Hahnemanni* II.
27. Basic mercuric sulphate II.
28. Ammonio-mercuric chloride II.
29. Sulphide of mercury, not in hydrochloric acid, not in nitric acid, but in warm aqua regia.
30. Sulphate of copper and ammonia I.
31. Sulphide of copper, decomposed by hydrochloric acid with difficulty, readily by nitric acid.
32. Basic acetate of copper partially in water, completely in acids.
33. Basic chloride of bismuth II.
34. Basic nitrate of bismuth II.
35. Chloride of sodium and gold I.
36. Sulphide of gold, insoluble in hydrochloric acid or in nitric acid, but soluble in warm aqua regia.
37. Platinochloride of potassium I–III.
38. Platinochloride of ammonium I–III.
39. Sulphide of platinum, not in hydrochloric acid, scarcely in boiling nitric acid (if precipitated hot), but in warm aqua regia.
40. Chloride of ammonium and tin I.
41. Stannous and stannic sulphide are dissolved by warm hydrochloric acid, converted by nitric acid into stannic oxide, insoluble in excess of the acid. Sublimed stannic sulphide only in warm aqua regia.
42. Teroxide of antimony in hydrochloric acid, not in nitric acid.
43. Basic chloride of antimony II.
44. Sulphide of antimony is dissolved by hydrochloric acid, particularly on heating; decomposed but only very partially dissolved by nitric acid.
45. Sulphide of antimony and calcium I–II.
46. Tartrate of antimony and potassa I.
47. Acid malate of lime I.

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ERRATA.

Page 91, line 2 from top, *for* "but the presence of cyanide of potassium," *read* "but the presence of free carbonic acid, acid carbonates, or cyanide of potassium."
Page 137, line 16 from top, *for* "barium carbonate," *read* "carbonate of baryta."
Page 362, line 24 from bottom, *for* "arsenic acid," *read* "arsenious acid."

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