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ELEMENTARY INSTRUCTION

IN

CHEMICAL ANALYSIS,

BY

Karl

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CHEMICAL ASSISTANT IN THE LABORATORY OF THE
UNIVERSITY OF GIESSEN.

WITH

A PREFACE BY PROFESSOR LIEBIG.

EDITED BY

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PREFACE

BY PROFESSOR LIEBIG.

Dr. Fresenius conducts the course of elementary instruction, in mineral analysis, in the laboratory of the University of Giessen. During the two last sessions he has followed the method described in his work, entitled, "Elementary Instruction in Qualitative Chemical Analysis." This method I can confidently recommend from my own personal experience to all who are desirous of obtaining instruction in inorganic analysis, for its simplicity, usefulness, and the facility with which it may be apprehended.

I consider Dr. Fresenius' work extremely useful as an introduction to Professor H. Rose's excellent manual, and for adoption in institutions where practical chemistry is taught, but it is especially adapted to the use of Pharmaceutical Chemists.

Further, a number of experiments and discoveries have been recently made in our laboratory, which have enabled Dr. Fresenius to give many new and simplified methods of separating substances, which will render his work equally welcome to those who already are familiar with the larger works on inorganic analysis.

JUSTUS LIEBIG.

EDITOR'S PREFACE.

THIS work of Dr. Fresenius has already gone through two editions in Germany. The abundant opportunities enjoyed by its author of discovering the wants felt by students in entering upon the practice of chemical analysis, and his position in the school at Giessen, has enabled him to devise a method of study of the highest value. That it has received the approbation of the illustrious HEAD of that school, and the benefit of three years' practical experience under his immediate observation, must powerfully recommend it to the English student of chemistry. Whoever is desirous of obtaining the knowledge necessary to become a practical chemist, will be in no small degree indebted to Dr. Fresenius for the facilities thus afforded him. Every one who knows any thing of Giessen, will bear testimony to the rigid economy of time, and the resolute adoption of every improvement in method which characterise that school, and serve to accomplish the many chemists annually flocking there for the completion of their studies. The author, in his preface to the first edition, tells us that he was led to compose this volume upon perceiving that the larger works on chemical analysis, such as H. Rose's, Duflos', and others, although admirable in themselves, present great difficulties to beginners, which difficulties may be summed up under three heads; 1st, Too great copiousness and detail; 2d, The absence of explanations of the causes of phenomena, i. e. the *theory* of the operations and reactions; and 3d, The omission altogether of many substances of very frequent occurrence, especially in the operations of the pharmaceutist, such as the organic acids, &c.

In avoiding these objections to former works on chemical analysis, Dr. Fresenius, I think, is not chargeable with having fallen into the opposite extreme of being too concise or elementary.

The student may, perhaps, at first be disappointed in taking up this work, to find that there are no tables constructed to furnish him at a glance with all he is desirous to know of tests and reactions, and to save him, as he may think, trouble and time. But this has not arisen from oversight; the question of the advantage or disadvantage of tables to the student has been fully considered, and the author has decided—and the decision is borne out by the highest authorities—that such tables serve no really good purpose; they rather, on the contrary, supply but very superficial information, and satisfy the student before they have really informed him. The information contained in this work, like every other professing to teach a practical science, requires application and perseverance to attain; but if begun at the beginning, if the student will carefully go over the necessary preliminary facts, the examination of his tests, and the reaction of the simple bodies consecutively, and make himself master of this very simple and elementary part of the course, he will find few or no difficulties when entering upon the more elaborate, and—what might appear, without this preparation—complex and intricate processes of the second part, the analysis of compound bodies. It is altogether another question whether the student should or should not exercise himself and his memory by tabulating the results of his experiments as he proceeds; and to this question we reply in the affirmative: but it must be left to individuals to act in this, according to their own judgment, and their own feeling of its necessity.

In the preface to the Second Edition, Dr. Fresenius tells us that his work has met with much success, having been adopted in the Pharmaceutical Institution of Bonn, &c., as well as in the laboratory of Giessen; and that he has improved it by many corrections and additions.

For my own part, I may be allowed to observe that the English edition was undertaken by the express desire of Professor Liebig, who kindly recommended its being entrusted to my care. The author has supplied me with many corrections, and some additions, and the hope is shared by us in common that it will facilitate the study of analytical chemistry to the English student, and in every way serve to promote the interests of the science.

J. LLOYD BULLOCK.

22, *Conduit Street, Oct.* 1, 1843.

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DEFINITION, DESIGN, AND UTILITY OF QUALITATIVE CHEMICAL ANALYSIS, AND CONDITIONS WHEREON SUCCESSFUL STUDY OF THIS SCIENCE DEPENDS.

CHEMISTRY is that science which teaches us the knowledge of the elements of which our earth consists, their composition and decomposition, and, in general, their relation to each other. A special branch of this science is designated by the name of *analytical chemistry*, inasmuch as it has a definite object in view, viz., the analysis of compound bodies, and the determination of their constituent parts. If this determination of the constituent parts merely refers to their *nature*, the analysis is called *qualitative;* but if the *quantity* of every single element is to be ascertained, the analysis is called *quantitative.* The object of the first, therefore, is to exhibit the constituent parts of an unknown substance in forms *already known*, so that these new forms admit of safe inferences as to the presence of the single elements. The value of its method depends on two circumstances, viz. it must attain the object in view infallibly, and in the quickest possible manner. Whereas, it is the object of quantitative analysis, to exhibit those elements rendered manifest by qualitative investigation, in such forms as admit of an exact determination of their amount.

The ways and means by which these various objects are attained, differ, of course, materially from each other. The study of qualitative analysis must, therefore, be separated from that of quantitative analysis, and, as a matter of course, must precede it.

After having thus generally defined the meaning and objects of qualitative analysis, we must now shortly consider, in the first place, the preliminary information which qualifies students to cultivate this science successfully, the rank which it occupies in the department of chemistry, the objects to which it extends, the advantages derived from it; and, in the second place, the main points whereon its study is based, and the principal branches into which it is distributed.

In order to enter with any prospect of success upon qualitative experiments, the student must previously have acquired some knowledge of the chemical elements, and of their most important combinations, as well as of the principles of chemistry generally, together with a certain readiness in the apprehension of chemical processes. This practical art demands, moreover, strict order, great neatness, and a certain degree of skill in manipulations. If the pupil combines with these qualifications a habit, in all cases in which phenomena contrary to experience appear, of imputing, first the fault to himself, or rather to the absence of some condition or other indispensable to the success of the experiment,—and a firm reliance on the immutability of the laws of nature cannot fail to create this habit, —he possesses every requisite to render his study of analytical chemistry successful.

Now, although chemical analysis is based on general chemistry, and cannot be cultivated without some knowledge of the latter, yet, on the other hand, we must consider it also as a kind of *corner stone*, upon which the entire structure of this science rests; for it is almost of equal importance for all branches of theoretical, as well as of practical chemistry; and we need not expatiate here on the utility and advantages which the physician, the apothecary, the mineralogist, the rational farmer, the artisan, and many others, derive from it.

This alone would be a sufficient reason to recommend a thorough and diligent study of this science, if even its cultivation possessed none of those attractions which, I may safely assert, without fear of contradiction, it must of necessity possess for every one who devotes himself zealously and ardently to its acquisition. For the human mind is constantly striving for the attainment of truth; it delights in the solution of enigmas, and where do we meet with a greater variety of problems, of more or less difficult solution, than in the province of chemistry? But as a problem, an enigma, for which, after long pondering, we can find no solution, wearies and discourages the mind; so, in like manner, do all chemical investigations, if the object in view be not attained, if our results do not bear the stamp of truth,—of unquestionable certainty. A half-knowledge is therefore, in every province of science, but principally here, to be considered worse than no knowledge at all, and the student must, therefore, be especially warned against a mere *superficial* cultivation of chemical analysis.

A qualitative experiment may be made with a twofold view, viz. either, 1st, to prove that some definite body or other is or is not contained in a substance, e. g. lead in wine; or, 2d, to ascertain *all* the constituents of a chemical combination or mixture. Any substance whatever may, of course, become the object of chemical analysis.

In the present work, however, we purpose to confine ourselves to those elements and combinations which are employed in pharmacy, arts, and trades, and understand thereby the following:

I. Bases.

Potash, Soda, Ammonia, Barytes, Strontian, Lime, Magnesia, Alumina, Oxide of Chromium, Oxide of Zinc, Protoxide of Manganese, Protoxide of Cobalt, Oxide of Nickel, Protoxide of Iron, Peroxide of Iron, Oxide of Cadmium, Oxide of Lead, Oxide of Bismuth, Oxide of Copper, Oxide of Silver, Protoxide of Mercury, Peroxide of Mercury, Oxide of Platinum, Oxide of Gold, Protoxide of Tin, Peroxide of Tin, Oxide of Antimony.

II. Acids.

Sulphuric Acid, Nitric Acid, Phosphoric Acid, Arsenious Acid, Arsenic Acid, Boracic Acid, Carbonic Acid, Chromic Acid, Chloric Acid, Silicic Acid, Oxalic Acid, Tartaric Acid, Paratartaric Acid, Citric Acid, Malic Acid, Benzoic Acid, Succinic Acid, Acetic Acid, Formic Acid.

III. Salt-radicals, and non-metallic substances.

Chlorine, Iodine, Bromine, Cyanogen, Fluorine, Sulphur, Carbon.

The study of qualitative analysis depends principally on four points, viz. 1st, on the knowledge of *operations;* 2d, on that of *reagents and of their application;* 3d, on that of the *relation of bodies to reagents;* and 4th, on that of the *systematic course* to be pursued in every experiment.

Chemical analysis, therefore, requires not only theoretical knowledge, but also practical skill; and it is obvious that a mere speculative study of it can no more lead to success, than experimenting at random; but in order to obtain satisfactory results, theory and practice must be combined.

CHAPTER I.

OPERATIONS.

§ 1.

The operations of analytical and synthetical chemistry are essentially the same, modified however to a certain extent, according to the object we have in view, and the quantities upon which we operate.

The following are the principal operations employed in qualitative investigations.

§ 2.

1. SOLUTION.

The general meaning of "solution" is "the combination" of a gaseous, liquid, or solid substance, with a fluid, forming a homogeneous liquid. But we call the solution more properly *absorption* when the dissolved substance is gaseous; and when liquid, the term *mixture* or *intermixture* is more frequently made use of. The term solution, in its usual and more restricted sense, is confined to the perfect union of a solid substance with a fluid. The more minutely we divide the substance to be dissolved, the more we facilitate its solution. The liquid, by means of which the solution is effected, is called the *solvent*. We call the solution *chemical*, if this solvent forms a chemical combination with the substance dissolved; *simple*, if no definite combination takes place.

A *simple* solution contains the dissolved body in a free and unconnected state, and with all its original properties, except those dependent on its form and cohesion; and when it separates from the solvent in the same unaltered state, as soon as the latter is withdrawn. Common salt dissolved in water is a familiar instance of a simple solution. The salt here imparts its peculiar taste to the water, and on evaporating the latter, we re-obtain common salt in its original form. A simple solution is called *saturated* when the solvent has received as much as it can hold of the substance to be dissolved. But as fluids, on an average, dissolve larger quantities of a substance, the higher their temperature, the term saturated can only refer to a certain temperature; and it must be considered a rule, that elevation of temperature facilitates and accelerates simple solution.

A *chemical* solution contains the substance dissolved, not in the same state nor with the same properties as before; the dissolved body is no longer free, but intimately combined with the solvent, which latter has likewise lost its original properties; the result of this combination has been the formation of a new body, the solution, therefore, now manifests the properties of this newly-formed substance. A chemical solution, too, may certainly be accelerated by elevation of temperature, and this is indeed usually the case, as heat generally promotes the action of bodies upon each other. But the quantity of the dissolved body remains always the same, in proportion to a given quantity of the solvent, whatever may be the difference of temperature; their combining proportions are invariable, and independent of the gradations of temperature.

In chemical solution, the solvent and the body, on which it acts, have always opposite properties, and their tendency is mutually to neutralize these opposite properties. Further, solution ceases as soon as this tendency is satisfied; if we add more of the solid body it remains unaltered. The solution in this case also is called saturated, or more properly *neutralized*, and the point which denotes it to be completely so, is called the point of saturation or neutralization. The substances by means of which chemical solutions are effected, are, in most cases, either acids or alkalies. They all require, first, a simple solvent to be converted to the fluid state. When the opposite properties of acid and base have mutually neutralized each other, and the new combination has been formed, the real conversion into fluid form takes place, only, if the product of this new combination possesses the property of forming a simple solution with the liquid present: e. g. when an aqueous solution of acetic acid 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 thereby produced acetate of lead, in the water of the menstruum.

Crystallization and precipitation are the reverse of solution, as they have for their object the conversion of a fluid or dissolved substance into the solid state. As both depend on the same cause, viz. on the absence of a solvent, it is impossible to assign exact limits to either, and in many cases they merge into each other. We must, however, consider them separately, since they essentially differ, as well in their extreme forms, as, in most cases, in the special objects we purpose to attain by their application.

§ 3.

2. CRYSTALLIZATION.

We understand by the term crystallization, in a more general sense, every operation, every process in which bodies pass from a fluid to a solid state, assuming certain regular, determinate, geometrical figures. But, as these figures, which we call crystals, are the more regular, and consequently the more perfect, the more slowly the operation is carried on, we always connect with the term "crystallization," the accessary idea of a slow separation,—of a gradual conversion to the solid state. The formation of crystals depends on the regular arrangement of atoms; it can only take place if these atoms possess perfect freedom of motion, and thus, generally, only when a substance, from the fluid or gaseous, changes to the solid state. Those cases, in which it is sufficient merely to heat or to soften a solid body, to induce crystallization, must be considered as exceptions,—as, e. g. barley-sugar becoming white and opaque, or crystallizing, when moistened.

To induce crystallization, we must remove the causes of the fluid or gaseous form of a substance. These causes, are either—*heat alone*, e. g. in metals in fusion, or *solvents alone*, as in an aqueous solution of common salt; or *both combined*, as in a hot and saturated aqueous solution of nitre. In the first instance, we can obtain crystals only by cooling the substance we wish to crystallize; in the second, only by evaporating the menstruum; and in the third, by either of these means. The most frequently occurring cases of crystallization are those by means of cooling hot and saturated solutions. The liquors which remain after the separation of the crystals, are called mother waters. The term, *amorphous* bodies, is applied to such solid substances as have no crystalline form.

We cause crystallization to take place, generally, either to obtain the substance crystallized in a solid form, or to separate it from other substances dissolved in the same menstruum.

§ 4.

3. PRECIPITATION.

This operation differs from crystallization inasmuch as in precipitation the substance dissolved is converted to the solid state, not in a slow and gradual manner, but suddenly; it is a matter of perfect indifference, as regards the application of the term precipitation to the process, whether this substance is crystalline or amorphous; whether it gravitates to the bottom of the vessel, or whether it ascends or remains suspended in the liquid. We may cause precipitation to take place, either, 1st, by modifying the solvent;—thus sulphate of lime (gypsum) separates immediately from its solution in water, if this water, by the addition of alcohol, is converted into diluted alcohol; or 2d, by separating some substance insoluble in the menstruum;—thus, if ammonia be added to a solution of sulphate of alumina, the decomposition of this latter salt takes place, and alumina, not being soluble in water, is precipitated. Precipitation takes place also when, by the action of simple or compound chemical affinity, new combinations ensue which are insoluble in the menstruum; thus oxalate of lime precipitates on adding oxalic acid to a solution of acetate of lime; chromate of lead on mixing chromate of potash with nitrate of lead. In decompositions of this kind, induced by simple or compound affinity, one of the new combinations generally remains in solution, and the same is sometimes the case with the substance separated,—thus in the instances just mentioned, the sulphate of ammonia, the acetic acid, and the nitrate of potash, remain in solution. Cases may, however, happen, where both products precipitate, so that nothing remains in solution, e. g. when a solution of sulphate of magnesia is mixed with water of barytes; or a solution of sulphate of silver with chloride of barium.

Precipitation is applied to the same purposes as crystallization: either, 1st, to obtain a substance in a solid form; or 2d, to separate it from other substances dissolved in the same menstruum. But in qualitative analysis we employ this operation especially, in order to detect substances by the colour, and the properties and relations in general, which they exhibit when precipitated, either alone or in combination with other substances. The solid body separated by this process, is called *precipitate*, and the substance, which is the immediate cause of this separation, is termed the *precipitant*. For the sake of a more particular designation, we apply various terms to precipitates, according to their different nature; thus we distinguish crystalline, pulverulent, flocculent, curdy, gelatinous precipitates, &c. &c.

The term *turbid* is made use of, when a precipitate is in a state of such minute division, and so small in quantity, that its particles cannot be clearly distinguished, and that the fluid in which it is suspended merely appears troubled. We may generally promote the separation of a precipitate by strongly agitating the menstruum, as well as elevating its temperature. The vessels used for the purpose of precipitation, must, therefore, admit of either of these operations. In qualitative analysis we principally make use of tubes of thin glass, closed at the bottom, such as are usually called test-tubes, or test-cylinders. Beside the advantages just mentioned, they permit the experimentalist closely to inspect the whole process, as well as the colour of the liquids and precipitates, and to experimentalize with very small quantities.

Two different operations, according to circumstances, are employed in analysis, in order mechanically to separate a fluid from matter suspended therein, namely, "*filtration*," and "*decantation*."

§ 5.

4. FILTRATION.

We purify liquids, by means of this operation, in pouring the fluid from which we wish to remove the mechanically-suspended solid particles, on a filter, for which purpose we usually employ unsized paper, supported by a funnel; for an apparatus of this description allows the liquid to trickle through with ease; and, on the other hand, completely retains the solid particles. We use smooth filters and plaited filters: the former, in such cases where the defiltrated solid substance is to be made use of; the latter, when we merely wish to clear the solution. Smooth filters are produced by folding a circular paper doubly together, so that the folds form right angles. The preparation of plaited filters is more properly a matter for ocular demonstration than for description, In minute operations, care should be taken that the filters do not reach over the brim of the funnel. It is in most cases advisable to moisten the filter previous to use, because then, not only the filtration proceeds more rapidly, but the solid particles of the substances to be filtered are less liable to pass through the pores of the filter. The paper selected for the purpose of filtration, must be as free as possible from inorganic substances, especially iron and lime. It is advisable to have always two sorts on hand, one of greater density for the separation of very minute precipitates, and one of greater porosity for the spėedy separation of grosser particles. The funnels must be either of glass or of porcelain.

§ 6.

5. DECANTATION.

This operation is frequently made use of instead of filtration, if the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended. They in such cases speedily gravitate to the bottom, and are deposited there, so that it becomes easy, either to decant the supernatant liquid by simply inclining the vessel, or to remove it by means of a syphon.

In such cases where we employ these operations (filtration or decantation) in order to obtain the solid substance out of the liquid in which it is suspended, we must afterwards free this substance by repeated washing or rinsing from the liquid still adhering to it. This operation is termed *edulcoration* or *rinsing*. In order to edulcorate a precipitate collected on a filter, we most frequently make use of the syringe bottle,—a glass vessel, stopped with a perforated cork, into which a small glass tube is adapted, drawn out at the top into a fine point. If air be blown through this tube, into the flask, and, when the air is sufficiently compressed, the flask be reversed, so that the inner aperture of the tube comes under water, a minute stream of water is expelled, peculiarly adapted to the rinsing of precipitates.

There are four operations by means of which we separate volatile substances from less volatile or from fixed bodies, viz. EVAPORATION, DISTILLATION, ROASTING, and SUBLIMATION. The two former of these operations always refer to fluids, the two latter only to solids.

§ 7.

6. EVAPORATION.

This is one of the most frequently-employed operations. We have recourse to it when a volatile fluid is to be separated from another less volatile, or from a fixed substance, (either fluid or solid,) if by this separation we only intend to obtain this residuary substance, without heeding the evaporating substance. Thus, evaporation serves, for instance, to remove from a saline solution part of its water, in order to induce the salt to crystallize, or, also, to remove all the water from the solution of an uncrystallizable substance, so as to obtain this latter in a solid form, &c. &c. The evaporating water is entirely disregarded, in either of these cases, and the only object in view is to obtain in the former case a more concentrated fluid, and, in the latter, a dry substance. These objects are always attained by converting the fluid to be removed, into the gaseous state; in ordinary cases, therefore, by exposing it to heat; sometimes, also, by leaving the fluid for a certain time, in contact with the atmosphere, or in confined air, constantly kept dry by hygroscopic substances; or, in many cases, by placing the fluid in a rarified air, with the simultaneous application of hygroscopic substances. The heating process is conducted either over a free fire, (coal-fire or flame of spirits of wine,) or in the sand-bath, or by means of steam, (in the water-bath,) &c. &c. Concentrated sulphuric acid and slaked lime, and also chloride of calcium, are used as the cheapest and most efficient hygroscopic substances. The vessels used in evaporation are of porcelain, glass, platinum, or silver, and have usually the shape of a shallow basin.

§ 8.

7. DISTILLATION.

This operation has for its object the separation of a volatile liquid from a less volatile or fixed substance, either solid or fluid, and the recovery of the evaporating fluid. In order to attain this object, it is necessary to reconvert the liquid from the gaseous form in which it evaporated, into the fluid state. A distilling apparatus, therefore, consists of three parts, whether separated from each other or not, is quite indifferent. These three parts are,—1st, a vessel in which the liquid to be distilled is heated, and thus converted into vapour; 2d, an apparatus in which this vapour is cooled again or condensed, and thus reconverted to the fluid state; and 3d, a vessel which receives the distilled fluid. In distillation on a small scale, we generally employ small glass retorts and receivers, but in the distillation of large quantities, either a metallic apparatus,—a copper still with helmet, and condensing tube of pewter, or large glass retorts.

§ 9.

8. ROASTING.

Roasting is, in a certain measure, for solid bodies, what evaporation is for fluids; for the object to which we apply it is, (at least generally,) the separation of a volatile substance from a less volatile, or from a fixed body, merely for the purpose of purifying this latter residuary substance. Roasting always presupposes the application of a high temperature, and in this it differs from exsiccation. The form or state which the volatilized substance assumes on cooling, is a matter of perfect indifference as to the name of the operation.

This is the usual design in the application of roasting. In some instances, however, substances are heated merely for the purpose of modifying their state, without any volatilization taking place; e. g. in the conversion of oxide of chromium into its insoluble modification, &c. &c. Crucibles are the vessels made use of in roasting. In analytical experiments we select, according to the substances to be heated, either porcelain, or platinum, or silver crucibles. In operations on a large scale, we employ either hessian or black-lead crucibles. The necessary heat we obtain either from a coal-fire, or in experiments on a small scale, most usually by means of a Berzelius spirit-lamp.

§ 10.

9. SUBLIMATION

Is that operation, whereby solid bodies are converted into vapours by the application of heat, and condensed again by cooling, to a solid state; the substance thus volatilized and recondensed is called a sublimate. Sublimation is consequently a distillation of solid bodies. We generally employ this process for the separation of substances of different degrees of volatility. Its application is of the highest importance in analysis, for the detection of divers substances, e. g. of arsenic. The vessels used in sublimation are of various shapes, according to the different degrees of volatility of the substance we have to operate upon. In sublimation for analytical purposes we generally employ glass tubes closed at both ends.

§ 11.

10. SMELTING AND FLUXING.

We designate by the term "smelting," the conversion of a solid substance into a fluid form, by the application of heat, and apply this operation generally to the purpose either of combination or of decomposition of bodies. The term "fluxing" is applied to this process in such cases where a substance, either insoluble or difficult of solution in water and acids, is, by being fused with some other body, modified or decomposed in such a manner, that the former or its new-formed combinations, afterwards admit of solution in water or acids. We employ in analysis, according to circumstances, either porcelain, silver, or platina crucibles, for the purposes of these operations. If we are unable to produce the necessary degree of heat by means of a Berzelius spirit-lamp, the crucible containing the substance or substances to be fused, may be placed in a larger, hessian crucible, and this latter exposed to a charcoal or coke fire.

The application of fluxing is especially required in the analysis of the sulphates of alkaline earths, and of many silicates. The flux most commonly used is carbonate of soda, or carbonate of potash, or, better still, a mixture of both, in equal atomic proportions, (vide § 75.) In certain cases, carbonate of barytes is used instead of carbonate of soda or potash, (vide § 76.) But in either case the operation is conducted in platina crucibles.

We will here briefly lay down a few precautionary rules for the prevention of damage to the platinum vessels used in these operations. No substance, evolving chlorine, ought to be treated in platinum vessels; no nitrate of potash, caustic potash, metals, sulphur or sulphurets, should be fused in such vessels, nor ought easily deoxidizable metallic oxides, organic metallic salts, and phosphoric salts, to be heated therein when organic compounds are present. It is also detrimental to platinum crucibles; and especially to their covers, to expose them directly to a strong coal-fire, (i e. without shielding them in larger, hessian crucibles,) because silicide of platinum is easily formed, in such cases, by the influence of the ashes, and this renders the vessels brittle.

§ 12.

11. THE USE OF THE BLOW-PIPE.

The application of the blow-pipe is of the utmost importance in analytical chemistry. We have here to consider, first, the necessary apparatus; then, the manner of its application; and, lastly, the results of the operation.

A blow-pipe is a small instrument, usually made of brass. It was originally used by metallurgists for the purpose of soldering, whence it derived the name of soldering-pipe. It consists of three distinct parts: viz. 1st, a tube through which air is blown from the mouth; 2d, a small vessel into which this tube is ground air-tight; this vessel serves to collect and retain the moisture of the air blown into the tube; and 3d, a smaller tube, also closely fitted into this vessel, forming a right angle with the large tube, and having a very fine aperture at its anterior extremity. The blow-pipe serves to conduct a fine and continuous stream of air into the flame of a candle or lamp. Such a flame, under ordinary circumstances, presents to the eye three distinct parts; viz. 1st, a dark nucleus in the centre; 2d, a luminous part surrounding this nucleus; and 3d, a kind of mantle encircling the whole flame, and but feebly luminous. The dark nucleus is formed by the gases which the heat evolves from the fuel; these gases cannot burn, from want of oxygen. In the luminoussphere they come into contact with a certain quantity of oxygen, although insufficient for their complete combustion. The hydrogen of the carburetted hydrogen gases evolved, therefore, burns principally here, whilst the carbon separates in a state of intense white heat, and is thus the cause of the luminousness of this part. In the outer coat, the access of air is no longer limited, and all the gases not yet consumed, are consumed there. This part of the flame is the hottest. Oxidizable bodies, therefore, oxidize with the greatest possible rapidity when placed in it, as the conditions of oxidizement are here combined, viz. high temperature, and an unlimited supply of oxygen. This part of the flame is therefore called the oxydizing flame. But the contrary ensues when we place oxydized bodies having a tendency to yield up their oxygen, within the luminous part of the flame, i. e. these substances *lose* their oxygen, the carbon and the still unconsumed carburetted hydrogen withdraw it from them, and thus reduce them. The luminous part of the flame is therefore called the reducing flame. Now, if we conduct a fine stream of air into a flame, we have oxygen, not merely around the outward flame, but also in its interior part. Combustion takes place, therefore, in either part. But this air rushes with a certain vehemence into the flame, and carries forward the gases evolved, mixes intimately with them, and effects their combustion at a certain distance from the point of the blow-pipe. This spot is marked by a bluish light. It is the hottest of the whole flame, since the combustion is most complete there, owing to the intimate intermixture of the air with the gases. The luminous part of the flame being thus surrounded on all sides by very hot flames, its temperature also becomes exceedingly elevated, and this elevation of temperature is the principal object in the application of the blow-pipe; the hottest point is then, of course, somewhat before the aperture of the blow-pipe. In this reducing flame many bodies fuse with ease, which remain unaltered in a common flame. The heat of the oxidizing flame also is considerably increased by the blow-pipe, since it becomes more concentrated upon one point.

As *fuel* we use either an oil-lamp, or a wax candle, or a lamp fed with a solution of oil of turpentine in spirits of wine. A common spirit-lamp does not yield, in all cases, the requisite degree of heat.

The *blowing* is effected by the cheek-muscles alone, and not by the lungs. This way of blowing may easily be acquired by practising for some time to breathe gently, with puffed up cheeks. If by this means the student has succeeded so far as to be able to continue calmly breathing in this manner, even when holding the blow-pipe between his lips, nothing except a little practice will be required to enable him to produce a continuous, correct and steady flame.

The *supports* on which the substances to be examined are exposed to the flame of the blow-pipe, are usually either charcoal, platinum wire, or platinum plate. In the choice of charcoal for the purpose of blow-pipe experiments, we must especially look to its being thoroughly charred, because, if not so, it will split and throw off the substances placed on it. The substances to be examined are put into small conical cavities carved into the piece of charcoal by means of a pen-knife. We generally employ charcoal as a support, when we want to reduce a metallic oxide, or to test its substance as to its fusibility. If metals are volatile in the heat of the reducing flame, they evaporate partly or entirely during their reduction. But these metallic vapours reoxidize in their transit through the external flame.

Many of them have a peculiar colour, by means of which the metals may be detected. The platinum wire, as well as the platinum plate, should be selected rather thin. We generally make use of platinum wire when fusing bodies together, by means of fluxes, in order to ascertain their nature, by the colour and other properties of the button produced.

The blow-pipe flame is of especial importance in chemical experiments, because its effects yield immediate results. These are of two different kinds; either, 1st, we obtain merely a knowledge of the general properties of the body, and are consequently only enabled to determine the class to which it belongs, i. e. we ascertain whether it is a fixed, volatile, or fusible substance, &c. &c.; or, 2d, the phenomena we observe at once point out what special body we have before us. The phenomena in question, we shall have occasion to examine when we treat of the relation of various substances to reagents.

APPENDIX TO THE FIRST CHAPTER.

§ 13.

APPARATUS AND UTENSILS.

As the student cannot be supposed to know the apparatus, &c., necessary for chemical analysis, it may be well here to furnish him with a list of indispensable articles, and to point out the qualities they should possess, in order to guide him in their purchase.

1. A BERZELIUS SPIRIT-LAMP. The vessel containing the spirit of wine should be connected with the wick by means of a narrow tube, to avoid explosions;—the chimney should not be too narrow. The aperture through which the spirit of wine is poured should not be air-tight.

2. A LAMP-STAND with moveable rings and brackets.

3. A GLASS SPIRIT-LAMP with ground cover and brass wick-tube.

4. A **BRASS BLOW-PIPE** with a mouth-piece made of horn or bone, (vide § 12.) The longer tube may be about seven inches, slightly varying, of course, according to the visual distance of the individual; the length of the smaller tube ought to be about two inches. Both must be ground air-tight into the small vessel, which, as we have stated, (§ 12,) collects and retains the moisture of the air blown through the pipe. It is advisable to keep two small tubes at hand, one with a wider, and the other with a narrower opening.

5. A **PLATINUM CRUCIBLE** with ground cover; this should not be too deep, in proportion to its breadth.

6. A **PLATINUM SPATULA**; this ought not to be selected too thin, and must be as clean and even as possible, and about two inches long and one inch in breadth.

7. A **FEW PIECES OF PLATINUM WIRE**, of the size of lute-strings, varying in length from three to four inches, and twisted at both ends into a small loop. It is advisable to keep these wires in a small glass containing water.

8. A **STAND WITH FROM TWELVE TO TWENTY TEST TUBES.** The latter may vary from four to six or eight inches in length, and must be of different width. They should be made of thin white glass, and so well annealed, that they do not crack even if boiling water be poured into them. Their brim must be quite round, and slightly turned down; it ought to have no lip whatever, as the latter is not of the slightest use, and prevents the tube from being closely stopped with the finger.

9. **SEVERAL BEAKER GLASSES AND SMALL RETORTS** of thin, well-annealed glass.

10. **SEVERAL PORCELAIN EVAPORATING DISHES, AND A VARIETY OF SMALL PORCELAIN CRUCIBLES.** Those of the royal manufacture of Berlin are quite unexceptionable in shape as well as durability.

11. **SEVERAL GLASS FUNNELS** of various sizes. They must be inclined at an angle of sixty degrees, and ought to merge into their tube at a definite angle.

12. A **SYRINGE BOTTLE**, capable of holding from twelve to sixteen ounces of water, (vide § 5.)

13. **SEVERAL GLASS RODS AND VARIOUS GLASS TUBES.**

The latter may be bent, drawn out, &c., over a Berzelius spirit-lamp.

14. A selection of WATCH-GLASSES.

15. A small AGATE MORTAR.

16. Several small IRON SPOONS.

17. A pair of small PINCERS, with scissor-handles, the blades close together, and bent at their extremity at an obtuse angle.

These should be varnished.

CHAPTER II.

REAGENTS.

§ 14.

VARIOUS phenomena may manifest themselves during the decomposition or combination of bodies. 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 if they accompany only the combination or decomposition of two definite bodies, it becomes evident that by means of one of these bodies the presence of the other may be detected and proved: e. g. if we know that a white precipitate, of determinate properties, is formed on mixing barytes with sulphuric acid, there can be no difficulty in understanding that, if by adding barytes to any liquid we obtain a precipitate of these determinate properties, the conclusion must follow, that this liquid contains sulphuric acid.

Those substances which indicate the presence of other bodies, by somewhat striking phenomena, are called *reagents*, on account of their mutual action upon each other.

Reagents are divided into *general* and *special*, according to the object obtained by their application. By *general* reagents, we understand those by means of which we determine the class or group to which the substance under investigation belongs; and by *special* reagents those, by means of which we detect a *single* definite substance. It cannot be considered an objection to this classification, that the limits between these two divisions cannot be drawn with any degree of exactness. I suggest it only to induce the student to keep distinctly in view his precise object, i. e. whether a group is to be determined or a single substance.

The value of reagents depends on two circumstances: 1st, whether they are *characteristic;* and 2d, whether they are *sensible.* We call a reagent *characteristic,* if the alteration it produces by the detection of the substance, the presence of which (in mixture or combination) we wish to ascertain, is of so distinct a character as to admit of no erroneous conclusion. Thus, iron is a characteristic reagent for copper, protochloride of tin for mercury, because the phenomena thereby produced, such as the separation of metallic copper and of globular mercury, admit of no mistake. We call a reagent *sensible,* if its action is still clearly perceptible, although but a very small quantity of the substance to be detected may be present, e. g. the action of starch upon iodine. We need scarcely mention that reagents must in general be chemically pure; they must contain no foreign substance, but simply consist of their essential constituents, for their evidence cannot be relied upon if this be not the case. We must therefore make it a rule carefully to test reagents as to their purity, before we use them in experiments, no matter whether they be articles of our own production or of purchase. As a matter of course, in the instruction we shall give when treating of each reagent in particular, and of the mode of testing its purity, we cannot take cognizance of all those substances with which the reagent may, accidentally, have become mixed, but only of those, the presence of which is probable from the manner of its preparation.

One of the most common sources of mistakes in qualitative analysis, proceeds from missing the proper measure —the right quantity—in the addition of a reagent to a substance under examination. Such terms as "addition in excess," "supersaturation," &c., often induce novices erroneously to suppose that they cannot add too much of the reagent, and, to avoid using too small quantities, many fill a test cylinder with acid for the supersaturation of a few drops of an alkaline fluid, whilst yet every drop of acid added, after the neutralization point has once been reached, must be considered an excess of acid. But, on the other hand, an insufficient addition is just as much to be avoided as a too copious one, since a reagent in insufficient quantity often produces phenomena quite different from those manifested when added in excess: e. g. chloride of mercury, when treated with a small quantity of sulphuretted hydrogen, gives a white precipitate; but when treated with sulphuretted hydrogen in excess, the precipitate is black. Experience has, however, proved that the most common mistake beginners are liable to, and which renders their operations difficult and uncertain, is to add the reagents in too copious quantities. The reason why the experiment loses thereby in certainty, is clear, if we recollect that all the changes effected by reagents are perceptible only within certain limits, and that consequently they become less and less evident, and may the easier be overlooked the more we approach this point by diluting the fluid.

No definite rules can be given for avoiding this source of errors; a general rule may, however, be laid down, and this even is sufficient to point out the proper measure in all, or at least in most cases. It is simply this: let the student always, before the application of a reagent, well consider to what purpose he applies it, and what are the phenomena he intends to produce.

We divide reagents into two classes, according as the fluid state of substances, indispensable to the action of the reagents, is caused either by the application of heat, or by means of liquid solvents; viz. 1, *Reagents in the humid way*; and 2, *Reagents in the dry way*. For the sake of facility and simplicity, we subdivide these two classes as follows:—

A. REAGENTS IN THE HUMID WAY.

I. GENERAL REAGENTS.

a. Reagents principally used as SIMPLE SOLVENTS.

b. Reagents principally used as CHEMICAL SOLVENTS.

c. Reagents which serve especially to separate, or otherwise to characterise groups of substances.

II. SPECIAL REAGENTS.

a. Reagents which serve especially for the detection of the various BASES.

b. Reagents which are particularly applied to the detection of the various ACIDS.

B. REAGENTS IN THE DRY WAY.

I. FLUXES.

II. BLOW-PIPE REAGENTS.

A. REAGENTS IN THE HUMID WAY.

I. GENERAL REAGENTS.

a. Reagents principally used as simple solvents.

§ 15.

1. WATER. (H O.)

Preparation.—Pure water is obtained by distilling spring-water from a copper still, or from a glass retort. This distillation should not be carried beyond three-fourths of its quantity. Rain-water received in the open air may in most cases be substituted for distilled water.

Testing.—Distilled water must leave no residue on evaporation, and must not alter the colour of Georgina paper. Nitrate of silver, chloride of barium, oxalate of ammonia, and lime-water, should not disturb its transparency.

Uses.—We use water* chiefly as a simple solvent for a great variety of substances. It has, moreover, a *special* application for the decomposition of several neutral metallic salts, giving rise to the formation of soluble acid, and insoluble basic compounds; this is particularly the case with the salts of bismuth and the chloride of antimony.

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* In chemical experiments we never make use of any other but distilled water; whenever therefore the term "water" occurs in the present work, distilled water is meant.

§ 16.

2. ALCOHOL. ($C^4H_6O_2 = E, O + Aq.$)

Preparation.—Two sorts of alcohol are used in chemical analysis; 1st. spirit of wine of 0·83 or 0·84, (*spiritus vini rectificatissimus* of the shops;) and 2d, absolute alcohol. The latter may be obtained by distilling the former, with the addition of fused chloride of calcium.

Testing.—Pure alcohol must completely volatilize, and ought not to cause any empyreumatic smell when rubbed between the hands, nor should it redden litmus paper.

Uses.—Many substances are soluble in alcohol, others remain insoluble. It may, therefore, frequently be employed for the separation of the former from the latter, e. g. of chloride of strontium from chloride of barium. We use alcohol also to precipitate from their aqueous solutions such substances as are insoluble in alcohol, e. g. to precipitate malate of lime. We employ alcohol, moreover, in the production of various kinds of ether, especially of ascetic ether, (which is so particularly characterised by its agreeable odour.) Alcohol serves also for the detection of various substances which impart a characteristic tint to its flame, especially boracic acid, strontian, soda, and potash.

§ 17.

3. ETHER. ($C_4H_5O = E\,O.$)

Ether has but a very limited application in the analysis of inorganic bodies. We use it in fact only to detect and isolate bromine, (§ 100, *b.*) and for this purpose commercial officinal ether is sufficiently pure and strong.

b. Reagents which are principally used as chemical solvents.

§ 18.

1. HYDROCHLORIC ACID. ($Cl\,H.$)

Preparation.—A mixture of thirteen and a half parts of oil of vitriol and four parts of water, when cold, is poured upon eight parts of common salt contained in a retort; the neck of the retort is then somewhat raised, and the heat of the sand-bath applied to the latter, as long as gas passes over. The gas evolved is by means of a bent tube, transmitted through twelve parts of water, in a glass flask, which must be constantly kept cool. In order to prevent the gas from receding, the tube is only permitted to dip about one line into the water of the receiver. If the sulphuric acid contains nitric acid, the gas which passes over first, (and which in that case contains chlorine,) must be received separately. The hydrochloric acid thus produced is tested as to its specific gravity, and diluted with water until its specific gravity is 1·11 or 1·12.

Testing.—Hydrochloric acid, used for the purposes of chemical analysis, must be colourless and leave no residue upon evaporation, nor ought it to discolour indigo-solution, even when heated with it to boiling. Chloride of barium ought not to produce any precipitate of barytes, neither in the highly diluted acid, (sulphuric acid,) nor even after having been boiled with nitric acid, (sulphurous acid.) Sulphuretted hydrogen must leave it unaltered. Ferrocyanide of potassium must not cause any precipitate in it, nor even impart the slightest blue tinge to it, after neutralization with ammonia and subsequent addition of some acetic acid in excess.

Uses.—We employ hydrochloric acid as a chemical solvent for a very great variety of bodies, especially for oxides and peroxides (on the solution of which, chlorine is liberated,) and salts with weaker acids. A solution of this kind, always depends on the formation of a chloride soluble in water. Muriatic acid serves also as a *simple* solvent for many salts, e. g. the phosphates, borates, and oxalates of the alkaline earths. We use it, moreover, to expel weaker acids from their salts; e. g. carbonic acid, hydrosulphuric acid. It has also a *special* application in the detection and precipitation of oxyde of silver, protoxyde of mercury, and oxyde of lead, (vide infrâ,) as well as in the detection of free ammonia, by producing dense white fumes with it, dependent on the formation of sal ammoniac, in the air.

§ 19.

2. NITRIC ACID. $(NO_5.)$

Preparation.—The nitric acid of commerce almost invariably contains sulphuric acid and hydrochloric acid. In order to purify it for the purpose of chemical analysis, a solution of nitrate of silver is added to it, as long as any precipitate of chloride of silver is formed; this precipitate is allowed to settle, and the supernatant acid decanted into a retort, and distilled to within a small fraction of its whole amount. The distillate is then, if necessary, diluted with water till the acid has a specific gravity of 1·2.

Testing.—Pure nitric acid must be colourless, and, when evaporated on a platinum plate, leave no residue behind. Nitrate of barytes, or nitrate of silver, must not render it turbid. It is advisable to dilute the acid highly with water before the application of these reagents, since nitrates will be precipitated if this precaution be neglected.

Uses.—Nitric acid serves, in the first place, as a chemical solvent for metals, oxides, sulphurets, oxygen salts, &c. Its action on metals and sulphurets depends on the oxidation of these bodies, at the expense of part of its oxygen, and on the subsequent chemical solution of the thereby formed oxides, giving rise to the formation of nitrates. Most oxides dissolve in nitric acid, directly as nitrates, and the same is the case with most insoluble—(i. e. in water)—salts with weaker acids, the nitric acids expelling the latter. For many salts with stronger acids it is (like hydrochloric acid) used as a simple solvent, e. g. the phosphates of the alkaline earths. Nitric acid serves, moreover, as the most common means of oxidation; thus we use it, for instance, to convert protoxide of iron into peroxide, to decompose hydriodic acid and the iodides, &c.

§ 20.

NITRO-MURIATIC ACID. AQUA REGIA. $(NO_4+Cl.)$

Preparation.—One measure of pure nitric acid is mixed with from three to four measures of pure hydrochloric acid.

Uses.—Nitric acid and hydrochloric acid decompose each other in such a manner as to give rise to the formation of chlorine, hyponitric acid, and water. This decomposition ceases as soon as the liquid is saturated with chlorine, but it is resumed immediately, if this state of saturation is disturbed, by the application of heat, or by the chlorine combining with some other substance. Thus we have, in aqua regia, 1st, a continuous source of chlorine; and 2d, hyponitric acid, and consequently a combination which has the property of readily yielding oxygen. The mixture of those two substances renders aqua regia the most powerful solvent we possess for metals, (those excepted which form insoluble compounds, with chlorine.) We use aqua regia chiefly for the solution of gold and platinum, (both of which are insoluble in hydrochloric acid alone, as well as in nitric acid alone,) and for the decomposition of various sulphurets, e. g. cinnabar, &c.

§ 21.

4. ACETIC ACID. ($C_4H_3O_3 = \bar{A}$.)

Preparation.—Pure acetic acid is best obtained by rubbing ten parts of crystallized neutral acetate of lead together, with three parts of anhydrous sulphate of soda, pouring the mixture into a retort, adding a cooled mixture of two and a half parts of sulphuric acid, with an equal weight of water, and distilling to dryness, in a sand-bath. The receiver is best connected with the retort by means of a Liebig's condensing apparatus.

Testing.—Pure acetic acid must leave no residue upon evaporation. Sulphuretted hydrogen, and solution of silver and of barytes, must not precipitate it when diluted, solution of barytes not even when the acetic acid has been previously boiled with nitric acid. Indigo solution must not be discoloured on being heated with the acid, (vide § 101, *a.*)

Uses.—The application of acetic acid in qualitative analysis is chiefly based upon its possessing an unequal power of solution for different substances, so it serves, for instance, to distinguish oxalate of lime from phosphate of lime. We apply acetic acid also for the acidulation of liquids, when we wish to avoid the use of mineral acids.

§ 22.

5. CHLORIDE OF AMMONIUM. ($N H_4 Cl.$)

Muriate of Ammonia.

Preparation.—The sal ammoniac of commerce may generally be purified for the purposes of chemical analysis by simple recrystallization. If it contains iron, a small quantity of hydrosulphuret of ammonia must be added to the solution; the precipitate formed is allowed to settle, the solution filtered, and hydrochloric acid added to it until a feeble acid re-action manifests itself; the mixture then is boiled, filtered, saturated with ammonia, and crystallized. For use as a reagent, one part of the salt is dissolved in eight parts of water.

Testing.—Solution of sal ammoniac, when evaporated on a platinum plate, must leave a residue which completely volatilizes upon a higher degree of heat being applied. Hydrosulphuret of ammonia ought not to change it. Its reaction ought to be completely neutral.

Uses.—We employ sal ammoniac chiefly to keep in solution certain oxides, e. g. protoxide of manganese, magnesia, or certain salts, e. g. tartrate of lime, when other oxides or salts are precipitated by ammonia or by some other reagents. This application of sal ammoniac is based on the tendency of the ammoniacal salts to form double combinations with other salts. Sal ammoniac also serves to distinguish between precipitates possessed of similar properties, e. g. to distinguish the basic phosphate of magnesia and ammonia which is insoluble in sal ammoniac, from other precipitates of magnesia. We employ sal ammoniac besides to precipitate from their solutions, various substances soluble in potash, and insoluble in ammonia, e. g. alumina, oxide of chromium; for in this process the sal ammonia decomposes with the potash, and chloride of potassium, water, and ammonia are formed. Sal ammoniac is moreover specially used to precipitate platinum as ammonio chloride of platinum.

c. *Reagents which serve especially to separate or otherwise to characterize groups of substances.*

§ 23.

1. REAGENT PAPERS: α. BLUE LITMUS PAPER.

Preparation.—One part of commercial litmus is digested with six parts of water; the intensely blue liquid obtained is divided into two parts, and the free alkali contained in the one half saturated by stirring it repeatedly with a glass rod dipped into very dilute sulphuric acid, until the colour exhibits a shade of red; then the other blue half is added, the whole poured into a cup, and slips of fine unsized paper are dipped into this tincture. These slips are then suspended on threads for the purpose of drying. The colour of litmus paper must be uniform, and neither too light nor too dark.

Uses.—Litmus paper serves for the detection of free acids in liquids, since its blue colour becomes thereby changed into red. It must, however, be borne in mind, that it undergoes the same alteration by the neutral salts of most metallic oxides.

β. REDDENED LITMUS PAPER.

Preparation.—Blue litmus tincture is repeatedly stirred with a glass rod dipped into dilute sulphuric acid, until its colour has assumed a distinct shade of red. Slips of paper are then dipped into this tincture. They must be distinctly red when dry.[1]

Uses.—The blue colour of reddened litmus paper is restored by pure alkalies and alkaline earths, as well as by their sulphur combinations, by alkaline carbonates, and also by the soluble salts of several other weak acids, especially of boracic acid. It serves, therefore, for the detection of these substances in general.

γ. GEORGINA PAPER.

Preparation.—The violet coloured petals of *Georgina purpurea* are boiled in water or digested with spirits of wine, and slips of paper dipped into the tincture. Care should be taken to concentrate the liquor only to such a degree as to impart to the paper when dry, a fine violet-blue colour, which must not be too dark (deep.) A small quantity of ammonia is added to the tincture, if the colour is too red.

Uses.—Georgina paper is reddened by acids; alkalies impart a beautiful green tinge to it. It is, therefore, of very convenient application, as a substitute for the blue as well as the red litmus paper. It is of extreme susceptibility, if properly prepared, for acids as well as for alkalies. Concentrated solutions of caustic alkalies, colour it yellow by destroying its colouring matter.

3. TURMERIC PAPER.

Preparation.—One part of bruised turmeric-root is digested and heated with six parts of dilute spirit of wine; the tincture obtained is filtered, and slips of fine paper are dipped into it. Turmeric paper, when dry, must have a fine yellow colour.

Uses.—It serves in the same manner as reddened litmus paper and Georgina paper, for the detection of free alkalies, &c.; as they change its yellow colour into brown. It is not so susceptible as the other reagent papers, but the change of colour it produces is highly characteristic, and can be especially well perceived in several coloured liquids; we consequently cannot well dispense with turmeric paper. It must be borne in mind, when using it as a test, that, besides the substances mentioned above, (vide reddened litmus paper,) several other bodies, e. g. boracic acid, change its yellow colour into brown.

All reagent papers should be cut into slips, and kept in well-closed glass jars or small boxes.

§ 24.

2. SULPHURIC ACID. $(S\,O_3.)$

English sulphuric acid may always be used in qualitative analysis, provided it contains no arsenic, and has previously been freed from nitric acid, by boiling.*

Testing.—Pure sulphuric acid, when boiled with a small quantity of indigo solution, must not destroy its blue colour. When mixed with pure zinc and water, it must yield hydrogen, which, on being passed through a tube heated to redness, does not deposit the slightest crust of arsenic. (Compare § 93, *d.*)

Uses.—Sulphuric acid having to most bases a greater affinity than almost any other acid, is principally employed for the liberation and expulsion of other acids, especially of phosphoric, boracic, muriatic, nitric, and acetic acids. Sulphuric acid serves also for the liberation of iodine from the iodides. It oxidizes, in this process, the metals at the expense of its own oxygen, and is converted into sulphurous acid. Several substances which cannot exist in an anhydrous state (e. g. oxalic acid) are decomposed when brought into contact with concentrated sulphuric acid; this decomposition is caused by the great affinity which sulphuric acid has for water. The nature of the decomposed body may in such cases be determined by the liberated products of its decomposition. Sulphuric acid is, moreover, frequently used for the evolution of several gases, especially of hydrogen and sulphuretted hydrogen. It is, besides, especially employed for the detection and precipitation of barytes, strontian, and lead. The acid used for this purpose is diluted with four parts of water.

§ 25.

3. SULPHURETTED HYDROGEN. (HS.)

Preparation.—Mix intimately thirty-two parts of iron filings with twenty-one parts of sublimed sulphur, divide into small portions, and gradually project them into a crucible heated to redness, and before adding new portions, wait until the last are red-hot. After the entire mixture has thus been fused, the crucible is well covered, and al-

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* The sulphuric acid of commerce often contains lead, which renders it turbid when diluted; this may be removed by allowing the lead to subside, or by distillation.—Ed.

lowed to remain a short time longer exposed to the fire. The sulphuret of iron thus obtained is broken into lumps, when cool, covered with water, in an evolution bottle (*a*,) and concentrated sulphuric acid added by means of (through) a funnel tube (*b*.) The gas evolved is transmitted through some water (*c*.) for the purpose of purifying it.

Sulphuretted hydrogen water is prepared by conducting the gas obtained in the preceding process into water of the lowest possible temperature (*d*,) until it is saturated, consequently until the whole volume of the gas added in excess begins to escape completely unabsorbed. Sulphuretted hydrogen water must be kept in well-closed vessels, as it soon undergoes complete decomposition, if this precaution is neglected. It keeps very long if it is immediately after preparation put into little flasks, and these latter, being well corked, are placed in an inverted position into small vessels filled with water. Sulphuretted hydrogen water must be clear, possess the odour of the gas to a high degree, and yield a strong precipitate of sulphur, when treated with chloride of iron. It must not assume a blackish tinge upon the addition of ammonia.

Uses.—Sulphuretted hydrogen has a strong tendency to decompose with metallic oxides, forming water and sulphurets. As these latter are mostly insoluble in water, a decomposition of this kind is usually attended with precipitation of the metallic oxides from their solutions. The conditions under which these precipitations take place, differ in such a manner, that by altering them we are enabled to divide all precipitable metals into groups, (as we shall afterwards explain, vide § 26, *uses.*) Sulphuretted hydrogen is, therefore, an invaluable means for the division of metals into groups. Some of these sulphuret precipitates have so distinct a colour, that we are enabled thereby to determine the particular metals they contain. Sulphuretted hydrogen serves for the special detection of the following metals: tin, antimony, arsenic, cadmium, manganese, and zinc. For more ample information we refer the reader to the third chapter. From its property of being readily decomposed, sulphuretted hydrogen serves also as means of reduction for many substances; thus, for instance, salts of peroxide of iron are converted by it into salts of protoxide of iron, chromic acid is changed into chromic oxide, &c. Sulphur separates in these reductions, in the form of a white powder.

§ 26.

2. HYDROSULPHURET OF AMMONIA. (NH_4SHS.)

Preparation.—This liquid is formed by transmitting sulphuretted hydrogen through liquor of ammonia, to complete saturation, consequently till it no longer causes precipitation in a solution of sulphate of magnesia. The solution obtained must be kept in well-closed bottles, since contact with the atmosphere decomposes it.

Testing.—Hpdrosulphuret of ammonia is transparent at first, and yields no sulphur on being mixed with acids; in contact with the atmosphere it assumes a yellow tint caused by the formation of sulphuret of ammonium, in excess.. This yellow tinge, however, does not render the reagent useless. But it now yields sulphur when mixed with acids, and this ought to be overlooked in experiments. Hydrosulphuret of ammonia must be transparent, and when heated evaporate without residue: and, as already mentioned above, ought not to precipitate solution of magnesia.

Uses.—The arrangement into groups of the metallic oxides, precipitable by sulphuretted hydrogen, depends upon certain conditions indispensable to their precipitation. The presence of an alkali is one of these conditions—its absence is another; i. e. certain sulphurets precipitate only if the liquid is alkaline, because they are soluble in acids; others precipitate only if the liquid is acid, as they are soluble in alkaline sulphurets. Now, hydrosulphuret of ammonia may be considered as a reagent in which sulphuretted hydrogen acts in conjunction with ammonia. Here, we have, therefore, as well as those conditions which are necessary for the precipitation of the first-mentioned group, as also those conditions which prevent the precipitation of the other group of sulphurets, or cause their resolution, when those precipitated from acid solutions are digested with the reagent. For the purposes of this latter application, the hydrosulphuret of ammonia must, in certain cases, contain sulphur in excess. Besides the sulphurets the precipitation of which is effected by the joint action of sulphuretted hydrogen and of ammonia, the hydrosulphuret of ammonia by the sole action of its ammonia, precipitates oxide of chromium and alumina as hydrated oxides, and also such substances as are only dissolved by free acids, e. g. phosphate of lime, dissolved in hydrochloric acid, and this property of hydrosulphuret of ammonia must not be lost sight of in experiments.

§ 27.

SULPHURET OF POTASSIUM. (KS_5)

Preparation.—This reagent must not be kept in store, but prepared immediately previous to its application. It may be produced by boiling sulphur, in proper proportions, with solution of caustic potash.

Uses.—Sulphuret of potassium must be substituted for hydrosulphuret of ammonia, when sulphuret of copper is to be separated from sulphur combinations soluble in alkaline sulphurets, e. g. from sulphuret of tin, because the sulphuret of copper is not quite insoluble in hydrosulphuret of ammonia.

§ 28.

6. POTASH. (KO.)

Preparation.—One ounce of pure carbonate of potash

(§ 29) is dissolved in twelve ounces of water, the solution boiled in a clean iron pan, and whilst the liquid is kept constantly at a boiling point, hydrate of lime added in small portions until a portion of the fluid thus obtained, causes no longer any effervesence when filtered into hydrochloric acid. (The proportions used are, the hydrate of about one part of the caustic lime in two parts of carbonate of potash.) The pan is then taken off the fire. If the process has been conducted exactly according to the direction here given, the carbonate of lime which has been formed will quickly subside. When all the carbonate of lime has settled at the bottom of the vessel, the supernatant solution of potash may be filtered through bleached linen, and the filtrate obtained rapidly evaporated in a clean iron pan, or more properly in a silver basin, until four ounces only remain, which, consequently, will give a specific gravity of 1·33. Solution of potash is kept best in small bottles, shut in the manner of glass spirit-lamps by a ground-glass cover, in default of which a small slip of paper ought to be rolled around the glass stopper of a common bottle. If this precaution be neglected, it will be found impossible, after a short time, to take the stopper off.

Testing.—Pure solution of potash ought to be colourless. It must form no precipitate with chloride of barium nor with nitrate of silver, when supersaturated with nitric acid, during which latter operation a slight effervesence only ought to take place. It must leave no silicic acid behind, when after evaporation to dryness the residue is washed off with water. It ought not to be rendered turbid on being heated with an equal measure of solution of sal ammoniac.

Uses.—By means of its great affinity for acids, potash decomposes the salts of most bases, and precipitates therefore from their solutions all those salts which are insoluble in water. Many of these oxides are dissolved by potash in excess, e g. alumina, oxide of chromium, oxide of lead; others are not, e. g. oxide of iron, oxide of bismuth, &c. Potash thus furnishes us with a means of separating the former oxides from the latter. Potash, besides, dissolves many salts, (e. g. chromate of lead,) sulphurets a. s. o., and thus enables us as well to separate as to distinguish them from other substances. Many of the precipitates produced by potash exhibit particular colour or other characteristic properties, as, e. g. suboxide of manganese, suboxide of iron, suboxide of mercury, and by means of these colours or properties we may detect the nature of the metals they contain. Potash expels ammonia from its salts, and thus enables us to detect the latter substance by its odour, its reaction on vegetable colours, &c.

§ 29.

7. CARBONATE OF POTASH. ($KO\ CO_2$.)

Preparation.—Pure carbonate of potash, for chemical purposes, is prepared by calcining purified bitartrate of potash in an iron pan, to complete carbonization; the residue is then boiled with water; the solution thus obtained is purified by filtration and evaporated to dryness, in a clean iron pan; towards the latter end of this process the mass must be constantly stirred. The residuary dry salt is kept in a well-closed bottle. For use, one part of it is dissolved in five parts of water.

Testing.—Pure carbonate of potash must be perfectly white. Its solution, when supersaturated with nitric acid, must not be rendered turbid by chloride of barium nor by nitrate of silver; and, when supersaturated with hydrochloric acid and evaporated to dryness, must leave no residue (silica) when redissolved in water.

Uses.—Carbonate of potash precipitates all bases, with the exception of the alkalies, most of them as carbonates, but also a few as oxides. Those bases which are soluble in water, as bicarbonates, are only on boiling completely precipitated from their acid solutions. Many of the precipitates produced by carbonate of potash exhibit particular colours, and may therefore serve for the detection of the various metals. The solution of carbonate of potash is moreover employed for the decomposition of many insoluble salts with metallic bases, or bases of the alkaline earths, especially of those with organic acids. For these salts, on being boiled with carbonate of potash, are converted into carbonates, whilst the acids combine with the potash, forming soluble salts. Carbonate of potash is also used to saturate free acids, in order to obtain them in combination with potash as salts, and is, moreover, *especially* used to precipitate platinum from solutions containing hydrochloric acid.

§ 30.

8. AMMONIA. (NH_4O.)

Preparation.—Pure liquor of ammonia is prepared by slaking four parts of quick lime with one and one-third part of water, mixing this hydrate of lime, in a glass retort, with five parts of sal ammoniac reduced to powder, and cautiously adding as much water as will cause the powder to form into lumps when agitated. The retort is then placed in a sand-bath, and brought into connexion with two gas conducting tubes, joined to each other in the middle by means of a rinsing apparatus, containing only a small quantity of water, such as has been described in the preparation of sulphuretted hydrogen, (vide § 25, and engraving.) The absorbing receiver should contain ten parts of water. This receiver is placed in a vessel filled with cold water; heat is then applied to the retort. The evolution of gas immediately ensues. The heat is continued until no more bubbles appear, and the stopper of the retort is then quickly taken off, to prevent the fluid from receding. The liquor of ammonia contained in the washing apparatus is impure, but that in the receiver is pure; it contains about sixteen per cent. of ammonia, and thus has a specific gravity of 0.93. It is kept in phials closed with glass stoppers.

Testing.—Pure liquor of ammonia must be colourless, and upon evaporation on a watch-glass not leave the slightest residue. It ought not to render lime-water turbid, (carbonic acid,) and after supersaturation with nitric acid, must not be rendered turbid by solution of barytes nor by solution of nitrate of silver, nor be coloured by sulphuretted hydrogen.

Uses.—Ammonia is one of the most frequently used reagents. It is especially applied for the saturation of acid liquids, for the precipitation of a great many metallic oxides and earths, as well as for their separation from each other, as many of them are dissolved as ammoniacal double salts, by ammonia in excess; such as the oxides of zinc, cadmium, silver, copper, nickel, and cobalt, whilst others remain insoluble in free ammonia. The precipitates, as well as their ammoniacal solutions, sometimes exhibit a very distinct and peculiar colour, by means of which we may at once detect the metals which they contain.

Many oxides which are precipitated by ammonia from neutral solutions, are not precipitated from acid solutions, their precipitation being here *prevented* by the formation of an ammoniacal salt. (Compare Chloride of Ammonium, § 22.)

§ 31.

9. CARBONATE OF AMMONIA. (NH_4O, CO_2.)

Preparation.—We use, for the purposes of chemical analysis, sesquicarbonate of ammonia, which must be entirely free from any smell of animal oil, (such as is prepared on a large scale, by the sublimation of sal ammoniac and chalk.) The outer and inner surface of the mass must be carefully scraped off; and then one part of the salt dissolved in a mixture of four parts of water, and one part of caustic liquor of ammonia.

Testing.—Pure carbonate of ammonia must completely evaporate, and after supersaturation with nitric acid, neither be coloured nor precipitated by solution of barytes, nor by solution of silver, nor by sulphuretted hydrogen.

Uses.—Carbonate of ammonia precipitates most metallic oxides and earths, like carbonate of potash. The complete precipitation of many of them takes place only on boiling. Several of the precipitated combinations redissolve again when this reagent is added in excess. Carbonate of ammonia dissolves many hydrates of oxides in a like manner, and thus enables us to separate them from others which are insoluble. This power of solution depends upon the tendency of ammoniacal salts, to form soluble double salts, indecomposible by free ammonia as well as by carbonate of ammonia.

Like caustic ammonia, and for the same reason, carbonate of ammonia does not precipitate from acid solutions, many oxides which it precipitates from neutral solutions. (§ 30.) We apply carbonate of ammonia, in chemical analysis, especially for the precipitation of barytes, of strontian and of lime, and for the separation of these substances from magnesia, as the latter is not precipitated in the presence of ammoniacal salts.

§ 32.

10. CHLORIDE OF BARIUM. ($Ba, Cl.$)

Preparation.—Six parts of heavy spar reduced to a fine powder are mixed with one part of powdered charcoal and one and a half part of flour; this mixture is put into a hessian crucible and exposed to the strongest possible red heat. The fused mass is rubbed to powder when cool; about nine-tenths of the powder are boiled with four times their weight of water, and hydrochloric acid is added, until no more effervescence of sulphuretted hydrogen takes place, and the liquid manifests an acid reaction. Then the last tenth of the fused mixture is added, and the boiling still continued for some time. The alkaline liquid is then filtered and chrystallized. The crystals when dry are digested and washed with alcohol, redissolved in water, and again crystallized. For use, one part of the crystals is dissolved in ten parts of water.

Testing.—Pure chloride of barium must not affect vegetable colours, nor ought its solution to be altered by sulphuretted hydrogen, nor by hydrosulphuret of ammonia. Pure sulphuric acid must precipitate every fixed particle from it, so that the filtered liquid leaves not the slightest residue when evaporated on a platinum plate.

Uses.—Barytes forms, with many acids, soluble salts; with others, insoluble combinations. This property of barytes affords us a means of distinguishing the former acids, which are not precipitated by chloride of barium, from the latter in saline solutions which are precipitated by chloride of barium. These barytes precipitates manifest to other substances (acids) relations differing from each other. Consequently, by subjecting them to the action of such bodies, we may subdivide again the group of precipitable acids, and even directly detect certain acids. Chloride of barium is one of our most important reagents, on account of its application, distinguishing one group of acids from another, and especially as a means of detecting sulphuric acid.

§ 33.

11. NITRATE OF BARYTES. $(Ba\,O, NO_5.)$

Preparation.—A dilute solution of chloride of barium is boiled, and carbonate of ammonia added as long as it causes any precipitate, and further until the liquid manifests an alkaline reaction. The carbonate of barytes obtained by this process is carefully washed, and then dissolved in hot and dilute nitric acid, until the liquid no longer manifests any acid reaction. The solution is then filtered, and afterwards crystallized by evaporation. One part of the crystallized salt is dissolved in ten parts of water, for use. The tests as to its purity are the same as in chloride of barium. Nitrate of silver must not render its solution turbid.

Uses.—Nitrate of barytes is analogous in its action to chloride of barium, and may be substituted for this latter substance, when we wish to avoid the formation of a chloride in a liquid.

§ 34.

CHLORIDE OF CALCIUM. $(Ca\,Cl.)$

Preparations.—Chalk is added to hot and dilute hydrochloric acid, until all acid reaction ceases; the solution is then filtered, and, with the addition of some ammonia, allowed to stand a few hours, at a moderate heat. It is then filtered again; the filtrate is heated to boiling, and carbonate of ammonia added until all the lime is precipitated; the thus obtained carbonate of lime is carefully washed. A mixture of one part of pure hydrochloric acid, with five parts of water, is then heated and the washed carbonate of lime added to complete neutralization; the solution is then boiled up several times, filtered, and preserved for use.

Testing.—Solution of chloride of calcium must be perfectly neutral, and neither be tinged nor precipitated by hydrosulphuret of ammonia; nor ought it to evolve ammonia when mixed with potash or with hydrate of lime.

Use.—Chloride of calcium is, in its action and application, analogous to chloride of barium. For, as the latter is applied to divide the *inorganic* acids into groups, so the former serves for the same purpose with the *organic* acids, since it precipitates some of them, whilst it forms soluble combinations with others. And, as is the case with the barytes precipitates, the different conditions under which the various insoluble lime salts are precipitated, furnish us with means for a more special classification of these acids.

§ 35.

13. NITRATE OF SILVER. ($Ag\,O, NO_5$.)

Preparation.—To obtain nitrate of silver in a state of purity, silver alloyed with copper, as e. g. a piece of standard coin, is dissolved in nitric acid. The solution is evaporated to dryness, and the residue fused in a small porcelain crucible, at a moderate heat, by means of a spirit-lamp, till all the nitrate of copper is decomposed, i. e. till the green colour of the salt has completely vanished, even in the portions adhering to the upper sides of the crucible, and a portion dissolved in water becomes no longer blue when ammonia in excess is added. The mass, when cooled, is boiled with water, filtered, and crystallized. One part of the crystals is dissolved in twenty parts of water, for use. The oxide of copper remaining after the solution of the fused mass, always contains some silver, to remove which the residue is dissolved in nitric acid, and the silver precipitated from the solution, as chloride of silver.

Testing.—Nitrate of silver may be considered pure, if the fixed part of its solution is completely precipitated by dilute hydrochloric acid, so that the fluid filtered from the chloride of silver leaves no residue upon evaporation on a watch-glass, and is neither precipitated nor tinged by sulphuretted hydrogen.

Use.—Oxide of silver forms, with many acids, soluble, with others, insoluble combinations; nitrate of silver may therefore be used, like chloride of barium, for the classification of acids into groups.

Most of the insoluble silver combinations are soluble in dilute nitric acid, chloride, iodide, bromide, and cyanide of silver excepted. Nitrate of silver is, therefore, an excellent means for distinguishing and separating the hydracids corresponding to the last-named silver combinations from all other acids. Nitrate of silver is also of great importance for the detection of individual acids, as many of the silver precipitates exhibit a particular colour, (chromate, and arseniate of silver, for example,) or a particular relation to other reagents, or peculiar properties, on being heated, e. g. formiate of silver.

§ 36.

14. PERCHLORIDE OF IRON. ($Fe_2 Cl_3$.)

Preparation.—To obtain pure perchloride of iron, two parts of hydrochloric acid, diluted with from six to eight parts of water, are heated with an excess of small iron nails free from rust, until the evolution of hydrogen ceases; the solution is then decanted, mixed with one part of hydrochloric acid, boiled in a very capacious vessel, and, whilst boiling, nitric acid in small portions cautiously and gradually added, till a further addition produces no longer any effervescence; i. e. till no more red vapours of nitrous acid appear, and solution of ferricyanide of potassium (§ 42) no longer tinges the mixture blue. A small excess of nitric acid does no harm whatever. The solution obtained is then diluted with water, boiled, ammonia added to alkaline reaction, and the produced precipitate of hydrated peroxide of iron well washed with hot water, and when still moist, added to a heated mixture of 272 parts of hydrochloric acid, and ten parts of water, till the last portions are not dissolved, even on continued heating. The solution is then filtered, and kept for use.

Testing.—Solution of perchloride of iron, for the purposes of chemical analysis, must not contain acid in excess; a portion of it must, therefore, when stirred with a small rod dipped in ammonia, yield a precipitate, which is not re-dissolved on shaking the vessel. Ferricyanide of potassium must not impart a blue tinge to it.

Use.—Chloride of iron serves for a further classification of those organic acids which are not precipitated by chloride of calcium, as it produces precipitates with benzoic and succinic salts, whilst it leaves acetic and formic salts in solution. The neutral salts which these latter acids form with peroxide of iron, dissolve in water, imparting an intensely red colour to the latter; chloride of iron affords, therefore, a useful means for their detection. (Vide § 98, *a* 7, for its application for the decomposition of phosphates of the alkaline earths, to which purpose it is exceedingly well adapted.) Chloride of iron serves also for the detection of ferrocyanide of hydrogen, producing Prussian blue with this substance.

II.—SPECIAL REAGENTS IN THE HUMID WAY.

a. Reagents which serve especially for the detection or separation of individual bases.

§ 37.

1. SULPHATE OF POTASH. (KO, SO_3.)

Preparation.—The sulphate of potash of commerce is purified by re-crystallization, and one part of the pure salt is dissolved in twelve parts of water, for use.

Uses.—Sulphate of potash precipitates from solutions of barytes and strontian the sulphates of the oxides, which are insoluble in water. It serves, therefore, for their detection and separation. It also produces a precipitate in very highly concentrated solutions of lime, but, in most cases, only after the lapse of some time. It does not precipitate dilute solution of lime. The action of sulphate of potash being analogous to that of dilute sulphuric acid, it is in many cases preferable to the latter reagent, since it does not disturb the neutrality of the solution.

§ 38.

2. PHOSPHATE OF SODA. ($2NaO, PO_5$.)

Preparation.—To obtain this reagent pure, dilute commercial phosphoric acid is heated, and solution of carbonate of soda added, till all effervescence ceases, and the liquid manifests a feeble alkaline reaction. The liquid is then filtered, evaporated, and crystallized. The crystals are dried, triturated with a portion of charcoal and flour, and the entire mass strongly heated in a hessian crucible. The heated mass is then boiled with water, filtered, and crystallized. One part of the salt obtained is dissolved in ten parts of water, for use. This solution must not become turbid on being heated with ammonia. The precipitates produced by the addition of solution of barytes, and of silver, must completely redissolve on the addition of dilute nitric acid.

Uses.—Phosphate of soda precipitates the alkaline earths, and all metallic oxides, by double affinity. It serves in the course of analysis, after the separation of the heavy metallic oxides, as a test for alkaline earths in general; and, after the separation of barytes, strontian, and lime, with simultaneous addition of ammonia, as a test for the detection of magnesia, which precipitates under these circumstances as basic phosphate of ammonia and magnesia.

§ 39.

3. NEUTRAL CHROMATE OF POTASH. ($KO, Cr\,O_3$.)

Preparation.—To obtain this reagent pure, the commercial bichromate of potash is dissolved in water, and carbonate of potash added, till the solution manifests a feeble alkaline reaction. The liquid, which is now of a yellow colour, is then crystallized. The crystals are well washed and re-dissolved in water, in the proportion of one part of the crystals to ten parts of water. The solution must be neutral.

Uses.—Chromate of potash decomposes, by double affinity, most of the soluble metallic salts. The precipitated metallic chromates are, for the most part, very difficult of solution, and often manifest such peculiar colourings, that the metals they contain may be easily detected. We use chromate of potash principally as a test for lead.

§ 40.

4. CYANIDE OF POTASSIUM. (KCy.)

Preparation.—To obtain this reagent pure, commercial ferrocyanate of potash is gently heated and stirred, till its water of crystallization is completely expelled; it is then pounded, and eight parts of the dry powder are mixed with three parts of perfectly dry carbonate of potash. This mixture is put into a crucible heated to redness, and the latter well closed and kept at a bright red heat, till the mass is in a state of clear and calm fusion. The fused cyanide of potassium is then poured into a heated porcelain basin; this must be done cautiously, in order to prevent the passing over of any particles of the iron which, in a highly-divided state, has separated from the mass, and subsided to the bottom of the crucible. The thus obtained cyanide of potassium is exceedingly well adapted for application in analysis, although it contains cyanate of potash. It must be perfectly white. One part is dissolved in four parts of cold water.

Uses.—Cyanide of potassium (containing cyanate of potash) produces in the solutions of most metallic salts in water, insoluble precipitates of cyanides, oxides, or carbonates. The former of these precipitates are soluble in cyanide of potassium; they may, therefore, by a further addition of the reagent, be separated from the oxides, &c. which are insoluble in cyanide of potassium. Some of the cyanides of metals always dissolve as cyanides combined with cyanides of potassium, even if free prussic acid be present; others combine with cyanogen, forming new radicals, and as such, combined with potassium, remain in solution. Cobalti-cyanide of potassium, ferro and ferri-cyanide of potassium, are the most common combinations of the latter kind. They differ from the double cyanogen compounds of the former description, especially inasmuch as dilute acids do not separate from them the cyanides of metals. Those metals forming such combinations may, therefore, by syanide of potassium, be separated from all those metals, the cyanides of which are precipitated by acids, from their solutions in cyanide of potassium. This reagent has a highly important special application, in analysis, for the separation of nickel from cobalt.

§ 41.

5. FERROCYANIDE OF POTASSIUM.

$$(C_6 N_3 Fe + 2 K = Cfy + 2 K.)$$

Preparation.—Commercial ferrocyanide of potassium is sufficiently pure for the purposes of chemical analysis. One part is dissolved in twelve parts of water, for use.

Uses.—Ferrocyanide forms with most metals combinations insoluble in water, and often very peculiarly coloured. These combinations occur 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, show the most characteristic colourings of all; and ferrocyanide of potassium is, therefore, especially applied as a reagent for the detection of oxide of copper and peroxide of iron.

§ 42.

6. FERRICYANIDE OF POTASSIUM.

$$(C_{12} N_6 Fe + 3 K = 2 Cfy + 3 K.)$$

Preparation.—This reagent is obtained by transmitting chlorine gas through a solution of one part of ferrocyanide of potassium in ten parts of water, till a portion of the fluid, when added to a solution of perchloride of iron, no longer produces a blue precipitate, or even a blue tinge. The solution is then concentrated by evaporation, and some carbonate of potash added, until a feeble alkaline reaction becomes manifest. The liquid is then filtered, and allowed to cool. The crystals obtained are of a magnificent red colour. One part is dissolved in ten parts of water, for use. The solution, as already remarked, must neither produce a blue precipitate nor a blue tinge, when added to solution of perchloride of iron.

Uses.—Ferricyanide of potassium decomposes with solutions of metallic oxides, in the same manner as ferrocyanide of potassium. Of all ferricyanides of metals, ferricyanide of iron is peculiarly characterized by its colour, and we apply, therefore, ferricyanide of potassium especially as a reagent for protoxide of iron. And for this purpose it may very well be prepared extempore, by gradually adding nitric acid to a solution of ferrocyanide of potassium, till a portion of the mixture no longer imparts a blue colour to a solution of chloride of iron. All elevation of temperature must be avoided in this process, and the vessel ought to be agitated whilst the nitric acid is added.

§ 43.

7. HYDROFLUO SILICIC ACID. ($3\,HF+2\,Si\,F_3$.)

Preparation.—This reagent is obtained in the following manner: equal parts of fluor spar and sand, in powder, are mixed in a glass retort, with six parts of English sulphuric acid; the opening of the retort is closed with a perforated cork, into which one end of a double-limbed tube is fitted air tight. The exit limb must reach to the bottom of a flat-bottomed glass jar, and its extremity be covered with a column of mercury, to the extent of a few lines; this glass-jar receiver contains four parts of water. A disengagement of the fluo-silicic gas immediately takes place, even without the application of heat; a gentle heat by the sand-bath is, however, required to aid the operation. Every bubble of gas, as it ascends through the mercury, produces a precipitate of hydrate of silicic acid. One equivalent of every three equivalents of the fluoride of silicon is decomposed in this process, and combines with three equivalents of water, forming silicic acid which precipitates, and hydrofluoric acid, which combines with the two remaining equivalents of the fluoride of silicon, forming hydrofluo silicic acid. The precipitated hydrate of silicic acid renders the liquid gelatinous, and it is on this account that the aperture of the exit tube must be placed under mercury, for it would speedily be choked if this precaution were neglected. It sometimes happens in the course, and especially towards the end, of the operation, that the gas forms complete tubes or channels of silica in the gelatinous liquid, through which it gains the surface without decomposition, if they are not broken from time to time [illegible]irring. When the disengagement of gas has ceased [illegible] gelatinous mass is poured on a piece of linen, and the fluid squeezed through. The liquid obtained is then filtered, and kept for use. The hydrofluo-silicic acid, mixed with two parts of water, produces no precipitate in the solution of salts of strontian.

Uses.—Bases decompose with hydrofluo-silicic acid, forming water, and metallic fluo-silicates. Many of these combinations are soluble, others insoluble; the latter may, therefore, by means of this reagent, be distinguished from the former. In the course of analysis it is only applied for the detection of barytes.

§ 44.

8. OXALIC ACID. ($2\,CO + O = C_2\,O_3 = \bar{O}$.)

Preparation.—This acid is prepared by pouring upon one part of starch, contained in a porcelain basin, five parts of nitric acid, of 1.42, diluted with two parts of water, and applying a gentle heat, till no more nitrous gas is evolved. The liquid is then filtered and crystallized; the crystals obtained are drained and purified by a second crystallization. Oxalic acid must be preserved in the form of a powder, as it soon decomposes in solution. Pure oxalic acid, when boiled with a small quantity of solution of indigo, does not discolour the latter.

Uses.—Oxalic acid combines with many bases, forming salts insoluble in water; it may, therefore, be used to precipitate these bases. Many of the oxalates insoluble in water, are easily dissolved by an excess of oxalic acid, whilst others dissolve with difficulty in the same menstruum. This relation affords us, therefore, a means of distinguishing the precipitated bases from each other. As all oxalates insoluble in water are soluble in stronger acids, (hydrochloric acid, nitric acid,) a complete precipitation by oxalic acid ensues, in most cases, only when the liberated acid is saturated by an alkali. In analysis, oxalic acid is of great importance for the detection and precipitation of lime.

§ 45.

9. OXALATE OF AMMONIA. $(NH_4+O, \bar{O}.)$

Preparation.—This reagent is prepared by dissolving oxalic acid in water, adding ammonia till a feeble alkaline reaction takes place, and crystallising. One part of the salt is dissolved in twenty-four parts of water, for use.

Uses.—Oxalate of ammonia is conveniently employed instead of oxalic acid and ammonia. It possesses this advantage over the free acid, that its solution does not decompose on keeping.

§ 46.

10. TARTARIC ACID. $(C_8 H_4 O_{10} = \bar{T}.)$

The tartaric acid of commerce is sufficiently pure for the purposes of analysis.* It is best preserved in powder, since it decomposes with the formation of a white film when kept in solution for some time.

Uses.—The addition of tartaric acid to solutions of iron, manganese, chromium, alumina, cobalt, and many other metals, prevents their precipitation by alkalies, by the formation of double tartrates indecomposible by alkalies. Tartaric acid may, therefore be employed to separate these metals from others, the precipitation of which it does not prevent. Tartaric acid forms with potash, but not with soda, a bi-salt difficult of solution; it is, therefore, one of the best means of distinguishing potash from soda.

§ 47.

11. BITARTRATE OF POTASH. $(KO, HO, \bar{T}.)$

The cream of tartar of commerce is sufficiently pure for the purposes of qualitative analysis. It should be preserved in powder.

Uses.—Many metals dissolve in hot solution of tartar, forming double tartrates; others do not. The former may, therefore, by means of this reagent, be separated from the

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* In cases where commercial salts are mentioned, well-defined crystals should be selected.—ED.

latt[illegible]analysis, tartar is employed in certain cases to sepa[illegible]xide of antimony from oxide of tin.

§ 48.

12. ACETATE OF BARYTES. ($BaO, \bar{A}$.)

Preparation.—This reagent is obtained in the same manner as nitrate of barytes, (vide § 33,) substituting, of course, acetic acid for the nitric acid. It may conveniently be preserved in a dry state, as it is but of rare application.

Uses.—The acetate of barytes is employed to convert sulphates into acetates, (especially sulphate of magnesia, and the alkaline sulphates). As these acetates are converted by heat into carbonates, and as carbonate of magnesia is insoluble, whilst the alkaline carbonates are soluble in water, acetate of barytes indirectly serves to separate magnesia from the alkalies.

§ 49

13. CAUSTIC BARYTES. (BaO.)

Preparation.—To prepare this reagent, one part of sulphuret of barium is boiled with twenty parts of water; copper scales are then added in excess to the solution, whilst boiling, till a filtered portion of the liquid ceases to blacken a solution of acetate of lead. The solution is then filtered, while still hot, and as much water added as will prevent any considerable portion of the hydrate of barytes in solution from crystallizing on cooling. The sa[illegible] water of barytes obtained is kept in well-closed [illegible]. Should it contain a small quantity of copper, some sulphuretted hydrogen must be cautiously added, and the liquid filtered from the precipitated sulphuret of copper.

Uses.—Caustic barytes is analogous in its ac[illegible] potash, i. e. it precipitates, as a strong base, from s[illegible] solutions, those metallic oxides and earths which are insoluble in water. In analysis, we apply this reagent only for the precipitation of magnesia. For this purpose a solution of sulphuret of barium may equally well be employed, inasmuch as (as is generally the case) it contains caustic barytes. Water of barytes may also, like the various salts of barytes, of which we have alre[illegible]ted, be used to precipitate those acids which for[illegible]luble combinations with barytes; we generally employ it thus only for the detection of carbonic acid.

§ 50.

14. PROTOCHLORIDE OF TIN. ($Sn\,Cl.$)

Preparation.—To obtain this reagent, English tin is reduced to powder, by being fused in an iron spoon, then taken from the fire and rubbed in a mortar till it has re-assumed the solid state. This powder is then, for some length of time, boiled with concentrated hydrochloric acid in a glass vessel; (care must always be taken that the mixture contains tin in excess;) the solution is diluted with four times its quantity of water, slightly acidulated with hydrochloric acid, and filtered. The clear solution is kept in a small closed bottle, containing small pieces of metallic tin. If this latter precaution be neglected, the reagent soon becomes useless, the protochloride being converted into perchloride of tin.

Testing.—Pure protochloride of tin, when mixed with perchloride of mercury, immediately produces a white precipitate of protochloride of mercury; it yields a dark brown precipitate with sulphuretted hydrogen, and is neither precipitated nor disturbed by sulphuric acid.

Uses.—The great tendency which protochloride of tin has to absorb oxygen, and thus to form peroxide of tin, or [illegible] perchloride of tin, as the oxide at the moment of its [illegible]ion, unites with the free hydrochloric acid present, [illegible]rs it one of the most powerful means of reduction. We employ it, in analysis, for the detection of gold, for which purpose it must first be mixed with some nitric acid, [illegible] the application of heat; we also use it to detect [illegible]presence of mercury.

§ 51.

15. CHLORIDE OF GOLD. ($Au\,Cl_3$.)

Preparation.—To obtain this reagent, fine shreds of gold, which may be alloyed either with silver or with copper, are drenched, in a small retort, with aqua regia in excess, and a gentle heat is applied till no more gold is dissolved. If the gold was alloyed with copper, which is detected by the brown red precipitate produced by ferrocyanide of potassium, in a portion of the solution diluted with water, the gold solution containing copper is mixed with sulphate of iron in excess. The gold becomes reduced, and separates as a fine brownish black powder; it is then washed in a small retort, re-dissolved in aqua regia, the solution evaporated to dryness in the water-bath, and the residue dissolved in thirty parts of water. If the gold is alloyed with silver, the latter metal remains undissolved as chloride of silver when treated with aqua regia. In this case, the first solution is evaporated to dryness, and the residue dissolved for use.

Uses.—Chloride of gold has a great tendency to yield its chlorine to other substances; it, therefore, easily converts protochlorides into perchlorides, protoxides into peroxides and perchlorides, &c. These oxidations usually manifest themselves by the precipitation of pure metallic gold, in the shape of a blackish brown powder. In analysis, chloride of gold serves only for the detection of protoxide of tin, as it produces a purple colour or precipitate in solutions containing this substance. (Vide infra.)

§ 52.

16. CHLORIDE OF PLATINUM. ($Pt\ Cl_2$.)

Preparation.—To obtain this reagent, platinum in powder is boiled with nitric acid, for the purpose of purification, and then, in a retort with narrow neck, drenched with concentrated hydrochloric acid, and some nitric acid; a gentle heat is applied, and, from time to time, some nitric acid added, until all the platinum is dissolved. The solution is, with the addition of hydrochloric acid, evaporated to dryness by a water-bath, and the residue dissolved in ten parts of water.

Uses.—Chloride of platinum forms very sparingly soluble double salts, with chloride of potassium and hydrochlorate of ammonia, whilst it enters into no such combinations with chloride of sodium. It serves, therefore, to detect ammonia and potash, and is, indeed, for the latter substance, nearly the most susceptible reagent we possess.

§ 53.

17. ZINC. (Zn.)

Pure, sublimed zinc, is selected for the purposes of chemical analysis; it must especially be free from arsenic. The method described in § 24 may be employed as a test to detect the presence of any trace of this latter substance. The pure zinc should be fused, and a portion of it gradually dropped into a large vessel, containing water; the remainder should be poured into wooden moulds, coated with chalk, for the purpose of casting it into little cylinders.

Uses.—Zinc precipitates many metals in their metallic state, by depriving them of their oxygen and acid, owing to the great affinity it possesses for oxygen, and its oxide for acids. As the precipitated metals vary in colour, form, &c., zinc may serve as well for their detection and distinction from each other, as for their precipitation. We employ it especially for the precipitation of antimony and of tin. Zinc is also frequently used for the production of hydrogen.

§ 54.

18. IRON. (Fe.)

Iron, like zinc, reduces many metals, and precipitates them in a pure state. We employ it especially for the detection of copper, which is precipitated on it with its characteristic colour. All clean surfaces of iron, such as knife-blades, needles, pieces of wire, &c., are well adapted to this purpose.

§ 55.

19. COPPER. (Cu.)

We employ copper exclusively for the reduction of mercury, which precipitates thereon as a white coating, which shines with silvery lustre when rubbed. Any copper coin scoured with fine sand, in fact, any clean copper surface, may be employed for this purpose.

b. Special reagents which are particularly employed for the detection and separation of acids.

§ 56.

1. ACETATE OF POTASH. ($KO, \bar{A}$.)

Preparation.—This reagent is obtained by dissolving one part of pure carbonate of potash in two parts of water, heating the solution and exactly saturating with acetic acid.

Uses.—Every salt of potash may serve to produce a precipitate of tartar, and, therefore, to detect tartaric acid. But the acetate of potash is peculiarly adapted for this purpose, as the precipitated tartar is insoluble in the liberated acetic acid. As this test is rarely employed, it is best to prepare it when needed.

§ 57.

2. CAUSTIC LIME. ($Ca. O.$)

Newly prepared hydrate of lime is agitated and digested for some time in cold distilled water, allowed to settle, and the clear fluid decanted and kept in well-closed bottles. Lime-water must impart a bright green tinge to Georgina paper, and yield with carbonate of potash no inconsiderable precipitate. It becomes useless as soon as it no longer manifests these properties, which soon takes place when it is exposed to the access of air. Besides lime-water, hydrate of lime also ought to be kept at hand.

Uses.—Lime forms with some acids insoluble, with others, soluble salts. Lime-water may, therefore, be employed to distinguish these acids from each other, as it precipitates the former whilst it yields no precipitate with the latter. Many of the precipitable acids are precipitated only under certain conditions, as e. g. on boiling, (citric acid ;) and it is therefore easy to distinguish them from each other by altering these conditions. We employ lime-water especially for the detection of carbonic acid, and to distinguish from each other paratartaric acid, tartaric acid, and citric acid. Hydrate of lime serves, like caustic potash, to liberate ammonia, and is in many cases preferable to the latter reagent.

§ 58.

3. SULPHATE OF LIME. (CaO, SO_3.)

Preparation.—To obtain this reagent, a concentrated solution of chloride of calcium is mixed with dilute sulphuric acid; the precipitate produced is well washed, digested, and for some time agitated with water, then allowed to settle, and the clear fluid decanted and kept for use.

Uses.—Sulphate of lime serves for the further subdivision of those acids which are precipitable by chloride of calcium, as, owing to its difficult solubility, a few acids only of that group (oxalic acid, paratartaric acid,) cause precipitates in its solution. The solution of sulphate of lime serves, moreover, as a reagent for bases, viz., to distinguish barytes, strontian, and lime from each other. For, of course, it cannot precipitate the latter, whilst it behaves with solutions of barytes and of strontian, in the same manner as highly dilute sulphuric acid, i. e. it precipitates barytes immediately, and strontian only after the lapse of some time.

§ 59.

4. CHLORIDE OF MAGNESIUM. ($Mg. Cl.$)

Preparation.—Chloride of magnesium is prepared by heating a mixture of one part of hydrochloric acid and two and a half parts of water, and adding basic carbonate of magnesia, (magnesiæ carbonas of the shops,) till the liquid ceases to manifest any acid reaction. The solution is once more boiled up, filtered, and kept for use. Sulphate of magnesia may, in most cases, be substituted for chloride of magnesium.

Uses.—Chloride of magnesium almost exclusively serves for the detection of phosphoric acid, as it precipitates from the aqueous solutions of phosphates, with presence of ammonia, a double salt, (basic phosphate of magnesia and ammonia,) which is almost insoluble and highly characteristic in its properties. Chloride of magnesium is, moreover, employed as a test of the purity of hydrosulphuret of ammonia. (Vide § 26.)

§ 60.

5. PROTO-SULPHATE OF IRON. ($Fe\,O, SO_3$.)

Preparation.—To obtain this reagent, a quantity of iron nails, (free from rust,) in excess, is heated with dilute sulphuric acid till no more hydrogen is evolved; the solution is then filtered, and after the addition of a few drops of dilute sulphuric acid, left to cool. Crystals are immediately obtained, if the solution was sufficiently concentrated, but if more dilute, evaporation must be had recourse to. The crystals are washed with water slightly acidulated with sulphuric acid, dried and preserved.

Uses.—Proto-sulphate of iron has a great disposition to change to persulphate of iron, i. e. to absorb oxygen. It acts, therefore, as a powerful means of reduction. We employ it especially for the reduction of nitric acid, from which it separates nitric oxide, by depriving it of three atoms of oxygen. As this decomposition is attended with the formation of a characteristic, intensely brownish-black coloured combination of nitric oxide with undecomposed protosulphate of iron, this reaction is particularly characteristic and susceptible for the detection of nitric acid. Protosulphate of iron serves, moreover, for the detection of ferricyanide of hydrogen, with which it produces a kind of Prussian blue, and for the detection of gold, which it precipitates from its solutions in its metallic state.

NEUTRAL ACETATE OF LEAD.

§ 61.

6. SOLUTION OF MAGNETIC OXIDE OF IRON (FERROSO-FERRIC OXIDE.) (FeO, Fe_2O_3.)

This reagent is not kept on hand, but prepared, when needed, by mixing solution of protosulphate of iron with some perchloride of iron. ($Fe\,O, SO + Fe_2Cl$.) It serves for the detection of hydrocyanic acid, which, when previously combined with alkalies, yields with it a precipitate of sesquiferrocyanide of iron (Prussian blue.)

§ 62.

7. OXIDE OF LEAD. ($Pb\ O$.)

Oxide of lead is employed for the detection of free acetic acid, as it forms with no other acid than this, a soluble combination with an alkaline reaction. Finely-washed litharge answers this purpose sufficiently well. (Compare § 104, *a*.)

§ 63.

8. NEUTRAL ACETATE OF LEAD. ($Pb\ O, \bar{A}$.)

The better sorts of commercial acetate of lead are sufficiently pure for the purposes of chemical analysis. One part is dissolved in ten parts of water for use.

Uses.—Oxide of lead forms, with a great many acids, combinations which are insoluble in water, and are distinguished by their colour, or by some characteristic property. The acetate of lead produces, therefore, precipitates in solutions of these acids or their salts, and essentially contributes to ascertain and characterize several of them. Thus, in particular, chromate of lead is distinguished by its yellow colour, phosphate of lead by its peculiar relation before the blow-pipe, and malate of lead by its easy fusibility.

§ 64.

BASIC ACETATE OF LEAD. ($3PbO, \bar{A}$)

Preparation.—This reagent is obtained by drenching in a well-stopped bottle, seven parts of finely-washed litharge, and six parts of neutral acetate of lead, with thirty parts of water, and allowing them to stand at a moderate heat, shaking it from time to time, till the sediment in it has become perfectly white. The clear fluid is then decanted and preserved in a well-stopped bottle. This acetate of lead is unfit for use, if it contains copper, which is detected by the blue colour it exhibits on the addition of ammonia. It must, in this case, be purified by digesting it with metallic lead, till all the copper is precipitated.

Uses.—The basic acetate of lead, like the neutral acetate, precipitates those acids which form insoluble combinations with oxide of lead, and, indeed, all those soluble in acetic acid, more completely than the former reagent. We employ it in analysis especially for the detection of sulphuretted hydrogen, for which substance it is nearly the most susceptible reagent. It serves, moreover, to neutralize free acids, in cases where it is desirable to avoid the application of an alkali, e. g. to render solutions of highly acid nitrate of bismuth precipitable by water.

§ 65.

HYDRATED OXIDE OF BISMUTH. ($Bi\,O+HO$.)

Preparation.—Bismuth reduced to a gross powder is projected into pure nitric acid, 1, 2 as long as solution takes place; this process may be promoted by the application of a gentle heat. The solution obtained is diluted with about an equal quantity of warm water, (slightly acidified with nitric acid,) and then filtered; the filtrate is mixed with from ten to twenty parts of water, and ammonia added to the milky fluid, till the reaction becomes perceptibly alkaline; the solution is then heated, and the precipitate obtained washed, first, by decanting the supernatant liquid, and then rinsing the precipitate upon a filter, and afterwards drying it between some sheets of blotting-paper, at a moderate heat.

Uses.—The oxide of bismuth, when boiled with alkaline solutions of sulphurets, decomposes with the latter, giving rise to the formation of metallic oxides, (corresponding with the various degrees of sulphuration of the sulphurets,) and of sulphuret of bismuth. It affords us, therefore, especially, a very proper and efficient means, to convert the sulphuret or bisulphuret of arsenic into arsenious or arsenic acid.

§ 66.

SULPHATE OF COPPER. ($Cu O, SO_3$.)

Preparation.—The blue vitriol of commerce may be purified by repeated recrystallization.

Uses.—Sulphate of copper is employed in qualitative analysis, for the precipitation of hydriodic acid, as protiodide of copper. For this purpose a solution of one part of the blue vitriol must be mixed with two and a quarter parts of protosulphate of iron, or else half of the iodine will separate in a free state. The protoxide of iron, in this process, changes to peroxide, by reducing the peroxide of copper to protoxide. Sulphate of copper is besides used as a test for the detection of arsenious and arsenic acid, and it is, indeed, as such very susceptible, but by no means characteristic. For this purpose it is best to prepare ammonio-sulphate of copper by adding ammonia to a solution of sulphate of copper till the precipitate which appears at first, is redissolved. We refer to § 94, *d.* 6, for the manner in which sulphate of copper is employed, in junction with caustic potash, to detect arsenious acid, and especially to distinguish it from arsenic acid. Sulphate of copper may, moreover, be employed for the detection of ferrocyanide of hydrogen.

§ 67.

12. PROTONITRATE OF MERCURY. ($Hg_2 O, NO_5$.)

Preparation.—To prepare this reagent, nine parts of nitric acid, of 1.23, are gently heated in a small retort, with ten parts of mercury, till no more red vapour of nitrous acid appear; the solution is then boiled for some time with the undissolved metallic mercury, taking care to replace the water lost by evaporation, till a solution of common salt in excess precipitates from a portion of the liquid, all the mercury it contains, as a protochloride, so that protochloride of zinc produces no precipitate in the filtered liquid. The original solution is then shaken until cold; the crystals obtained are pounded, and agitated with twenty parts of cold water, to which a very small quantity of nitric acid is added. The solution is then filtered, if necessary, and kept in a glass bottle, the bottom of which is covered with mercury.

Uses.—The protonitrate of mercury acts in a manner analogous to the corresponding salt of silver. In the first place, it precipitates many acids, especially the hydracids; and 2, it serves for the detection of several substances of easy oxidation, e. g. of formic acid, since their oxidation at the expense of the oxygen of the black oxide of mercury, is attended by the highly characteristic precipitation of metallic mercury.

§ 68.

13. PEROXIDE OF MERCURY. ($Hg\,\dot{O}$.)

The peroxide of mercury of commerce is reduced to a fine powder, after having been moistened with some alcohol, in order to prevent its minute particles from rising into the air. This powder is then kept for use. As a reagent it affords us a certain means of detecting hydrocyanic acid, since it dissolves in an alkaline fluid only when this acid is present. (Compare § 100, *d.*)

§ 69.

14. PERCHLORIDE OF MERCURY. ($Hg\,Cl$.)

The commercial perchloride of mercury is sufficiently pure for the purposes of chemical analysis. For use, one part is dissolved in sixteen parts of water.

Uses.—Perchloride of mercury yields with various acids, e. g. with hydriodic acid, precipitates of the characteristic colour, but it is, nevertheless, one of the less essential reagents for the determination of acids. It acts, moreover, as a means of oxidation, and allows us to detect the presence of easily oxidizable bodies, e. g. of protoxide of tin, by the precipitation of protochloride of mercury.

§ 70.

AMMONIO-NITRATE OF SILVER. ($Ag\,\dot{O}, \dot{N}O_5 + 2NH_3$.)

This reagent is not kept on hand, but prepared, when needed for use, by cautiously dropping caustic ammonia into a solution of nitrate of silver, till the precipitate which at first appears is re-dissolved. It serves for the detection of arsenious and arsenic acid in solutions which contain a free acid.

§ 71.

SULPHUROUS ACID. (SO_2.)

Preparation.—To obtain this acid, small pieces of charcoal are heated in a retort with six or eight times their weight of English sulphuric acid, and the evolved gas is transmitted through water (which must be kept cool) till no more sulphurous acid is absorbed. The solution obtained must be kept in well-closed bottles.

Uses.—Sulphurous acid has a great disposition to be converted into sulphuric acid, by the absorption of oxygen. It is, therefore, one of our most powerful means of reduction; it precipitates metallic mercury from its solutions, and converts chromic acid into oxide of chromium, in the same manner as protochloride of tin. We employ sulphurous acid principally for the conversion of arsenic acid into arsenious acid, in order to be enabled to precipitate arsenic more rapidly and more completely, by means of sulphuretted hydrogen. (Vide § 93, *e.*) Before applying this reagent, it is always necessary to ascertain by its odour whether it has undergone decomposition.

§ 72.

17. CHLORINE. (Cl.)

Preparation.—One part of pounded peroxide of manganese is drenched in a retort, with from four to five parts of commercial hydrochloric acid; a gentle heat is then applied to the retort, and the evolved gas is conducted into a jar containing about from thirty to forty parts of water at the lowest possible temperature. The chlorine water obtained must be kept in a well-closed bottle, and cautiously protected from the influence of light, for if this precaution be neglected, it will soon become completely decomposed, i. e. converted into dilute hydrochloric acid, with evolution of oxygen, (owing to the decomposition of the water.)

Uses.—Chlorine has a greater affinity for metals and for hydrogen than iodine and bromine. Chlorine water is, therefore, an efficient means of expelling iodine and bromine from their combinations. Free chlorine forms with bromine chloride of bromine, and with iodine, chloride of iodine, and these combinations present a different relation to that of the uncombined metalloids; we must, therefore, in certain cases, e. g. when testing for iodine by means of starch, (§ 100,) carefully avoid adding chlorine water in excess. Chlorine serves, moreover, for the destruction of organic substances, by depriving water, which contains these substances, of its hydrogen, so that the liberated oxygen is enabled to combine with the vegetable elements, and thus to effect their decomposition. For this latter purpose it is most advisable to evolve chlorine in the fluid which contains the organic substances, by adding hydrochloric acid to it, heating it to boiling, and then adding chlorate of potash. In this process chloride of potassium and water are formed, and chlorous acid and chlorine liberated.

§ 73.

18. SOLUTION OF INDIGO.

Preparation.—One part of pounded indigo is heated with seven parts of fuming sulphuric acid. The solution obtained is diluted for use, with so much water that the fluid just appears still distinctly blue.

Uses.—Indigo becomes decomposed when boiled with nitric acid, giving rise to the formation of oxidation-products of a yellow colour. It is, therefore, employed for the detection of nitric acid, either in its free and uncombined state or in its salts; in which latter case, however, the nitric acid must first be liberated by means of sulphuric acid.

§ 74.

19. STARCH-PASTE.

Common starch is rubbed with cold water, and the mixture then heated to the boiling point, being at the same time constantly stirred. The paste must be uniform, and so thin as almost to run.

Uses.—Starch, when brought into contact with free iodine, forms, with this latter substance, a peculiar dark-blue combination, the colour of which is so intense that it is distinctly perceptible, even when the two substances are brought together, in a highly dilute state. Starch-paste is, therefore, a most excellent and delicate test for free iodine. It is by far less susceptible with regard to bromine, as the fiery yellow colour of bromide of starch is far less characteristic and intense than that of iodide of starch.

B. REAGENTS IN THE DRY WAY.

1. *Fluxes and means of decomposition.*

§ 75.

1. MIXTURE OF CARBONATE OF SODA AND CARBONATE OF POTASH.

$$(\mathrm{Na\,O,\,CO_2 + KO,\,CO_2.})$$

Preparation.—Ten parts of dried carbonate of soda are rubbed together with thirteen parts of dry carbonate of potash; the mixture is kept in a closed vessel.

Uses.—When silicic acid or silicates are fused with about four parts, (and consequently with an excess,) of carbonate of potash or soda, a basic alkaline silicate is formed, (carbonic acid escaping with effervescence,) which, being a combination soluble in water, may be separated from such metallic oxides as it may peradventure contain, and from which hydrochloric acid always separates silicic acid in its soluble modification. When a fixed alkaline carbonate is fused together with sulphate of barytes, of strontia, or of lime, carbonates of the alkaline earths and sulphate of the alkali present. are formed, in which combinations the base, as well as the acid of the previously insoluble salts, may now be ascertained with facility. In order to enable us to render soluble the insoluble silicates and sulphates, we use neither carbonate of potash nor carbonate of soda, separately, but the above mixture of both, because this mixture requires a far lower degree of heat for fusion than either of its components, and thus renders it possible to conduct the operation over a Berzelius lamp. This should always be done in a platinum crucible, when no easily reducible metallic oxides are present.

§ 76.

2. CARBONATE OF BARYTES. ($Ba\,O, CO_2$.)

For the preparation of this reagent we refer the reader to § 33.

Uses.—When silicates are heated with about six times their weight of carbonate of barytes till they begin to fuse together, the silicates decompose with the salt of barytes, in the same manner as with alkaline carbonates, i. e. superbasic silicate of barytes is formed, which is easily decomposed by hydrochloric acid, the carbonic acid escapes and the oxides separate. It is, however, by far more difficult to render silicates completely soluble by this method, than by means of alkaline carbonates; and we use carbonate of barytes, therefore, only, when we intend to test silicates as to the presence of alkalies. The operation with carbonate of barytes is conducted in a platinum crucible.

§ 77.

3. NITRATE OF POTASH. (KO, No_5.)

Preparation.—Commercial saltpetre is dissolved to saturation in boiling water. The solution is then diluted with a small quantity of water, filtered hot into a glass beaker ; this latter put into cold water, and the solution stirred till cold. The crystalline powder obtained is thrown on a filter and washed with cold water till the filtrate is no longer disturbed by nitrate of silver. It is then well dried and kept for use.

Testing.—A solution of pure nitrate of potash must neither be disturbed by solution of silver, nor by solution of barytes, nor precipitated by carbonate of potash.

Uses.—Saltpetre serves as a very powerful means of oxidation, by yielding oxygen to combustible substances when heated with them. We use it principally to convert several metallic sulphurets, especially the sulphurets of tin, of antimony, and of arsenic, into oxides and acids; and also for the rapid and complete combustion of organic bodies. For this latter purpose, however, nitrate of ammonia is, in most cases, preferable: we obtain this by saturating nitric acid with carbonate of ammonia.

II. BLOW-PIPE REAGENTS.

§ 78.

1. CHARCOAL. (C.)

Any kind of completely calcined wood charcoal may be used for blow-pipe experiments. The charcoal of pine or linden-wood is, however, preferable to any other sort. Smooth pieces ought to be selected, as knotty pieces split and throw off fragments of the test specimen when heated.

Uses.—Charcoal is principally used as a support for the matter under examination in blow-pipe experiments, (vide § 12.) The following are the properties which render it so valuable in this respect. First, its infusibility; 2d, its low conducting power for heat, which admits of a substance being heated more strongly upon a charcoal than on any other support; 3d, its porosity, by means of which it imbibes easily fusible substances, such as borax, soda, &c., whilst infusible bodies remain on its surface; 4th, its property of reducing oxidized bodies, by means of which it co-operates in the reduction of oxides by the inner flame of the blow-pipe. Charcoal serves, moreover, for the reduction of arsenious acid and of arsenic acid, by depriving them of their oxygen, at a red heat. Charcoal, for this purpose, is employed either in the shape of small splinters, or reduced to powder. Sometimes the simultaneous application of an alkaline carbonate is necessary for the separation of arsenic; in such cases it is best to use a mixture of soda in powder and lamp-black; this mixture is heated in a covered crucible, and kept in a well-stopped bottle.

§ 79.

2. CARBONATE OF SODA. ($Na\ O, CO_2$.)

Preparation.—One part of chrystallized and three parts of dried carbonate of soda are intimately mixed together and then put into the broken-off neck of a retort, or into a wide glass tube, or some vessel of that description; one aperture is closed by means of a perforated cork, the other remains open. To the perforated cork a tube is fitted, which is connected with a gas evolution flask, in which, when the entire apparatus is ready, carbonic acid is evolved from limestone and hydrochloric acid. We obtain in this manner bicarbonate of soda. The complete saturation of the carbonate of soda with carbonic acid is known by the falling of the temperature of the mixture which had become elevated in the course of the operation, and by the immediate extinction of an ignited wood-splint, when held before the open aperture of the tube. The salt is then thrown on a filter-funnel and washed with cold water, till the liquid which runs off, after supersaturation with nitric acid, is no longer disturbed by chloride of barium, or by nitrate of silver; the salt is then dried, and heated in a crucible of silver, platinum, or porcelain. Carbonate of soda is thus obtained, one atom of carbonate acid being expelled. The purity of carbonate of soda is tested like that of carbonate of potash. Hydro-sulphuret of ammonia must not alter its solution.

Uses.—We employ carbonate of soda, on account of its fusibility, to promote the reduction of oxidized substances by the inner flame of the blow-pipe. In fusing it brings the oxides into most intimate contact with the charcoal support, and allows the flame of the blow-pipe to embrace every part of the specimen. But it does not co-operate in this process by its matter, or by decomposition. If the quantity operated upon is very minute, the reduced metal will often be found in the pores of the coal. In such cases, the parts surrounding the little hole which contained the sample, are taken off with a knife, triturated in a mortar, and the coal washed off from the metallic particles, which then become visible, either as powder or as small and flat spangles, according to their various nature.

In many cases, e. g. in the reduction of peroxide of tin, it is advantageous to add some borax to the carbonate of soda, in order to render the mass more easily fusible. In the second place, carbonate of soda serves as solvent. It is best to use platinum wire as the support, when testing whether bodies are soluble in carbonate of soda. For this purpose the substance is made into a paste with some carbonate of soda and water; this paste is placed on the loop of a platinum wire, and heated. A few only of the bases dissolve in melting carbonate of soda, but acids dissolve with facility therein. Silicic acid differs from all other acids, inasmuch as the glass which it forms with carbonate of soda, remains clear on cooling, if, of course, the two constituents are present in the right proportion to each other. Carbonate of soda is, moreover, applied as a means of decomposing, and rendering other bodies soluble, especially the insoluble sulphates, with which it exchanges acids, whilst, at the same time, a reduction of the new-formed sulphate of soda to sulphuret of sodium takes place; when fused together with sulphuret of arsenic, both are decomposed, giving rise to the formation of sulphuret of arsenic and sodium, and of arsenite, or asseniate of soda, and thus converting it into such a form as to admit of its being reduced by means of hydrogen. Finally, carbonate of soda is the most susceptible reagent in the dry way, for the detection of manganese, since, when fused together in the outer flame of the blow-pipe, with a substance containing manganese, it produces a green, turbid button, owing to the formation of manganate of soda.

§ 80.

3. CYANIDE OF POTASSIUM. (KCy.)

For the preparation of this reagent, vide § 40.

Uses.—Cyanide of potassium is so powerful as a reducing agent in the dry way, that it excels in its action almost all other reagents, and, indeed, it separates the radicals not only from oxygen combinations, but also from sulphur combinations, giving rise, in the first case, to the formation of cyanate of potash, by absorbing oxygen, and, in the latter case, to the formation of sulphocyanide of potassium. We may, by means of this reagent, in the easiest manner (commonly merely in a porcelain crucible over a spirit-lamp) obtain pure metals from their combinations, as e. g. antimony from antimonious acid or from sulphuret of antimony, iron from peroxide of iron, &c. &c. The separation of these metals is much promoted by the easy fusibility of cyanide of potassium. In analysis, this reagent is of the highest importance, for the reduction of arsenites and arseniates, especially of some of those salts which have the heavy metals for bases, and the reduction of which by the usual means of deoxidizing succeeds only with difficulty. As cyanide of potassium is not yet universally known as a reagent in this respect, I invite particular attention to its superior usefulness in the reduction of arsenic. For experiments on a larger scale, glass tubes are selected, rounded at their closed end. The salt which it is intended to reduce, e. g. arseniate of silver, is thrown into a tube of this description, and covered by a small piece of cyanide of potassium; all moisture is first removed from the tube by gently heating it from below upwards; the cyanide of potassium is then heated to fusion and allowed to act on the test specimen. The deoxidation begins in a brisk manner, and with ignition; it is, therefore, unnecessary to apply much external heat, at this point of the operation. Up to this time, generally, no incrustation of arsenic appears, but if the melting mass be now somewhat more strongly heated, the arsenic will, after some time, completely sublime; and as the fused mass does notspout, if the interior of the tube is perfectly dry and clean, exceedingly beautiful mirror-incrustations will be obtained. For the reduction of very small quantities of compounds of arsenic, we use a perfectly dry mixture of equal portions of carbonate of soda and of cyanide of potassium, and cover the test specimen with about six times its quantity of this mixture; conducting the operation in a small glass tube expanded at one end into a small bulb. From sulphuret of arsenic also we may completely sublime the arsenic, by fusing the sulphuret together with cyanide of potassium. Several arsenious and arsenic metallic-salts, when fused together with cyanide of potassium, are reduced in such a manner as to give rise to the formation of fixed arseniuret, (e. g. arseniate of iron.) In such cases no mirror incrustations of arsenic are obtained, which must be borne in mind. As a blow-pipe reagent, cyanide of potassium is also highly useful; its action is indeed extraordinary; substances like peroxide of tin, sulphuret of tin, &c. &c., which for their reduction with carbonate of soda, require rather a strong flame, are reduced with the greatest facility when cyanide of potassium is used. In blow-pipe experiments we always use a mixture of equal parts of carbonate of soda and of cyanide of potassium, since the cyanide of potassium alone fuses too easily. This mixture, besides its more powerful action, has another advantage over carbonate of soda: it is with extreme facility imbibed by the porous charcoal, so that the purest metallic globules are obtained.

§ 81.

BIBORATE OF SODA. (BORAX.) $(NaO, 2B, C_3.)$

The purity of commercial borax may be tested, by adding to its solution, either carbonate of potash, or, after a previous addition of nitric acid, solution of nitrate of barytes or solution of nitrate of silver. The borax may be considered pure if these reagents cause no alteration; but if they either disturb or precipitate its solution, it must be purified by recrystallization. The pure crystallized borax is exposed to a gentle heat, in a platinum crucible, till it no longer swells up; it is then triturated and kept for use.

Uses.—Boracic acid shows a grea affinity for oxides, when brought into contact with them whilst fusing. It combines, therefore, in the first place, directly with oxides. 2. It expels weaker acids from their salts; and 3, with the co-operation of the outer flame of the blow-pipe, it disposes metals, sulphur combinations, and haloid combinations to oxidize, in order to combine with the oxides. The borates produced, generally fuse readily by themselves, but by far more easily when fused together with borate of soda; the latter salt acts in this operation either as a mere flux, or by giving rise to the formation of double salts. In the biborate of soda, we have 1, free boracic acid; and 2, borate of soda; and thus, both conditions united, by which, as before stated, oxides, sulphurets, metals, &c. are disposed for solution and fusion; borax is, therefore, as a blow-pipe reagent, of the greatest importance in analytical chemistry. We generally select platinum wire as support in this operation, heating the loop of it to redness, dipping it into the borax powder, and holding it in the outer flame, whereby a colourless pearl is obtained. This pearl is brought into contact with the test specimen, either when still hot, or after being moistened, and thus a small quantity of the latter attached to it; it is then again exposed, first, to the flame of a spirit-lamp, then to that of the blowpipe, observing the phenomena which appear. The following points ought to be examined with especial care: 1. Whether the specimen dissolves transparent or not, and whether it retains this transparency on cooling or not. 2. Whether this specimen shows a distinct and definite colour, which in many cases, e. g. with cobalt, leads to an instantaneous and certain detection; and 3. Whether the pearls show the same or a different relation in the outer and inner flame. Phenomena of the latter kind depend on the mutation from higher degrees of oxidation to lower, or even to the metallic state, and are for some substances particularly significant.

§ 82.

5. PHOSPHATE OF SODA AND AMMONIA. (MICROCOSMIC SALT.)

(NaO, NH_4O, PO_5.)

Preparation.—This salt is obtained by dissolving six parts of phosphate of soda and one part of pure sal-ammoniac in two parts of hot water, and allowing the mixture to cool. The crystals of the double salt thus obtained are purified by recrystallization from the chloride of sodium which still adheres to them. They are then dried, powdered, and kept for use.

Uses.—When phosphate of soda and ammonia is heated, the ammonia escapes together with the water of crystallization. There remains, consequently, a compound, which, with regard to composition, (free acid and fusible salt,) very nearly approaches borax. The action of microcosmic salt is, therefore, quite analogous to that of biborate of soda. We prefer it, however, to borax in many cases as a solvent or flux, knowing, by experience, that the glasses which it forms with many substances, are more beautifully and distinctly coloured than those of borax. Platinum wire is equally used as a support when employing microcosmic salt as a flux; it ought, however, here to be remarked, that the loop of the wire must be small and narrow, or else the pearl will not stick to it. The operation is conducted as stated § 81 in the preceding paragraph.

§ 83.

PROTO-NITRATE OF COBALT. ($Co\,O, NO_5$.)

Preparation.—To obtain this reagent, an intimate mixture of two parts of very finely pounded cobalt, four parts of saltpetre, one part of effloresced carbonate of soda, and one part of dry carbonate of potash, is projected in small portions into a crucible heated to redness; the latter is then left exposed to the strongest possible heat, till the mass, although perhaps not in perfect fusion, yet is melting. The mass is then allowed to cool, and afterwards reduced to powder and boiled with water; the impure peroxide of cobalt obtained is completely washed, digested and heated with hydrochloric acid until dissolved. This solution is of a dark green colour, and generally gelatinous, owing to the separation of silicic acid. It is evaporated to dryness, the residue boiled with water, filtered, and carbonate of ammonia added to the filtrate, whilst kept at the boiling point, till all acid reaction ceases. The filtered solution is precipitated by means of carbonate of potash, the precipitate obtained washed, and then dissolved in nitric acid. The solution is evaporated to dryness, at a gentle heat, and one part of the residue dissolved in ten parts of water, for use.

Uses.—The protoxide of cobalt, when heated with certain infusible substances, forms with them combinations of divers various characteristic colours, and may, therefore, serve for the detection of those substances. Experiments of this kind are conducted in the following manner. The substance under examination, reduced to powder, is heated to redness, on a charcoal support, the smallest possible drop of solution of proto-nitrate of cobalt is then dropped upon it, and it is again heated to redness. In this process, oxide of zinc assumes an intensely green colour, alumina a blue, and magnesia a feeble rose tint. The rose tint of magnesia is of so little intensity that beginners may easily overlook this reaction. Silica also, when moistened with solution of nitrate of cobalt and heated to redness, assumes a feeble blue tint, which ought to be borne in mind when testing for alumina. The blue compound of the latter is, however, by far more beautifully and intensely coloured, than that of silica.

CHAPTER III.

ON THE RELATION OF THE VARIOUS SUBSTANCES TO REAGENTS.

§ 84.

As we have stated in our introductory remarks, qualitative analysis is based on experiments by means of which we endeavour to convert the unknown constituents of a substance into forms with the relations and properties of which we are familiar, so as to enable us to determine the nature of constituents. It is the same with such experiments as with inquiries and investigations in general. They are the better the more certainly they lead to a definite result, no matter whether of a positive or negative character. But as a question does not render us a whit the wiser, if we do not understand the language in which the answer is returned, so an experiment cannot avail us if we do not know the manner of expression in which the information is conveyed to us, i. e., if we do not know what conclusion we are to draw from a reagent leaving a body unaltered, or producing some phenomenon or other, owing to a mutation of form, or state, in the substance operated upon.

Before we can, therefore, proceed to the practice of analysis, we must, as an indispensable condition, first really and completely know those forms and combinations of substances, which are supposed to be known. But this perfect knowledge depends first, on a comprehensive conception of the conditions which are necessary for the formation of the new combinations, and thus, in short, for the manifestation of the various reactions ; and 2dly, on a distinct impression of the colour, form, and physical properties in general which characterize the new combinations.

It is, therefore, of paramount importance to the student, not merely theoretically to study this branch of qualitative analysis, but also, by actual experiments, to verify every part of it. To teach the relation of the various bodies to reagents, it is usual, in works like the present, to treat of the substances individually and separately, and to point out their characteristic reactions. I have, however, in the present work, deemed it more judicious and better adapted to its elementary character, to collect into groups those substances which are in many respects analogous, and thus, by confronting their analogies with their differences, to place the latter in the clearest possible light.

A.—RELATION OF THE METALLIC OXIDES.

§ 85.

First Group.

POTASH, SODA, AMMONIA.

Properties of the Group.—The alkalies are easily soluble in water, as whether in their pure—or caustic state—or as sulphurets and carbonates. They, therefore, do not precipitate each other, neither in their pure state nor as carbonates, nor are they precipitated by sulphuretted hydrogen under any condition whatever. The solutions of the purer alkalies, as well as of their sulphurets and carbonates, tinge reddened litmus paper blue, and impart an intensely brown tint to turmeric paper.

Special reactions characteristic of the individual substances.

a. POTASH. (K O.)

1. The salts of potash are not volatile in the heat of a

spirit-lamp. They almost all dissolve in water with facility. Their solutions are colourless provided the constituent acid be so. The neutral salts of potash with strong acids, do not affect vegetable colours. Carbonate of potash is of difficult crystallization. The dry salt as well as the crystals, ($KO, CO_2, 2\,aq.$) which are formed in concentrated aqueous solutions of carbonate of potash, when allowed to stand for some time, deliquesce with rapidity when exposed to humid air.

2. *Chloride of platinum* produces in the neutral and acid solutions of the salts of potash, a yellow crystalline heavy precipitate. (CHLORIDE OF PLATINUM AND POTASSIUM. $K\,Cl + P + Cl_2$.) In concentrated solutions, the formation of this precipitate is immediate, in dilute solutions it takes place after a short time, and frequently even after the lapse of some time. The presence of free hydrochloric acid promotes its formation. It is difficultly soluble in water, and wholly insoluble in alcohol. Chloride of platinum is, therefore, a particularly delicate test for salts of potash when the latter is in alcoholic solution. Care should be taken to avoid confounding chloride of platinum and potassium with chloride of platinum and ammonium.

3. *Tartaric acid* produces, in neutral or alkaline solutions of salts of potash, (to alkaline solutions the reagent must be added till a strongly acid reaction becomes manifest,) a white, quickly subsiding, *granular* crystalline precipitate of BI-TARTRATE OF POTASH. ($KO, HO, \bar{T}$.) In concentrated solutions this precipitate is formed immediately, in dilute solutions frequently only after the lapse of *some time.* Violent agitation of the liquid considerably promotes the formation of the precipitate. Free alkalies and free mineral acids dissolve the precipitate; it is difficultly soluble in cold, but more easily so in hot water.

4. When salts of potash, by means of a platinum wire, are held in the summit of the inner *blow-pipe flame*, the outer flame assumes a VIOLET tint, owing to a reduction of potash, and a reoxidation of the potassium thus formed. This reaction is hardly perceptible in phosphates and borates of potash. The presence of soda renders it completely imperceptible.

5. When a salt of potash is heated with a small quantity

of water, *alcohol* added, and the latter ignited, the flame appears VIOLET. The presence of soda renders this reaction also imperceptible.

b. SODA. ($Na\,O$.)

1. The salts of soda present the same general relations as those of potash. Carbonate of soda crystallizes readily; the crystals ($Na\,O, CO_2 + 10$ aq.) effloresce rapidly when exposed to dry air.

2. If a neutral or alkaline solution of a soda salt be mixed with a solution of *neutral antimoniate of potash*,* a white granular crystalline precipitate, ANTIMONIATE OF SODA ($Na\,O, Sb\,O_5$) is formed, (in concentrated solutions, almost immediately, in dilute solutions after the lapse of some time.) Violent agitation of the mixture promotes the separation of the precipitate very much; rubbing the inner sides of the vessel with a glass rod is even more effective. Even in solutions of soda, diluted to the extent of 1000 to 1, we observe, after the lapse of some time, a certain milkiness, and, finally, the formation of a crystalline precipitate. This reaction is not interfered with by the presence of salts of potash; the presence of *carbonate of potash*, in excess, alone has a preventive influence on the formation of the precipitate, since antimoniate of soda dissolves more readily in solution of carbonate of potash, than in water. The presence of free acids must always be avoided, since they separate from the reagent, bi-antimoniate of potash, or hydrate of antimonic acid, in the form of a white precipitate.

3. Salts of soda exposed on a platinum wire to the inner blow-pipe flame, colour the outer flame INTENSELY YELLOW, owing to a reduction of soda, and a re-oxidation of the sodium formed. This reaction is visible even if a large quantity of potash is mixed with the soda.

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* This reagent is prepared by exposing fifty parts of antimonium diaphoreticum ablutum, mixed with twenty and four tenth parts of pure carbonate of potash, to a red heat for half an hour. The crumbling mass is kept in a well-stopped glass vessel. The solution is prepared by drenching four parts of the powder with one hundred parts of warm water, allowing it to digest, and to cool completely, and then filtering the solution and preserving the clear filtrate, protected from the access of air.

* Bi-antimoniate of potassa

4. When a salt of soda is heated with a small quantity of water, *alcohol* added, and the latter ignited, the flame appears strongly YELLOW. The presence of a salt of potash has no preventive influence on this reaction.

5. *Chloride of platinum* produces no precipitate in solutions of soda: *tartaric acid* only when they are highly concentrated. The BITARTRATE OF SODA, ($Na\,O, HO, \bar{T} + 2\,aq.$) which crystallizes out in such cases, appears always in the shape of small needles and columns, and not, like the corresponding salt of potash, in the form of a granular crystalline precipitate.

c. AMMONIA. ($NH_4\,O.$)

1. All salts of ammonia are volatile at a high temperature, either with decomposition, or remaining in combination. Most of them are easily soluble in water. Their solutions are colourless. The neutral ammoniacal compounds with strong acids do not alter vegetable colours.

2. When salts of ammonia are triturated with *hydrate of lime*, with the addition of a few drops of water, or when they are heated, either in a solid form or in solution, with solution of potash, ammonia becomes liberated in its gaseous state, and manifests itself, 1, by its characteristic *odour*; 2, by its reaction on moistened test-papers; and 3, by giving rise to the formation of *white fumes*, when any object (e. g. a glass rod) moistened with hydrochloric acid, nitric acid, acetic acid, any volatile acids, is brought in contact with it. These fumes are caused by the formation of fixed salts, produced by the contact of the gases in the air. Hydrochloric acid is the most delicate test in this experiment; acetic acid, however, less easily admits of any mistake.

3. *Chloride of platinum* shows the same relation to salts of ammonia as to salts of potash; the yellow precipitate of CHLORIDE OF PLATINUM AND AMMONIUM ($NH_4\,Cl + P + Cl_2$) has, however, a somewhat lighter colour than chloride of platinum and potassium.

c. *Tartaric acid* produces in solutions of salts of ammonia a precipitate of BITARTRATE OF AMMONIA, ($NH_4\,O, HO, \bar{T},$) which is formed in the same manner, and under the same circumstances as the corresponding salt of potash, but is somewhat more soluble than the latter.

Recapitulation and remarks.—Salts of potash and of soda are not volatile at a common red heat; salts of ammonia volatilize easily. The latter may, therefore, be easily separated from the former by the application of a red heat. The surest test of ammonia is its expulsion by lime or potash. Salts of potash can only be detected when salts of ammonia are removed, since both show the same or similar relations to chloride of platinum and tartaric acid. Potash is characterized with certainty by either of these two reagents, when ammonia is removed. Soda can only be positively detected by the figure of crystallization, and the properties of some of its salts by its behaviour with antimoniate of potash, and by the colour which its salts impart to the flame of the blow-pipe, and to that of alcohol. When testing for soda with antimoniate of potash, ammoniacal salts must not be present, as they also yield precipitates with the same reagent. If the soda is combined with potash in *alkaline* solution, and we intend to test for it with antimoniate of potash, acetic acid, or hydrochloric acid, must first be added, until the alkaline reaction has nearly but yet not completely disappeared. If the fluid under examination contains a *free acid*, pure carbonate of potash is added, until the solution has acquired an incipient alkaline reaction.

§ 86.

Second Group.

BARYTES, STRONTIAN, LIME, MAGNESIA.

Properties of the group.—The alkaline earths are soluble in water, in their caustic state and as sulphurets. Magnesia, however, is very difficult of solution. These solutions manifest alkaline reactions. The neutral carbonates and phosphates of the alkaline earths are insoluble in water. The solutions of the salts of the alkaline earths are, therefore, not precipitated by sulphuretted hydrogen, under any condition, but alkaline carbonates and phosphates do precipitate them. This relation distinguishes the oxides of the second group from those of the first. The salts of the alkaline earths are colourless, partly soluble, partly insoluble, and not volatile.

Special Reactions.

a. BARYTES. (Ba O.)

1. *Ammonia* causes no precipitate in the solutions of salts of barytes; POTASH only when they are concentrated. Water re-dissolves the precipitate of HYDRATE OF BARYTES (Ba O+aq.) which is formed.

2. *Alkaline carbonates* throw down from solutions of barytes CARBONATE OF BARYTES, (Ba O, CO_2.) in the form of a white precipitate. In acid solutions, however, complete precipitation takes place only on boiling; the same is the case when carbonate of ammonia is employed as the precipitant. The presence of salts of ammonia does not prevent this precipitation.

3. *Sulphuric acid*, and all the soluble sulphates, produce, even in the most highly diluted solutions of barytes, immediately, a fine white precipitate, SULPHATE OF BARYTES, (Ba O, SO_3,) which is insoluble in acids and alkalies.

4. *Hydrofluo-silicic acid* precipitates from solution of barytes SILICOFLUORIDE OF BARIUM, (3 Ba Fl+2 Si Fl_3,) in the form of a colourless, crystalline, quickly-subduing precipitate. In dilute solutions this precipitate is formed only after the lapse of some time; hydrochloric acid and nitric acid dissolve it, but only to a hardly perceptible extent.

5. *Phosphate of soda* causes in neutral or alkaline solution, a white precipitate of PHOSPHATES OF BARYTES, (Ba O, PO_5) which is soluble in free acids. Addition of ammonia neither increases the quantity of this precipitate, nor promotes its formation.

6. *Oxalic acid* causes only in concentrated solutions a white precipitate of OXALATE OF BARYTES, (Ba O, $\bar{O}$+aq.) which is soluble in acids. But if ammonia be added, the reaction is by far more susceptible, and the solution must be highly dilute indeed if no precipitate is formed.

7. Salts of barytes, when heated with diluted *spirit of wine*, impart to the flame of the latter a but little characteristic YELLOWISH colour.

b. STRONTIAN. (Sr O.)

1. Salts of strontian show completely the same relations as salts of barytes, to *ammonia* and *potash*, as well as to the *alkaline carbonates* and to *phosphate of soda.*

2. *Sulphuric acid* and *sulphates* precipitate from solutions of strontian, SULPHATE OF STRONTIAN, (Sr O, SO_3,) in form of a white powder, which is insoluble in acids and alkalies. Sulphate of strontian is by far more soluble in water than sulphate of barytes, owing to which the precipitate in rather dilute solutions is generally only formed after the lapse of some time; and this is always the case (even in concentrated solutions) if *solution of gypsum* is employed as the precipitant.

3. *Hydrofluo-silicic acid* does not cause any precipitate, even in concentrated solutions of strontian.

4. *Oxalic acid* precipitates even from rather highly dilute solutions, after the lapse of some time, OXALATE OF STRONTIAN, (Sr O, $\bar{O}$ + aq.) as a white powder. Addition of ammonia promotes the formation of the precipitate, and considerably increases its quantity.

5. If such salts of strontian as are soluble in water or alcohol, be heated with diluted *alcohol*, and the latter ignited, they impart to its flame, especially on stirring, an intense CARMINE RED colour. This colour must not be confounded with that which salts of lime communicate to the flame of alcohol.

c. LIME. (Ca O.)

1. *Ammonia, potash, alkaline, carbonates,* and *phosphate of soda*, show the same relations to salts of lime as to salts of barytes.

2. *Sulphuric acid* and *sulphate of soda* produce in highly-concentrated solutions of lime immediately, white precipitates of SULPHATE OF LIME, (Ca O, SO_3, HO+aq.) which are completely dissolved by a large proportion of water, but are far more soluble in acids than in water. In less concentrated solutions the precipitates are only formed after the lapse of some time; and no precipitation whatever takes place in highly dilute solutions. Solution of gypsum, of course, cannot produce any precipitate; but

even a cold saturated solution of sulphate of potash, mixed with an equal quantity of water, produces no precipitate in solutions of lime, at least never immediately. If solutions of lime are so highly dilute, that sulphuric acid causes no precipitation in them, a precipitate is immediately formed on the addition of alcohol.

3. *Hydrofluo-silicic acid* does not precipitate salts of lime.

4. *Oxalic acid* produces a white precipitate of OXALATE OF LIME, (Ca O, $\bar{O}+2$ aq.) even in highly dilute neutral solutions of lime. Addition of ammonia promotes the formation of this precipitate, and increases its quantity. Oxalate of lime is easily soluble in hydrochloric acid and nitric acid, but not in acetic acid, nor in oxalic acid.

Soluble salts of lime, when heated with dilute *alcohol*, impart to the flame of the latter a YELLOWISH RED colour, which is often confounded with that caused by strontian.

d. MAGNESIA. (Mg O.)

1. *Ammonia* throws down from the solutions of neutral salts of magnesia, a portion of the magnesia as HYDRATE OF MAGNESIA, (Mg O, HO,) in the form of a white bulky precipitate. The other portion of magnesia remains in solution, combined with the salt of ammonia to which the decomposition has given rise, and forming with it a double salt, not decomposible by ammonia. This disposition of the salts of magnesia to form such double salts with salts of ammonia, is the cause that salts of magnesia are not precipitated when salts of ammonia are present, or, what is in fact the same, that ammonia does not produce any precipitate in acid solutions of magnesia, and that a precipitate caused by ammonia, in neutral solutions, is re-dissolved on the addition of a salt of ammonia.

2. *Potash* and *caustic barytes* precipitate from solutions of magnesia, HYDRATE OF MAGNESIA. The formation of this precipitate is much promoted by boiling. Salts of ammonia redissolve the precipitated hydrate ; and no precipitate is formed at all, if they are mixed in sufficient quantity with the magnesia solution, before the addition of the precipitant. But it will, of course, make its appearance if the

solution be then boiled with an excess of potash, for in that case the condition of its remaining in solution, i. e. the salt of ammonia, becomes decomposed and is thus removed.

3. *Carbonate of potash* causes in neutral solutions of magnesia a white precipitate, A COMPOUND OF ONE EQUIVALENT OF HYDRATE OF MAGNESIA, AND THREE EQUIVALENTS OF CARBONATE OF MAGNESIA. ($Mg\,O, HO+3\,Mg\,O, CO_2$.) The fourth part of the carbonic acid contained in the carbonate of potash becomes liberated on the decomposition of this salt, and combining with a portion of the new-formed carbonate of magnesia, keeps this part in solution as a bicarbonate of magnesia. This carbonic acid may be expelled by boiling; the application of heat to the solution, therefore, promotes the formation and increases the quantity of the precipitate. Salts of ammonia prevent this precipitation also, and re-dissolve a precipitate already formed.

4. *Carbonate of ammonia* does not precipitate solutions of magnesia when cold, and but imperfectly when boiling. The addition of salts of ammonia completely prevents the formation of a precipitate.

Phosphate of soda precipitates PHOSPHATE OF MAGNESIA ($2\,Mg\,O, PO_5$) as a white powder, from solutions of magnesia, provided they be not too highly dilute. The precipitation is much promoted by boiling the solution. But if ammonia be added to even a highly diluted solution of magnesia, no matter whether before or after the addition of the phosphate of soda, a white crystalline precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2\,Mg\,O, NH_4\,O$,) ($PO_5 + 2\,HO + 10$ aq.) is formed. Its separation from dilute solutions is much promoted by violent stirring (with a glass rod,) if even the solution is too highly diluted as to admit of the formation of a precipitate; yet, white lines appear after some time in those places of the sides of the vessel which have been touched by the glass rod whilst stirring the fluid. Muriate of ammonia and salts of ammonia, in general, do not dissolve the basic phosphate of magnesia and ammonia, but it is soluble in free acids, (even in acetic acid.)

6. *Oxalate of ammonia* (but not free oxalic acid) pro-

duces a white precipitate of OXALATE OF MAGNESIA. ($MgO, \bar{O} + 2$ aq.) Salts of ammonia prevent its formation.

7. *Sulphuric acid* and *hydrofluo-silicic acid* do not precipitate salts of magnesia.

8. If magnesia, or a salt of magnesia, be moistened with solution of *protonitrate of cobalt*, and for some time exposed on a coal to a strong *blow-pipe flame*, a FEEBLY FLESH-COLOURED mass is obtained, the tint of which only becomes distinct on cooling, but is never very intense.

Recapitulation and remarks.—The difficult solubility of the hydrate of magnesia, the easy solubility of the sulphate of magnesia, and the disposition of salts of magnesia to form double salts with salts of ammonia, are the three main points in which magnesia differs from the other alkaline earths. To detect magnesia, we remove always first barytes, strontian, and lime, if they are present; and we effect this purpose, either by boiling with carbonate of ammonia with addition of sal ammoniac, or by means of sulphate of potash and of oxalate of ammonia, with addition of sal ammoniac, and then select for the detection of magnesia, the reaction with phosphate of soda, with addition of ammonia. The detection of barytes is always easy, for the immediately forming precipitate which it yields with solution of gypsum, and its reaction with hydrofluo silicic acid, leave no doubt as to its presence. Strontian may also easily be detected by its relation to solution of gypsum, except in cases where barytes is present. It must, therefore, in such cases first be separated from barytes. This separation may best be effected by converting both earths into dry chlorides, and digesting the latter with absolute alcohol. The chloride of strontian dissolves whilst the chloride of barium remains undissolved. When testing for strontian by means of the alcohol flame, we must avoid confounding the colour it imparts to it, with that communicated by salts of lime. For the detection of lime, oxalic acid is always selected. Barytes and strontian must, however, first have been removed by means of sulphate of potash, since they manifest with oxalic acid an analogous reaction, only varying in intensity. On the separation of barytes and strontian, by means of sulphate of potash, it may possibly happen that also a portion of the lime precipitates. This is, however, a matter of indifference, since, at any rate, sufficient remains dissolved in the fluid to admit of its presence being ascertained with indubitable certainty, by means of oxalic acid.

§ 87.

Third Group.

ALLUMINA, OXIDE OF CHROMIUM.

Properties of the group.—Alumina and oxide of chromium are both in their pure state, and, as hydrates, insoluble in water. They form no neutral salts with carbonic acid. Their sulphur combinations cannot be formed in the humid way. Sulphuretted hydrogen, therefore, does not precipitate solutions of alumina or oxide of chromium; hydrosulphuret of ammonia precipitates the hydrated oxides from these solutions. This relation to hydrosulphuret of ammonia distinguishes the oxides of the third from those of the two preceding groups.

Special Reactions.

a. ALUMINA. $Al_2\ O_3$,)

1. The salts of allumina are colourless, for the most part not volatile; some of them are soluble, others insoluble. The soluble salts redden litmus paper and lose their acids when heated to redness.

2. *Potash* throws down from the solutions of alumina a bulky precipitate of HYDRATE OF ALUMINA, ($Al_2\ O_3 + HO$,) containing potash, which easily and completely dissolves in an excess of the precipitant, but may again be precipitated from this solution by the addition of hydrochlorate of ammonia, even when the solution is cold, but more completely on heating it. The presence of salts of ammonia does not prevent this precipitation by potash.

3. *Ammonia* also produces a precipitate of HYDRATE OF ALUMINA; and this precipitate also is redissolved by a very considerable excess of the precipitate, but only in such cases where the solution of alumina contains no salts of potash or soda. But if a certain quantity of these salts is present, ammonia is not able to redissolve the precipitate first formed.

Upon this relation, the complete precipitation of the hydrate of alumina from a potash solution, by means of hydrochlorate of ammonia, depends. For in this process, potash and hydrochlorate of ammonia mutually decompose, giving rise to the formation of chloride of potassium and of ammonia; and ammonia not being able to maintain the hydrate of alumina in solution, when a salt of potash is present, this hydrate of course precipitates.

4. If alumina, or a compound of alumina, be heated to redness, on charcoal, before the blow-pipe, and then moistened with a few drops of solution of *protonitrate of cobalt*, and again strongly heated, an unfused mass of a deep SKY-BLUE colour is obtained, a compound of the two oxides. The colour becomes distinct only on cooling. By candle-light it appears violet.

b. OXIDE OF CHROMIUM. ($Cr_2\ O_3$.)

1. The solutions of the compounds of oxide of chromium, have always, even when highly diluted, either an emerald-green or a nigrescent violet colour. The soluble neutral salts of oxide of chromium redden litmus paper, and are decomposed by heat.

2. *Potash* produces in solutions of oxide of chromium, a bluish green precipitate of HYDRATED OXIDE OF CHROMIUM ($Cr\ 2O_3+HO$) which easily and completely redissolves in an excess of the precipitant, imparting an emerald-green colour to the fluid. If this solution is kept *constantly* boiling for a certain time, the precipitate completely separates again, so that the supernatant liquor appears perfectly colourless. The dissolved hydrated oxide of chromium is also precipitated, if the potash solution is mixed with hydrochlorate of ammonia and heated.

3. *Ammonia* produces the same precipitate of HYDRATED OXIDE OF CHROMIUM. An excess of the precipitant redissolves it to a small extent, at a low temperature, but the precipitation is complete, if the solution is boiled after the addition of ammonia in excess.

4. If oxide of chromium, or a compound of this substance, are fused together with *nitre*, CHROMATE OF POTASH, ($KO,\ Cr\ O$,) is obtained in all cases; in this process a portion of the oxygen of the nitric acid leaves its com-

bination, and forms with the oxide of chromium, chromic acid, which then combines with the potash of the decomposed saltpetre. For the Reaction of Chromic Acid, vide infra, § 95, *b*.

5. *Phosphate of soda and ammonia* dissolves oxide of chromium and its salts, as well in the oxidizing as in the reducing flame of the blow-pipe, giving rise to the formation of clear, FEEBLY YELLOWISH-GREEN GLASS, the colour of which changes to emerald-green, on cooling. Borax manifests a similar relation.

Recapitulation and remarks.—The solubility of the hydrates of chromium and alumina, in potash and their precipitation from potash solutions, by means of hydrochlorate of ammonia, allows us, in the first place, to separate them from the oxides of other groups, and affords us, in the second place, a certain means of detection for alumina, when no oxide of chromium is present. If the latter, therefore, is present—which we may ascertain either by the colour of the solution, or, at any rate, by the reaction with phosphate of soda and ammonia,—it must be separated before we can proceed to test for alumina. This separation may be effected most completely by fusing the mixed oxides together with nitre. The precipitation of oxide of chromium, by means of boiling its potash solution, is also a sufficiently exact indication; it gives, however, frequently rise to mistakes.

§ 88.

Fourth Group.

OXIDE OF ZINC, PROTOXIDE OF MANGANESE, OXIDE OF NICKEL, PROTOXIDE OF COBALT, PROTOXIDE OF IRON, PEROXIDE OF IRON.

Properties of the group.—The sulphurets corresponding with these oxides, are more or less soluble in dilute acids, but insoluble in water, alkalies, and alkaline sulphurets. The solutions of the salts of these oxides, are, therefore, not at all precipitated by sulphuretted hydrogen, when they contain free acid, and either not at all, or at least but incompletely, when they are neutral, but completely, when they are alkaline, or when an alkaline sulphuret is employed instead of sulphuretted hydrogen.

Special Reactions.

a. OXIDE OF ZINC. (Zn O.)

1. The compounds of oxide of zinc are colourless. Its soluble neutral salts redden litmus paper, and are easily decomposed by heat, with the exception of sulphate of zinc, which can bear a slight degree of red heat.

2. *Sulphuretted hydrogen* precipitates from neutral zinc solutions, a portion of the zinc as white SULPHURET OF ZINC (Zn S.) In acid solutions no precipitate is formed, if the free acid present be one of the stronger acids.

3. *Hydrosulphuret of ammonia* throws down from neutral as sulphuretted hydrogen does from alkaline solutions, all the zinc they contain, as SULPHURET OF ZINC, in the form of a white precipitate. This precipitate is not redissolved by hydrosulphuret of ammonia in excess, nor by potash or ammonia; it is sparingly soluble in hydrochloric acid, but easy of solution in aqua regia.

4. *Potash* and *ammonia* throw down from solutions of zinc, HYDRATED OXIDE OF ZINC (Zn O, HO) in the form of a white gelatinous precipitate, which is easily and completely redissolved by an excess of the precipitant.

5. *Carbonate of potash* produces a precipitate of BASIC CARBONATE OF ZINC 3 (Zn O, HO) + 2 (Zn O, CO_2) which is insoluble in an excess of the precipitant. The presence of salts of ammonia prevents its formation, or they redissolve it when already formed, giving rise to the formation of double salts of oxide of zinc and ammonia.

6. *Carbonate of ammonia* produces the same precipitate as carbonate of potash; addition of carbonate of ammonia in excess redissolves it.

7. Oxide of zinc, or a salt of oxide of zinc mixed with *carbonate of soda*, and exposed to the *reducing flame* of the blow-pipe, covers the coal support with an incrustation of OXIDE OF ZINC, presenting a yellow colour, as long as it is hot, and changing to white, on cooling. This is caused by the reduced metallic zinc volatilizing at the moment of

its reduction, and reoxidizing in passing through the outer flame.

8. If oxide of zinc, or a salt of zinc, be moistened with solution of *protonitrate of cobalt*, and heated before the blow-pipe, an unfused beautifully GREEN coloured mass is obtained, consisting of a combination of oxide of zinc with protoxide of cobalt.

b, PROTOXIDE OF MANGANESE. ($Mn\,O$.)

1. The protosalts of manganese are colourless or of a pale red; some of them are soluble, others insoluble. The soluble salts are decomposed by a red heat, with the exception of protosulphate of manganese. The solutions of the manganese salts do not alter vegetable colours.

2. *Sulphuretted hydrogen* does not precipitate acid nor neutral solutions of prototoxide of manganese.

3. *Hydrosulphuret of ammonia* throws down from neutral solutions, as sulphuretted hydrogen does from alkaline, all the manganese they contain, as SULPHURET OF MANGANESE ($Mn\,S$) in the form of a bright flesh-coloured precipitate, which changes to a dark-brown when exposed to the air; this precipitate is insoluble in hydrosulphuret of ammonia and in alkalies, but easily soluble in hydrochloric acid and nitric acid.

4. *Potash* and *ammonia* produce whitish precipitates of HYDRATED PROTOXIDE OF MANGANESE, ($Mn\,O, HO$,) which, when exposed to the air, soon change to a brownish, and at last, to a dark blackish brown colour, owing to the hydrated protoxide being converted into hydrated peroxide, by the absorption of oxygen from the air. Ammonia and carbonate of ammonia do not redissolve this precipitate; but sal ammoniac prevents the precipitation by ammonia completely, and that by potash partly. Solution of sal ammoniac redissolves only those parts of the already-formed precipitates which have not yet undergone a higher degree of oxidation. The solution of the hydrated protoxide in sal ammoniac depends on the disposition of the protosalts of manganese to form double salts with salts of ammonia. The pellucid solutions of these double salts become brown, when exposed to the air, and depose dark-brown peroxide of manganese.

5. If any compound of manganese be fused with *carbonate of soda*, on a platinum wire, in the *outer* flame, MANGANATE OF SODA is formed, which makes the test specimen appear GREEN, as long as it is hot, but, after cooling, of a bluish green and opaque. This reaction enables us to detect the smallest quantities of manganese. The delicacy of the test is still further increased if a minute quantity of nitre is added to the carbonate of soda.

6. *Borax* and *phosphate of soda and ammonia* dissolve manganese compounds, in the outer flame of the blow-pipe, giving rise to the formation of clear and VIOLET-RED glasses, which, on cooling, appear of an amethyst red, and lose their colour when exposed to the inner flame, owing to the peroxide becoming reduced to protoxide. The glass which borax forms with manganese, appears black when containing a considerable proportion of peroxide of manganese, but the glass formed by phosphate of soda and ammonia never loses its transparency. The latter, when exposed to the inner flame, becomes colourless far more easily than the former.

c. OXIDE OF NICKEL. (Ni O.)

1. The salts of nickel are yellow or green; their solutions are of a bright green colour. The soluble neutral salts redden litmus paper and are decomposed at a red heat.

2. *Sulphuretted hydrogen* precipitates neither acid nor neutral solutions of nickel; or the latter at least but very incompletely.

3. *Hydrosulphuret of ammonia* produces in neutral, as sulphuretted hydrogen does in alkaline solutions, a black precipitate of SULPHURET OF NICKEL, (Ni S,) which is not altogether insoluble in hydrosulphuret of ammonia, owing to which property the fluid from which it has been precipitated, presents always a brownish colour. Sulphuret of nickel is dissolved with difficulty by hydrochloric acid, but easily by aqua regia.

4. *Potash* produces a bright green precipitate of HYDRATED OXIDE OF NICKEL, (Ni O, HO,) which is insoluble in potash, and does not alter when exposed to the air. Carbonate of ammonia re-dissolves this precipitate to a

greenish-blue fluid, from which potash again precipitates the nickel it contains, as a yellow-green hydrated oxide of nickel.

5. *Ammonia* precipitates also HYDRATED OXIDE OF NICKEL, but an excess of the precipitant easily re-dissolves it to a blue fluid, as a double salt of oxide of nickel and ammonia. Potash precipitates hydrated oxide of nickel from this solution.

6. *Cyanide of potassium* produces a yellowish-green precipitate of CYANIDE OF NICKEL, (Ni Cy,) which by an excess of the precipitant is easily redissolved to a brownish-yellow fluid, containing cyanide of nickel and cyanide of potassium combined. Sulphuric acid and hydrochloric acid again precipitate from this solution cyanide of nickel, which is very difficultly soluble in an excess of these acids, at a low temperature.

7. *Borax* and *phosphate of soda and ammonia* dissolve compounds of oxide of nickel, in the outer flame of the blow-pipe, giving rise to the formation of clear glasses of a dark yellow colour, with a tinge of red-brown, which become clearer and almost colourless on cooling. Addition of nitre or carbonate of potash changes the colour to blue or to dark purple. The glass which phosphate of soda and ammonia forms with nickel remains unaltered when exposed to the inner flame, but that of borax becomes grey and troubled owing to the reduction of nickel.

d. PROTOXIDE OF COBALT. (Co O.)

1. The protosalts of cobalt are blue in their anhydrous, and of a characteristic bright red tint in their hydrated state. Their solutions show their colour even when considerably diluted. The soluble neutral salts redden litmus paper, and are decomposed by a red heat.

2. *Sulphuretted hydrogen* does not precipitate acid solutions of cobalt, and neutral solutions at the most, very incompletely, when they contain weak acids; these latter precipitates are of a black colour.

3. *Hydrosulphuret of ammonia* precipitates from neutral, as sulphuretted hydrogen do esfrom alkaline solutions, all the cobalt they contain, as black SULPHURET OF COBALT.

(Co S.) This substance is insoluble in alkalies and hydrosulphuret of ammonia, difficultly soluble in hydrochloric acid, easily soluble in aqua regia.

4. *Potash* produces in solutions of cobalt BLUE precipitates of basic salts of cobalt, which become GREEN when exposed to the air, owing to the absorption of oxygen, and are converted into hydrates of a pale red colour when boiled. They are insoluble in potash. But neutral carbonate of ammonia dissolves them completely to intensely violet-red fluids, in which potash does not cause any, or, at least, but a very scanty precipitate.

5. *Ammonia* produces the same precipitate as potash, but an excess of the precipitant redissolves it to a reddish-brown fluid, in which potash does not cause any, or at least but a very scanty, precipitate.

6. If to a solution of cobalt acidified with some hydrochloric acid, *cyanide of potassium* be added, a brownish-white precipitate of PROTOCYANIDE OF COBALT is formed, which by an excess of the precipitant, with presence of free hydrocyanic acid, is easily dissolved to COBALTOCYANIDE OF POTASSIUM. (Cy_6 Co_2+3 K.) Acids cause no precipitation in the solutions of this salt.

7. *Borax* dissolves compounds of cobalt in the inner as well as in the outer flame of the blow-pipe, TO CLEAR SPLENDIDLY BLUE COLOURED GLASSES which appear almost black, when cobalt is present in any considerable proportion. This test is as delicate as it is characteristic. Phosphate of soda and ammonia manifest the same reaction, but in a lesser degree.

e. PROTOXIDE OF IRON. (Fe O.)

1. The protosalts of iron have a greenish colour; their solutions appear coloured only when quite concentrated. The soluble neutral salts redden litmus paper and are decomposed by a red heat.

2. Acid solutions are not precipitated by *sulphuretted hydrogen*, and neutral solutions, with weak acids, at the most but incompletely. These precipitates are of a black colour.

3. *Hydrosulphuret of ammonia* precipitates from neutral, as sulphuretted hydrogen does from alkaline solutions,

all the iron they contain, as black SULPHURET OF IRON, ($Fe S$,) which is insoluble in alkalies and alkaline sulphurets, but easy of solution in hydrochloric acid and nitric acid.

4. *Potash* and *ammonia* produce a precipitate of HYDRATED PROTOXIDE OF IRON, ($Fe O, HO$,) which, in the first moment, appears almost white, but, after a very short time, becomes of a dirty green, by absorption of oxygen from the air, and at last assumes a red-brown colour. The presence of salts of ammonia prevents the precipitation by potash partly, and that by ammonia totally.

5. *Ferrocyanide of potassium* produces in solutions of protoxide of iron a bluish-white precipitate of FERROCYANIDE OF POTASSIUM AND IRON, ($2 Cfy+K+3 Fe$,) which, by absorption of oxygen from the air, soon becomes blue. In this change, all the potassium of three equivalents of the compound, and one equivalent of iron, become oxidized, and Prussian blue ($3 Cfy+2 Fe_2$) remains. Nitric acid or chlorine causes this oxidation immediately.

6. *Ferricyanide of potassium* produces a splendidly blue precipitate of FERRICYANIDE OF IRON, ($2 Cfy+3 Fe$.) This precipitate does not differ in colour from Prussian blue. It is insoluble in hydrochloric acid, but easily decomposed by potash. When the solution of protosalt of iron is highly dilute, the reagent imparts to it only a dark bluish green colour.

7. *Borax* dissolves protosalts of iron in the oxidising flame, forming DEEP RED GLASSES, the colour of which changes to bottle green when exposed to the inner flame, owing to the reduction of the first formed peroxide to magnetic-oxide. Both tints disappear totally, or in a great measure, when the glasses become cool. Phosphate of soda and ammonia shows a similar relation to the protosalts of iron, but the colour of its glass vanishes even more decidedly than is the case with borax.

f. PEROXIDE OF IRON. ($Fe_2 O_3$.)

1. The persalts of iron are of a more or less red yellow colour. Their solutions present this colour even when pretty highly diluted. The soluble neutral salts redden litmus paper and are decomposed by heat.

2. *Sulphuretted hydrogen* produces in neutral and acid solutions a slight precipitate of SULPHUR, which renders the solution turbid and imparts a milky white tint to it. Peroxide of iron and sulphuretted hydrogen decompose each other; in this process the hydrogen withdraws from the peroxide of iron, one-third of its oxygen combining with it to form water; the persalt of iron is thus converted into a protosalt, and the sulphur of the decomposed sulphuretted hydrogen separates.

3. *Hydrosulphuret* of *ammonia* precipitates from neutral, as sulphuretted hydrogen does from alkaline solutions, all the peroxide of iron they contain, as black SULPHURET OF IRON; this precipitation is preceded by the conversion of the persalt into a protosalt. The reagent produces only a blackish-green tint in the fluid, if the solution is very dilute. The minutely divided sulphuret of iron subsides in such cases only after the lapse of some time. For the several degrees of solubility of sulphuret of iron in various substances, vide *e.* (Protoxide of iron.) 3.

4. *Potash* and *ammonia* produce bulky red-brown precipitates of HYDRATED PEROXIDE OF IRON, which are insoluble in an excess of the precipitant, as well as in salts of ammonia.

5. *Ferocyanide of potassium* produces even in highly dilute solutions a splendidly blue precipitate of SESQUIFERROCYANIDE OF IRON, (3 Cfy+4 Fe,) (Prussian blue) which is insoluble in hydrochloric acid, but easily decomposed by potash, with precipitation of peroxide of iron.

6. *Ferricyanide* of *potassium* imparts a reddish-brown tint to solutions of peroxide of iron, but it causes no precipitate.

7. The persalts of iron present the same appearances as the protosalts, when exposed to the action of the blow-pipe flame, vide *e.* (Protoxide of iron) 7.

Recapitulation and remarks.—Of the metallic oxides belonging to the fourth group, oxide of zinc alone is soluble in potash. It is this property which distinguishes it from the other oxides of this group, and connects it with those of the third group. But it differs from oxide of chromium and from alumina, inasmuch as sulphuretted hydrogen precipitates it from its solutions in potash. This characteristic property is the surest test of oxide of zinc. Protoxide of manganese, oxide of nickel, protoxide of cobalt, and protoxide of iron form with salts of ammonia double salts, from which the metallic oxides are not precipitated by free ammonia; but peroxide of iron, just like the oxides of the third group, is completely precipitated by ammonia, even when salts of ammonia are present. Hence it follows, in the first place, that by means of this property, manganese, nickel and cobalt may be separated, as well from peroxide of iron as from oxide of chromium and from alumina; and, in the second place, that, in order to separate these metals from protoxide of iron, the latter substance must first be peroxidized, which operation is best performed by boiling its solution with nitric acid. The peroxide of iron differs from oxide of chromium, and from alumina, inasmuch as it is insoluble in potash; and peroxide of iron may be distinguished from protoxide, by means of ferrocyanide of potassium. Hydrated oxide of nickel and hydrated protoxide of cobalt dissolve in carbonate of ammonia, whilst hydrated protoxide of manganese is insoluble in this substance. We may, therefore, by means of this solvent, separate the protoxide of manganese from the two other oxides. The brown tint assumed by the white hydrated protoxide when exposed to the air, and the blow-pipe reactions, especially that with soda, are the surest test of protoxide of manganese. Cyanide of nickel, and cyanide of cobalt are soluble in cyanide of potassium. But cyanide of nickel may be precipitated from this solution by acids, which is not the case with cyanide of cobalt. This property, i. e. the formation of a precipitate in a solution of these two cyanides in cyanide of potassium, by the addition of hydrochloric acid, is, under all circumstances, a perfectly sure test of the presence of nickel. Whether this precipitate be cyanide of nickel or cobalticyanide of nickel, is quite immaterial as far as the detection of nickel is concerned; we have only to bear in mind that no precipitate forms if cobalt alone be contained in the solution, since cobalticyanide of potassium is not decomposed by hydrochloric acid. To explain the composition of the precipitates formed, and the process in general, we will now proceed to consider and examine three special cases, the difference of which depends on the unequal relative proportion of the nickel and the cobalt.

1, Ni : Co = 3 eq. : 2 eq.
2, Ni : Co = 3 eq. : 2 eq.+x
3, Ni : Co = 3 eq.+x : 2 eq.

Consequently, we get in solution in the first case, one eq.: of cobalticyanide of potassium, (Cy_6, Co_2+3 K,) and 3 eq.: of cyanide of nickel and cyanide of potassium combined, (Cy_3 Ni,+Cy_3 K,) and if we add hydrochloric acid in excess to this solution, we obtain a dirty green precipitate of cobalticyanide of nickel, (Cy_6 Co_2+3 Ni,) which contains all the nickel and cobalt of the solution; in this process the combination of cyanide of nickel and cyanide of potassium is decomposed, and the potassium in the cobalticyanide of potassium changes places with the nickel in the cyanide of nickel. Besides the cobalticyanide of nickel, chloride of potassium and hydrocyanic acid are formed. In the second case we obtain also a precipitate of cobalticyanide of nickel, but this precipitate, though containing all the nickel, does not contain all the cobalt of the solution, for the excess of cobalticyanide of potassium is not decomposed. In the third case, at last, we obtain a precipitate of cobalticyanide of nickel, which contains all the cobalt and a portion of the nickel, mixed with insoluble cyanide of nickel, which contains the remaining part of the nickel. The precipitate of cobaltcyanide of nickel has been formed, as in the first case, whilst the cyanide of nickel is formed by the decomposition of the double cyanide of nickel and potassium in excess. Hence it is evident, that nickel is, in all cases, a necessary condition to the formation of a precipitate, and consequently that this precipitate can leave no doubt as to its presence. As cobalt may, under all circumstances, be safely and easily detected by its characteristic properties before the blowpipe, any further indications for the mere detection of either metal, would almost seem superfluous; but since we are now already far advanced towards the complete separation of these two substances from each other, we may as well briefly state how to effect it. In the first and second of the above-mentioned cases, we have, after the addition of the hydrochloric acid, only to heat the fluid together with the therein suspended precipitate of cobalticyanide of nickel, till the free hydrocyanic acid is expelled, (the cobalticyanide of nickel as well as the cobalticyanide of potassium present in the second case, remain unaltered during this operation;) and then we may, by addition of caustic potash, easily decompose the cobalticyanide of nickel, into cobalticyanide of potassium, which remains in solution, and oxide of nickel which precipitates as hydrated oxide. But in the third case we must add a larger quantity of hydrochloric acid, and boil the solution therewith, till the cyanide of nickel contained in the precipitate (which would only be incompletely decomposed by potash) is converted into chloride of nickel, and till the hydrocyanic acid, formed during this operation, is completely expelled; and then, after this preparatory process, we may, by boiling with caustic potash, obtain all the nickel as an insoluble hydrated oxide, and all the cobalt as soluble cobalticyanide of potassium. Lastly, we must still mention, that the oxides of the fourth group are not precipitated by alkalies, if non-volatile organic substances, (such as sugar, tartaric acid, &c.) are contained in their solutions. The same is the case with alumina and oxide of chromium.

§ 89.

Fifth Group.

OXIDE OF SILVER, PROTOXIDE OF MERCURY, PEROXIDE OF MERCURY, OXIDE OF LEAD, OXIDE OF BISMUTH, OXIDE OF COPPER, OXIDE OF CADMIUM.

Properties of the group.—The sulphurets corresponding with the oxides of this group, are insoluble both in dilute acids and in alkaline sulphurets. The solutions of these oxides are, therefore, completely precipitated by sulphuretted hydrogen, no matter whether their reaction be neutral, alkaline, or acid.

We divide the oxides of this group into two sections, and distinguish

1. OXIDES PRECIPITABLE BY HYDROCHLORIC ACID, viz.: oxide of silver, protoxide of mercury, and oxide of lead, from

2. OXIDES, NOT PRECIPITABLE BY HYDROCHLORIC ACID, ivz.: peroxide of mercury, oxide of copper, oxide of bis-

muth, oxide of cadmium. Lead must be considered in both sections, as the difficult solubility of its chloride renders it possible to confound it with protoxide of mercury and oxide of silver, without affording us any means of separating it completely from the oxides of the second section.

§ 90.

FIRST SECTION. OXIDES PRECIPITABLE BY HYDROCHLORIC ACID.

Special Reactions.

a. OXIDE OF SILVER. (Ag O.)

1. The salts of oxide of silver are fixed and colourless; most of them blacken when exposed to light. The soluble neutral salts do not alter vegetable colours, and are decomposed at a red heat.

2. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* precipitate black SULPHURET OF SILVER, (Ag S,) which is insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium. Boiling concentrated sulphuric acid easily decomposes and dissolves this precipitate, with separation of sulphur.

3. *Potash* and *ammonia* precipitate OXIDE OF SILVER, in the form of a BRIGHT BROWN powder, which is insoluble in potash, but easy of solution in ammonia. The presence of salts of ammonia prevents this reaction either totally or partly.

4. *Hydrochloric acid* and soluble *chlorides* produce a white curdy precipitate of CHLORIDE OF SILVER. (Ag Cl.) In very dilute solutions, this precipitate merely imparts to the fluid a bluish white opalescent appearance. The white chloride of silver, when exposed to light, acquires first a violet tint, and at last a black colour, but without any alteration in its composition; it is insoluble in nitric acid, but dissolves easily in ammonia, giving rise to the formation of chloride of silver and ammonia. Acids precipitate it again from this combination. Chloride of silver, when heated, fuses without decomposition, forming a transparent horny mass.

5. When silver compounds, mixed with *carbonate of soda*, are on a charcoal support, exposed to the *inner* flame of the blow-pipe, **WHITE, SHINING, AND DUCTILE METALLIC GLOBULES** are obtained, whilst no incrustation takes place.

b. PROTOXIDE OF MERCURY. (Hg_2 O.)

1. The salts of protoxide of mercury, when exposed to a red heat, either volatilize without decomposition, or decompose; in the latter case the mercury separated volatilizes in a metallic state. They are colourless. The soluble salts, when neutral, redden litmus paper; when mixed with much water, they separate into insoluble basic and soluble acid salts.

2. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce black precipitates of **SULPHURET OF MERCURY**, (Hg_2 S,) which are insoluble, as well in dilute acids as in alkaline sulphurets, and in cyanide of potassium. Potash resolves this sulphuret into bisulphuret and globules of metallic mercury. Sulphuret of mercury is easily decomposed and dissolved by aqua regia, but not by boiling concentrated nitric acid.

3. *Potash* and *ammonia* produce black precipitates, which are insoluble in an excess of the precipitants. The potash precipitates consist of **PROTOXIDE OF MERCURY**; those of ammonia, of **BASIC SALT OF PROTOXIDE OF MERCURY AND AMMONIA.**

4. *Hydrochloric acid* and *soluble chlorides* precipitate **PROTOCHLORIDE OF MERCURY** (Hg_2 Cl) as a shining white, fine powder. Cold hydrochloric acid, and cold nitric acid, do not dissolve this precipitate; but it dissolves, although very difficultly and slowly, when long boiled with these acids, being converted by hydrochloric acid into chloride of mercury, by nitric acid into chloride of mercury and per-nitrate of mercury. Ammonia and potash decompose protochloridc of mercury, giving rise to the formation of black protoxide of mercury.

5. If a drop of a neutral or feebly acid solution of protoxide of mercury be poured on a *clean and smooth surface of copper*, washed off after some time, and the spot rubbed with cloth or paper, &c. &c., it will appear of a **SILVERY**

WHITE COLOUR, with metallic lustre. This apparent silvering vanishes when the copper is heated, owing to the volatilization of the metallic mercury precipitated on its surface.

6. *Protochloride of tin* produces in solutions of protoxide of mercury, a gray precipitate of METALLIC MERCURY, which may be united into globules by heating and agitating it, but most easily by boiling it with hydrochloric acid.

7. If mercury compounds, intimately mixed with effloresced *carbonate of soda*, and covered with a layer of carbonate of soda in a distended glass-tube, are heated before the blow-pipe, a decomposition always takes place to the effect of liberating metallic mercury, which sublimes as a gray crust above the heated part of the tube. The fine particles of mercury unite into globules on this crust being rubbed with a glass rod.

c. OXIDE OF LEAD. ($Pb\,O$.)

1. The salts of oxide of lead are colourless and not volatile; the soluble salts, when neutral, redden litmus paper, and are decomposed at a red heat.

2. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce black precipitates of SULPHURET OF LEAD, ($Pb\,S$,) which are insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium. This sulphuret of lead is decomposed by boiling concentrated nitric acid; all the lead is first converted into nitrate of lead, the greater portion of the sulphur separates, another portion is converted into sulphuric acid, and this again decomposes a part of the nitrate of lead, and thus, besides the precipitated sulphur, sulphate of lead is formed, and remains undissolved as a white powder.

3. *Potash* and *ammonia* throw down BASIC SALT OF LEAD in the form of white precipitates, which are insoluble in ammonia, and of difficult solution in potash.

4. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions heavy white precipitates of CHLORIDE OF LEAD, ($Pb\,Cl$,) which are soluble in much water, especially if the water be heated. This chloride of lead

is not altered by ammonia, and is more difficult of solution in hydrochloric acid and in nitric acid than in water.

5. *Sulphuric acid* and *sulphates* produce white precipitates of SULPHATE OF LEAD, ($Pb\,O, SO_3$,) which are almost insoluble in water and dilute acids, but to a small extent soluble in concentrated nitric acid, difficult of solution in boiling concentrated hydrochloric acid, and more easily soluble in solution of potash. Salts of ammonia, and especially sulphate of ammonia, prevent the precipitation partly or altogether.

6. *Chromate of potash* produces a yellow precipitate of CHROMATE OF LEAD, ($Pb\,O, Cr\,O_3$) which is easily soluble in potash, but insoluble in dilute nitric acid.

7. Lead compounds, mixed with *carbonate of soda*, and on a charcoal support, exposed to the *reducing blow-pipe flame*, very easily yield soft and ductile METALLIC GLOBULES; whilst the coal is, at the same time, covered with a YELLOW incrustation of OXIDE OF LEAD.

Recapitulation and remarks.—The metallic oxides of the first section of the fifth group are the most easily characterized in their corresponding chlorides, since the divers relations of these different chlorides to ammonia afford us means as well of detecting as of separating them from each other. For chloride of silver, as we have stated, is dissolved by ammonia, whilst protochloride of mercury and chloride of lead remain undissolved. By adding nitric acid to a solution of chloride of silver and ammonia, we may again precipitate the chloride of silver; and as this reaction admits of no mistake, we want in fact no further means for the detection of silver. Of the two remaining chlorides, the protochloride of mercury is converted by ammonia into black protoxide of mercury, whilst the chloride of lead remains unaltered. The new-formed protoxide of mercury may be separated from the chloride of lead by treating with nitric acid, whereby the protoxide of mercury is dissolved; or by boiling with water, when solution of the chloride of lead takes place. These relations sufficiently characterize the protoxide of mercury; as further tests for lead, its reaction with sulphuric acid or with chromate of potash may be employed.

§ 91.

SECOND SECTION OF THE FIFTH GROUP. OXIDES WHICH ARE NOT PRECIPITATED BY HYDROCHLORIC ACID.

Special Reactions.

a. PEROXIDE OF MERCURY. (HgO.)

1. The salts of peroxide of mercury volatilize when heated to redness, some with, some without decomposition. Most of them are colourless. The neutral soluble salts redden litmus paper. The nitrate and sulphate of peroxide of mercury are decomposed by much water into soluble acid and insoluble basic salts.

2. If *sulphuretted hydrogen*, or *hydrosulphuret of ammonia*, be added in very small proportions to solutions of peroxide of mercury, and these solutions be then agitated, a perfectly white precipitate is obtained. The addition of somewhat large quantities of these reagents causes the precipitate to acquire a yellow, orange, or brown-red colour, as more or less of them is added; an excess of the precipitate produces a black precipitate of BISULPHURET OF MERCURY, CINNABAR. (HgS.) This variation of colour depends on the different proportions added of sulphuretted hydrogen, distinguishing the peroxide of mercury from all other substances. It is caused by the formation, at first, of a white-coloured double compound of bisulphuret of mercury, with still undecomposed salt of peroxide of mercury, which then, becoming more and more mixed with black bisulphuret, causes the precipitate successively to assume the various tints described above. Bisulphuret of mercury is not dissolved by hydrosulphuret of ammonia, nor by cyanide of potassium; it is quite insoluble in hydrochloric acid and nitric acid, even on being boiled with these acids. Potash ley dissolves it completely, and aqua regia decomposes and dissolves it with facility.

3. *Potash*, when added in insufficient quantity to neutral or feebly acid solutions of peroxide of mercury, yields with them a RED-BROWN precipitate, which acquires a YELLOW tint when the reagent is added in excess. The *red-brown* precipitate is a BASIC SALT; the yellow, on the contrary, consists of pure HYDRATED PEROXIDE OF MERCURY. (Hg.

O, HO.) An excess of the precipitant does not re-dissolve these precipitates. In very acid solutions this reaction either does not take place at all, or is at least incomplete. If salts of ammonia be present, the precipitates formed are neither red, brown, nor yellow, but white; consisting of basic compounds of peroxide of mercury and ammonia.

4. *Ammonia* causes the same WHITE PRECIPITATE, which potash produces when salts of ammonia are present.

5. *Protochloride of tin*, when added in small proportions to salts of peroxide of mercury, causes a reduction of this peroxide to protoxide, in consequence of which a white precipitate of PROTOCHLORIDE OF MERCURY forms; but when added in excess, it completely withdraws the oxygen and acid or the salt-radical from the mercury and causes the latter to separate in a metallic form, just as is the case with protoxide of mercury, (vide § 90, *b* 6.) The precipitate, therefore, which in the first place was white, acquires now a gray tint, and may be united into globules of metallic mercury, by being boiled with hydrochloric acid.

5. The salts of peroxide of mercury present the same relation to metallic *copper* as those of the protoxide; and the same is the case with regard to their behaviour before the blow-pipe, when mixed with *carbonate of soda.*

b. OXIDE OF COPPER. (Cu O.)

1. The salts of oxide of copper undergo decomposition, even at a gentle red heat, with the exception of blue vitriol, which can bear a somewhat higher temperature. They present in their anhydrous state a white, but as hydrates, a blue or green colour, which their solutions still retain, though rather highly diluted. Most of the neutral salts of oxide of copper are soluble in water; those which are soluble redden litmus paper.

2. *Sulphuretted hydrogen* and *hydrosulphuret* of ammonia produce, under any circumstances, brown-black precipitates of BISULPHURET OF COPPER (Cu S.) This substance is insoluble in dilute acids and caustic alkalies, as well as in hot solutions of sulphuret of potassium and

of sulphuret of sodium; but it is not quite insoluble in hydrosulphuret of ammonia, on account of which this reagent is not applicable for the separation of bisulphuret of copper from other metallic sulphurets. Boiling concentrated nitric acid readily decomposes and dissolves bisulphuret of copper. Solution of cyanide of potassium dissolves it completely.

3. *Potash* produces a bright blue, bulky precipitate of HYDRATED OXIDE OF COPPER, ($Cu\,O,\ HO.$) In highly concentrated solutions this precipitate becomes, on addition of potash in excess, black, and loses its bulkiness, even at a low temperature, after some time, but at any rate on being boiled with the fluid wherein it is suspended. In this process the hydrated oxide is converted into oxide.

4. *Ammonia,* when added in a small proportion, produces a GREENISH BLUE precipitate, consisting of a BASIC SALT OF COPPER. This precipitate is easily redissolved when the addition of ammonia is continued and a PERFECTLY TRANSPARENT MAGNIFICENTLY AZURE BLUE SOLUTION obtained, which owes its colour to the new-formed BASIC AMMONIACAL SALT OF OXIDE OF COPPER. This tint vanishes only when the solution is highly diluted. Potash causes in this blue solution—(at a low temperature only after having been allowed to stand at rest for some time)—a precipitate of BLUE HYDRATED OXIDE, but at the boiling point, it precipitates the entire copper as BLACK OXIDE. Carbonate of ammonia presents the same relation to salts of copper, as pure ammonia.

5. *Ferrocyanide of potassium* produces even in highly-dilute solutions, a reddish-brown precipitate of FERROCYANIDE OF COPPER ($Cfy + 2\,Cu$) which is insoluble in dilute acids, but decomposed by potash.

6. *Metallic iron,* when in contact with concentrated solutions of copper, is almost immediately covered with a COPPERY RED CRUST OF METALLIC COPPER; but when the copper solution is highly dilute, this coating only takes place after the lapse of some time. This test is very delicate, but especially so, when the solution contains a free acid, (e. g. hydrochloric acid.)

7. If copper compounds, mixed with *carbonate of soda,* be exposed on a charcoal support to the *reducing flame of*

the blow-pipe, METALLIC COPPER is obtained without simultaneous incrustation of the coal. The best method of examining this copper, so as to leave no doubt of its presence, is to triturate the fused mass together with the surrounding particles of the charcoal support, in a mortar with some water, and then to wash off the charcoal powder. The coppery-red metallic spangles will remain.

c. OXIDE OF BISMUTH. ($Bi\,O$.)

1. The salts of bismuth are not volatile, with the exception of a few, (chloride of bismuth.) Most of them decompose at a red heat. They are colourless; some are soluble in water, whilst others are insoluble. The soluble salts, when neutral redden litmus paper, and are decomposed by much water into soluble acid and insoluble basic salts.

2. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce, under all circumstances, black precipitates of SULPHURET OF BISMUTH ($Bi\,S$) which are insoluble in dilute acids, alkalies, alkaline sulphurets, and cyanide of potassium. Boiling concentrated nitric acid readily decomposes and dissolves it.

3. *Potash* and *ammonia* throw down from solutions of salts of bismuth, HYDRATED OXIDE OF BISMUTH ($Bi\,O, HO$) as a white precipitate, which is insoluble in an excess of he precipitants.

4. *Chromate of potash* precipitates CHROMATE OF BISMUTH ($Bi\,O, Cr\,O_3$) as a yellow powder. This substance differs from chromate of lead, inasmuch as it is soluble in dilute nitric acid, and insoluble in potash.

5. The reaction which particularly characterizes the oxide of bismuth, is the decomposition of its neutral salts by *water* into acid soluble and basic insoluble salts. For when a solution of bismuth is diluted with much water, a shining white precipitate immediately forms, provided free acid be not present in a too large proportion. This reaction is the most susceptible with chloride of bismuth, the basic chloride of bismuth being almost absolutely insoluble in water. If water causes no precipitate in nitric solutions of bismuth, owing to the presence of a too large quantity of free acid, precipitation may immediately be induced by the addition of basic acetate of lead in excess.

Before recurring to this means, we must, of course, be convinced of the absence of sulphuric acid, &c. &c. The precipitates of bismuth are easily to be distinguished by means of their insolubility in tartaric acid, from the basic salts of antimony which are formed under analogous circumstances.

6. If bismuth compounds, mixed with *carbonate of soda*, be exposed on a charcoal support, to the *reducing flame*, BRITTLE GRAINS OF BISMUTH are obtained, which fly into pieces under the stroke of the hammer. The charcoal at the same time becomes covered with a slight yellow incrustation of OXIDE OF BISMUTH.

d. OXIDE OF CADMIUM. ($Cd\,O.$)

1. The salts of oxide of cadmium are either colourless or white; most of them are soluble in water. The soluble salts, when neutral, redden litmus paper and decompose at a red heat.

2. *Sulphuretted hydrogen* and *hydrosulphuret of ammonia* produce, under all circumstances, precipitates of a rich yellow colour, consisting of sulphuret of cadmium ($Cd, S.$) This substance is insoluble in dilute acids, in alkalies, alkaline sulphurets, and cyanide of potassium. Boiling concentrated nitric acid readily decomposes and dissolves it.

3. *Potash* produces a white precipitate of HYDRATED OXIDE OF CADMIUM ($Cd\,O, HO$) which is insoluble in an excess of the precipitant.

4. *Ammonia* also precipitates white HYDRATED OXIDE OF CADMIUM, but readily redissolves into a colourless fluid, when added in excess.

5. *Carbonate of potash* and *carbonate of ammonia* produce white precipitates of CARBONATE OF CADMIUM ($Cd\,O, CO_2$) which are insoluble in an excess of the precipitants. The presence of salts of ammonia does not prevent the formation of these precipitates.

6. If cadmium compounds mixed with *carbonate of soda* be exposed on a charcoal support, to the *reducing flame*, the charcoal becomes covered with a REDDISH YELLOW incrustation of OXIDE OF CADMIUM, owing to the re-

duced metal immediately volatilizing, and then becoming reoxidized in passing through the oxidizing flame.

Recapitulation and remarks.—The metallic oxides of the second section of the fifth group may, as we have stated, be completely separated, by means of hydrochloric acid, from protoxide of mercury and oxide of silver, but only incompletely from oxide of lead. The peroxide of mercury is distinguished from the other oxides of this section, by the insolubility of its bisulphuret in boiling nitric acid. This property affords a convenient means for its separation. Moreover, the reactions with protoxide of tin, or with metallic copper, as well as those in the dry way, readily admit of its detection when the protoxide has been previously removed.

Of the still remaining oxides, those of copper and cadmium are distinguished, inasmuch as the precipitates which ammonia causes in their solutions, are soluble in an excess of ammonia, whilst the precipitates which this reagent produces in solutions of lead and bismuth, are not redissolved by an excess of the precipitant. The oxide of bismuth may be separated from the oxide of lead by means of sulphuric acid, but is most safely detected by the decomposibility of its salts by water. The other tests of lead have already been stated in the first section of this group. The oxide of copper may be separated from the oxide of cadmium, by means of carbonate of ammonia; the former is especially characterized by the reactions with ferrocyanide of potassium and with iron, as well as by its relations before the blow-pipe; and oxide of cadmium may always be detected by its yellow sulphuret, which is insoluble in hydrosulphuret of ammonia, and by the characteristic incrustation with which it covers charcoal when exposed to the reducing flame. For a separation of the oxides of the fifth group from each other, by means of cyanide of potassium, we refer to the second section of Part II.

§ 92.

Sixth Group.

PEROXIDE OF GOLD, PEROXIDE OF PLATINUM, OXIDE OF ANTIMONY, PEROXIDE OF TIN, PROTOXIDE OF TIN, ARSENIOUS AND ARSENIC ACID.*

Properties of the group.—The sulphurets corresponding with the oxides of the sixth group are insoluble in dilute acids. They combine with alkaline sulphurets, forming soluble sulphur salts, in which compounds they perform the part of an acid. Sulphuretted hydrogen, therefore, precipitates them completely from acidified, but not from alkaline solutions. The precipitated sulphurets dissolve in hydrosulphuret of ammonia, sulphuret of potassium, &c. &c., and are again precipitated from these solutions by the addition of acids.

We divide the oxides of this group into two classes, and distinguish,

1. OXIDES THE CORRESPONDING SULPHURETS OF WHICH ARE INSOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID, viz. peroxide of gold and peroxide of platinum, from

2. THOSE THE CORRESPONDING SULPHURETS OF WHICH ARE SOLUBLE IN HYDROCHLORIC ACID OR NITRIC ACID, viz. oxide of antimony, protoxide and peroxide of tin, arsenious and arsenic acid.

§ 93.

First Class.

Special Reactions.

a. PEROXIDE OF GOLD. ($Au\ O_3$.)

1. Salts of gold with oxygen acids are, at present, almost unknown. The haloid salts of gold are yellow, and their

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* The two acids of arsenic will be again referred to, when we treat of the relations between acids and reagents. We join them here to the metallic oxides, since the relation of sulphuret of arsenic easily admits of their being confounded with several oxides of the sixth group, and because in analysis we always obtain the sulphuret of arsenic as a precipitate, together with sulphuret of antimony, sulphuret of tin, &c. &c.

solutions present this tint up to a high degree of dilution. They all readily decompose at a red heat; the soluble salts, when neutral, redden litmus paper.

2. *Sulphuretted hydrogen* precipitates from neutral and acid solutions all the gold they contain, as black SULPHURET OF GOLD ($Au\ S_3$) which is insoluble in potash and in any single acid, but soluble in alkaline sulphurets and in aqua regia.

3. *Hydrosulphuret of ammonia* produces the same precipitate. A considerable excess of the precipitant redissolves it.

4. *Potash* in excess causes no precipitation, but a small proportion of potash produces in concentrated solutions, especially when heated, a reddish yellow precipitate of PEROXIDE OF GOLD, which is always mixed with an auric salt of chloride of gold, as well as with potash.

5. *Ammonia* produces also only in concentrated solutions, reddish yellow precipitates of AURATE OF AMMONIA (fulminating gold.)

6. *Protochloride of tin*, containing perchloride of tin, produces even in highly dilute solutions of gold, a purple-red precipitate or tint at least, which sometimes inclines more to violet or to brown-red. This precipitate has received the name of PURPLE OF CASSIUS; it is a mixture of peroxide of tin and metallic gold, and is insoluble in hydrochloric acid.

7. *Protosalts of iron* reduce the peroxide of gold when added to its solutions, and precipitate metallic gold as a very fine brown powder, which shows a metallic lustre, when pressed upon with the blade of a knife, or when rubbed. The fluid in which the precipitate is suspended, appears of a blackish-blue colour, by transmitted light.

b. PEROXIDE OF PLATINUM. ($Pt\ O_2$.)

1. The persalts of platinum decompose at a red heat. They are of a red-brown colour, which their solutions still show, though considerably diluted. The soluble salts when neutral redden litmus paper.

2. *Sulphuretted hydrogen* precipitates from acid and neutral solutions—(but not from alkaline solutions)—after

the lapse of some time blackish-brown SULPHURET OF PLATINUM ($Pt S_2$.) Potash and alkaline sulphurets dissolve it when added greatly in excess. Sulphuret of platinum is insoluble in hydrochloric acid as well as in nitric acid, but dissolves readily in aqua regia.

3. *Hydrosulphuret of ammonia* produces the same precipitate, which completely redissolves in a large excess of the precipitant. Acids precipitate it again unaltered from this solution.

4. *Potash* and *ammonia* produce in solutions of platinum when not too highly dilute, yellow crystalline precipitates of CHLORIDE OF PLATINUM AND POTASSIUM and of CHLORIDE OF PLATINUM AND AMMONIA, which are insoluble in acids, but soluble in an excess of the precipitants, upon the application of heat. The presence of free hydrochloric acid promotes the precipitation in a high degree, by effecting the conversion of the free alkalies into chlorides.

5. Protochloride of tin [illegible]parts an INTENSE DARK BROWNISH RED COLOUR to solutions of persalts of platinum, but without yielding a precipitate; this reaction is owing to a reduction of the peroxide or the perchloride to protoxide or protochloride.

Recapitulation and remarks.—The reactions of gold and platinum afford, at least partly, the means of detecting these metals as well when many other oxides are present, as also and especially, when platinum and gold are contained in one and the same solution. Protochloride of tin and protoxide of iron must be mentioned here as particularly characteristic tests of gold, and with regard to platinum the same may be said of potash and ammonia with the presence of free hydrochloric acid, or what, in fact, is the same, of chloride of potassium and muriate of ammonia.

§ 94.

Second Class of the Sixth Group.

Special Reactions.

a. OXIDE OF ANTIMONY. ($Sb O_3$.)

1. The salts of oxide of antimony partly decompose at a red heat; the haloid salts volatilize readily, and without

undergoing decomposition. The soluble neutral salts of antimony redden litmus paper. The solution of oxide of antimony in hydrochloric acid is characterized by the nature of the decomposition it undergoes when diluted with water; in this decomposition, an acid salt remains in solution whilst a basic salt is thrown down as a white, bulky precipitate, which, however, after some time, becomes dense and crystalline. Tartaric acid readily dissolves this precipitate, and, consequently, prevents its precipitation when added to the solution before the dilution with water. It is by this property that the basic protochloride of antimony is distinguished from the basic salts of bismuth formed under analogous circumstances. The oxide of antimony, in whatever manner it may have been prepared, is completely soluble in a hot solution of bitartrate of potash.

2. *Sulphuretted hydrogen* precipitates the oxide of antimony from neutral solutions very incompletely, from alkaline solutions not at all, but from acid solutions completely, as orange-red SULPHURET OF ANTIMONY ($Sb\ S_3$.) This precipitate is readily dissolved by potash and by alkaline sulphurets, especially if the latter contain sulphur in excess, whilst it is almost insoluble in ammonia, and totally so in bicarbonate of ammonia, when free from any admixture of sulphur, as well as from sulphantimonious and sulphantimonic acid. It is insoluble in dilute acids. Concentrated boiling hydrochloric acid dissolves it, with evolution of sulphuretted hydrogen gas. When heated, with free access of air, it is converted into a mixture of antimonious acid with sulphuret of antimony. When deflagrated with saltpetre, it yields sulphate of potash and antimoniate of potash. If a potash solution of sulphuret of antimony be boiled together with oxide of copper, sulphuret of copper is formed, and oxide of antimony dissolved in potash remains in solution.

3. *Hydrosulphuret of ammonia* produces an orange-red precipitate of SULPHURET OF ANTIMONY, which readily redissolves in an excess of the precipitant. Acids precipitate from this solution the sulphuret of antimony unaltered. But the colour of this second precipitate usually appears somewhat lighter, owing to an admixture of sulphur.

4. *Potash, ammonia, carbonate of potash,* and *carbonate of ammonia,* throw down from the solutions of simple salts of oxide of antimony,—but not, at least not immediately, from those of tartar emetic or analogous compounds, —a white and bulky precipitate of HYDRATED OXIDE OF ANTIMONY $Sb\ O_3,\ HO$) which readily redissolves in an excess of potash, but is very difficult of solution in an excess of the other three precipitants.

5. *Metallic zinc* precipitates from all solutions of oxide of antimony, unless containing free nitric acid, METALLIC ANTIMONY as a BLACK POWDER. But if they contain free nitric acid, a precipitate of oxide of antimony forms simultaneously with the metallic precipitate.

6. If a solution of oxide of antimony is mixed with *zinc* and *sulphuric acid,* the zinc oxidizes not only at the expense of the oxygen of the water, but also at the expense of that of the oxide of antimony. Antimony, therefore, separates in its METALLIC STATE, but a portion of the metal in the moment of its separation combines with the liberated hydrogen of the water, forming ANTIMONIURETTED HYDROGEN ($Sb\ H_3$.) If this operation be conducted in a gas-evolution flask, connected by means of a perforated cork with one limb of a bent tube, the other limb of which ends in a finely drawn-out point, pinched off at the top,*) and the hydrogen passing through this fine aperture, be kindled, after all atmospheric air has been previously expelled, the flame appears of a bluish-green, owing to the antimony separating in a state of intense heat, during the combustion of the antimoniuretted hydrogen; white fumes of oxide of antimony rise from the flame, which readily condense upon cold substances, and are not dissolved by water. If a cold substance (such as a porcelain plate) be depressed upon the flame, a deep black and almost lustreless spot of metallic antimony in a state of minute division is formed upon the surface of the plate. If the tube through which the gas is passing be heated to redness in the middle, the bluish-

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* In very minute and exact experiments, it is necessary further to transmit the gas through another connecting tube, loosely filled with cotton, in order to prevent it from carrying with it any moisture with which it may be charged, into the emission part of the tube. Vide engraving of Marsh's apparatus for the reduction of arsenic, § 94 *d* 7.

green tint of the flame disappears, and a metallic mirror of antimony of silvery lustre is formed within the tube on both sides of the heated spot. If a stream of dry sulphuretted hydrogen be now very slowly transmitted through this tube, and the mirror be heated by a spirit-lamp, from its outer towards its inner extremity, i. e. in a direction opposite to that of the gas stream, the mirror of antimony changes into sulphuret of antimony, which appears of a more or less red-yellow colour, and almost black when in thick layers. If a weak stream of dry hydrochloric acid gas be then transmitted through the same glass tube, the sulphuret of antimony disappears, immediately, when only present in thin layers, and, after a few seconds, when the incrustation is somewhat thicker. For sulphuret of antimony readily decomposes with hydrochloric acid gas, and the nascent chloride of antimony is very volatile in the stream of hydrochloric acid gas. If this gas stream be transmitted through water, the presence of antimony in the latter may easily be proved by means of sulphuretted hydrogen. By this combination of reactions, antimony may be distinguished with certainty from all other metals.

7. If compounds of antimony mixed with *carbonate of soda*, on a charcoal support, be exposed to the *reducing blow-pipe flame*, BRITTLE GLOBULES OF METALLIC ANTIMONY are obtained. At the same time, volatilization of the reduced and reoxidized metal takes place, which, even after the removal of the test specimen from the flame, continues for some time, and becomes especially evident when a stream of air is directed by means of the blow-pipe upon the surface of the cooling mass. The oxide formed is partly deposed on the charcoal as a white crust, and partly surrounds the metallic globule in the form of fine crystalline needles.

b. PROTOXIDE OF TIN. (SnO.)

1. The protosalts of tin are colourless, and decompose when heated. The soluble salts when neutral, redden litmus paper. When solutions of neutral stannous salts are diluted with water, they become turbid and of a milky-white colour, owing to their decomposition into soluble acid and insoluble basic salts. The addition of hydrochloric acid causes the milkiness to disappear.

2. *Sulphuretted hydrogen* precipitates from neutral and acid, but not from alkaline solutions, dark brown SULPHURET OF TIN, (SnS,) which is soluble as well in potash and in alkaline sulphurets, especially in such as contain larger proportions of sulphur, as also in concentrated boiling hydrochloric acid. Boiling nitric acid converts it into insoluble peroxide of tin.

3. *Hydrosulphuret of ammonia* occasions the same precipitate of SULPHURET OF TIN, which very sparingly dissolves in an excess of the precipitant. If the hydrosulphuret of ammonia has already turned yellow, i. e. if it contains an excess of sulphur, or if finely powdered sulphur be added, the solution is much facilitated. From this solution, in hydrosulphuret of ammonia, with excess of sulphur, acids precipitate yellow bisulphuret of tin mixed with sulphur.

4. *Potash, ammonia, carbonate of potash,* and *carbonate of ammonia,* produce a white and bulky precipitate of HYDRATED PROTOXIDE OF TIN, (SnO, HO,) which readily dissolves in an excess of potash, but is insoluble in an excess of the other three precipitants.

5. *Perchloride of gold* produces in solutions of protochloride or protoxide of tin, a precipitate or tinge of PURPLE OF CASSIUS, on the addition of some nitric acid, (without the application of heat,) vide § 93, *a.* 6.

6. If to a solution of protochloride or protoxide of tin, solution of *perchloride of mercury* be added in excess, a white precipitate of PROTOCHLORIDE OF MERCURY will be formed owing to the salt of tin depriving the perchloride of mercury of half its chlorine.

7. If proto-compounds of tin be mixed with *carbonate of soda* and some *borax*, or better still, with equal parts of *carbonate of soda* and *cyanide of potassium*, and then, on a charcoal support, be exposed to the *inner blow-pipe flame*, ductile grains of METALLIC TIN will be obtained, without simultaneous incrustation. They may be most easily detected by scraping off the specimen and the particles surrounding, that part of the charcoal which contained the specimen, strongly triturating them in a mortar, and washing the coal off from the metallic particles.

c. PEROXIDE OF TIN. ($Sn O_2$.)

1. Peroxide of tin exists in two modifications which exhibit a different relation to solvents. When precipitated from its salts, by alkalies, it is easily soluble both in potash and acids, but when produced by oxidation of metallic tin by means of nitric acid, it is insoluble in these solvents, (the precipitated oxide of tin also becomes insoluble on being heated to redness.) The insoluble modification is converted into the soluble, by fusion with carbonate of soda.

2. The persalts of tin are colourless and decompose at a red heat. The soluble neutral persalts of tin redden litmus paper.

3. *Sulphuretted hydrogen* throws down, from acid and neutral solutions, a yellow precipitate of BISULPHURET OF TIN, ($Sn S_2$.) Alkaline solutions are not precipitated. The bisulphuret of tin is soluble in pure alkalies, in alkaline carbonates and bicarbonates, in alkaline sulphurets, and in concentrated and boiling hydrochloric acid. Nitric acid converts it into insoluble peroxide of tin. On deflagrating bisulphuret of tin with nitre, sulphate of potash, and stannate of potash are formed. If a solution of bisulphuret of tin in potash be boiled with oxide of copper, sulphuret of copper and peroxide of tin will be formed, which latter substance remains in solution in the potash.

4. *Hydrosulphuret of ammonia* produces the same precipitate of BISULPHURET OF TIN, which readily redissolves in an excess of the precipitant. Acids reprecipitate from their solution, the bisulphuret of tin in its unaltered state.

5. *Potash* and *ammonia*, *carbonate of potash* and *carbonate of ammonia*, precipitate a white HYDRATED PEROXIDE OF TIN, which readily redissolves in potash and carbonate of potash (in excess,) but is sparingly soluble in ammonia, and quite insoluble in carbonate of ammonia.

6. *Metallic zinc* precipitates, from solutions of perchloride or persalts of tin, when containing no free nitric acid, METALLIC TIN, in the shape of small gray leaves or as a spongy mass. If, on the contrary, nitric acid be present, white peroxide or a mixture of metallic tin and of peroxide of tin will precipitate.

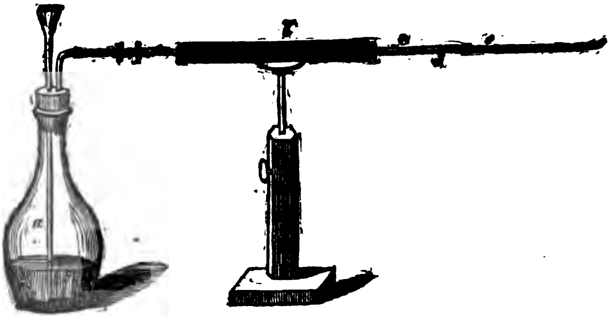
7. The per-compounds of tin exhibit the same properties before the blow-pipe as the proto-compounds.

d. ARSENIOUS ACID. ($As\,O_3$.)

1. Arsenious acid on being heated volatilizes in white inodorous vapours. Its salts, on being heated to redness, generally are decomposed into fixed arseniates and arsenic, which volatilizes. Of the arsenites, only those with an alkaline base are soluble.

2. *Sulphuretted hydrogen* precipitates the solutions of arsenious acid and of neutral arsenites, slowly and incompletely, but when a free acid is present, totally and immediately; these precipitates have a lively yellow colour. Alkaline solutions are not precipitated. The yellow precipitate of SULPHO-ARSENIOUS ACID, ($As\,S_3$,) is readily and completely redissolved in pure alkalies, in alkaline carbonates and bicarbonates, and in alkaline sulphurets, but is almost insoluble in hydrochloric acid. Boiling nitric acid readily decomposes and dissolves it. On deflagrating it with carbonate of soda and nitrate of potash, arseniated alkali and sulphated alkali are obtained. When a solution of sulpharsenious acid in potash is boiled with oxide of copper, sulphuret of copper and arseniate of potash are formed; and when the same solution is boiled with pure oxide of bismuth, or with a carbonate of basic nitrate of the same substance, sulphuret of bismuth and arsenious acid are formed. If sulpharsenious acid be mixed with from three to four parts of carbonate of soda, with the addition of some water, and the magma be then spread over some small glass splinters, and the latter, after having been well dried, be rapidly heated to redness, in a glass tube, (*c.* vide sketch,) through which dry hydrogen gas is transmitted, half of the arsenic contained in the mixture forms a metallic mirror within the tube. For when fusing two eq. of sulpharsenious acid, together with four eq. of soda sulpharsenico sulphuret of sodium and arsenite of soda are formed; heating these products in hydrogen gas, all the arsenic is expelled, if the heat is strong and continuous. This method, although a great portion of the reduced arsenic is carried off, suspended in the hydrogen gas, yields, nevertheless, very good results. If the hydrogen

gas be kindled at the exit aperture of the tube *c*, and a cold porcelain plate depressed on the flame, this arsenic (carried away with the hydrogen gas) will condense upon the plate. If a red heat be applied to another part of the tube *c*, more towards its anterior aperture, (the part first heated being at the same time maintained at a red heat,) another sublimate will be formed beyond the heated spot, the particles of arsenic carried away with the stream of the hydrogen gas, being reconverted, at the red hot spot, into arsenic vapours in a state of expansion, and thus condensing again as a sublimate, on coming into contact with the cold part of the glass tube. If the heat thus simultaneously applied to two parts of the tube be strong, whilst the stream of the hydrogen gas is feeble, scarcely any arsenic will be carried away with the gas. No arseniuretted hydrogen is formed in this operation and those who explain the phenomena just described, by the formation of arseniuretted hydrogen, are in error. (Fresenius and Babo.) The apparatus may be constructed as in the annexed sketch.



a is the evolution flask, *b* a tube containing chloride of calcium, *c* the tube in which, at the point *d*, the glass splinter with the specimen is placed. This part is then (the apparatus being completely filled with pure hydrogen gas) exposed to a slight heat, at first, in order to expel all moisture, and then suddenly to a very strong heat, (this is best done with a blow-pipe,) to prevent the sublimation of undecomposed sulphuret of arsenic. The metallic mirror is formed near the point *e*.

3. *Hydrosulphuret of ammonia* causes also the formation of SULPHARSENIOUS ACID. In neutral or alkaline solutions, however, this substance is not precipitated, but remains in solution as sulpharsenico sulphuret of ammonia. On the addition of free acid it precipitates immediately from this solution.

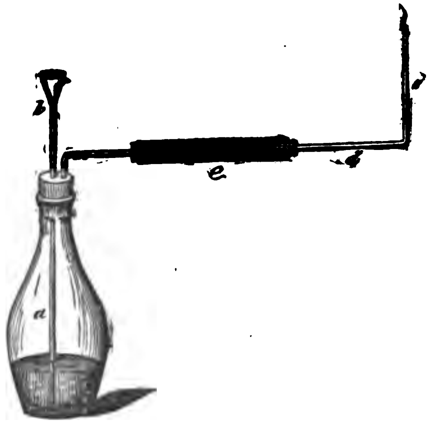
4. *Nitrate of silver* produces in neutral solutions of the arsenites, a yellow precipitate of ARSENITE OF SILVER, ($2\ Ag\ O,\ As\ O^3$.) which is soluble both in dilute nitric acid and in ammonia. AMMONIO-NITRATE OF SILVER yields the same precipitate with solutions of arsenious acid or arsenites when containing free acid.

5. *Sulphate of copper* and *ammonio-sulphate of copper* produce, under the same circumstances as the salts of silver, yellow-green precipitates of ARSENITE OF COPPER, ($2\ Cu\ O,\ As\ O^3$.)

6. If arsenious acid be dissolved in solution of caustic potash in excess, or if the solution of an alkaline arsenite be mixed with caustic potash, and a few drops of a dilute solution of sulphate of copper be added and the mixture boiled, a red precipitate of protoxide of copper is formed, and arseniate of potash remains in solution. This reaction is highly sensible, provided only a minute quantity of solution of blue vitriol be used. If the red precipitate of protoxide of copper is no longer distinctly visible on the light falling through the tube in which the solution is contained, it will yet be distinctly seen on looking in at the top of the tube. That this reaction, though really important in individual cases as a confirmatory test of arsenious acid, and especially as a means of distinguishing arsenious acid from arsenic acid, yet cannot be employed as a means of directly detecting the presence of arsenic, is a matter of course, since grape sugar and other organic substances in the same manner separate protoxide of copper from salts of copper.

7. If an acid or neutral solution of arsenious acid, or of an arsenite, be mixed with zinc, water, and sulphuric acid, ARSENIURETTED HYDROGEN ($As\ H_3$) will be formed; for the mode of its formation we refer to § 94, *a* 6. This property of arsenic affords us a most delicate test for its detection, and a highly important means for its isolation. The

operation is, under all circumstances, conducted in the apparatus alluded to, § 94, *a* 6, of which we annex a sketch.



a is the evolution flask, containing fragments of metallic zinc, and water; *b* a funnel tube, through which the sulphuric acid, and afterwards the liquor to be tested for arsenic, are poured into the flask; *c* is a glass tube, loosely filled with smooth cotton, to which a bent tube, *d*, is fitted by means of a perforated cork; this tube is drawn out into a point, at its emission extremity, *e*, and pinched off at the top. When the evolution of hydrogen has proceeded for some considerable time, so that it may safely be inferred that all atmospheric air has been expelled from the apparatus, the gas is kindled at the emission aperture of the tube, *d*, *e*. (It is advisable to envelop the flask with a piece of cloth before kindling the gas, as an effectual means of preventing any accident, should an explosion take place.) It is absolutely necessary to ascertain, first, whether the zinc and the sulphuric acid are quite free from arsenic. For this purpose, 1st, a porcelain plate is depressed upon the flame, and, 2d, the tube *d e* is heated to redness in the middle, the limb *e* being turned into a horizontal position for this purpose. If no incrustation be formed, neither on the plate nor in the tube, the zinc and sulphuric acid contain no arsenic. The liquor to be tested is then introduced into the flask through the funnel tube. If it contain arsenic, arseinuretted hydrogen will be evolved together with the hydrogen, imparting a bluish tint to the flame, owing to the arsenic separating at a red heat. At the same time white fumes of arsenious acid are observed, which condense upon cold objects. If a porcelain plate be now depressed upon the flame, black spots are formed on its surface, owing to the reduced and not yet reoxidized arsenic condensing on the plate. (Vide antimony, § 94, *a* 6.) Arsenic spots are of a rather blackish brown colour, and bright metallic lustre; whilst those of antimony are of a deep black colour, and but very feebly lustrous. If the tube *d e* be heated to redness in the middle of its limb *d*, the arsenic will condense in the cold part of the tube, forming a particularly beautiful and distinct metallic crust, which is of a darker appearance and less silvery than that formed by antimony under similar circumstances; it may, moreover, be clearly detected by the characteristic odour of garlic which is perceived, if the tube is cut off near the incrustation, and the latter then volatilized by heat. The characteristic odour of alcarsin (vide 10 seq.) is even a safer indication than that of garlic. If the metallic spots of crust formed on the porcelain plate seem to indicate the presence of arsenic, it is still necessary to make quite sure that it is really arsenic and not antimony we have before us, for even the characteristic odour of garlic or alcarsin is not sufficient to set all doubts at rest as to this point. The following are the best methods of ascertaining the presence of arsenic beyond doubt:—

a, fine and distinct metallic mirror is formed within the tube through which the arseniuretted hydrogen passes, on heating its middle part to redness. A very feeble stream of dry sulphuretted hydrogen is then transmitted through this tube, with simultaneous application of the heat of a spirit-lamp to the metallic crust, from its outer towards its inner extremity. If arsenic alone be present, a yellow sulphuret of arsenic will be formed within the tube; and if antimony alone be present, an orange or black sulphuret of antimony: but if both metals be present, both sulphurets will be formed side by side, the sulphuret of arsenic, as the more volatile, always preceding the sulphuret of antimony. Not long ago, this conversion of antimony and arsenic into sulphurets was suggested as the surest means of distinguishing these two metals from each other. Experience has, however, taught us that these differences in colour and volatility are not striking enough to prevent the possibility of mistakes. But if dry hydrochloric acid gas be transmitted through the tube containing the deposit under examination, without application of heat, no alteration whatever will take place if sulphuret of arsenic alone is present, even if the gas be transmitted through the tube for a considerable time. If sulphuret of antimony alone be present, it will entirely vanish, and if both sulphurets be present, the sulphuret of antimony will vanish immediately, whilst the yellow sulphuret of arsenic remains. If a small quantity of ammonia be then introduced into the tube, the sulphuret of arsenic will dissolve, and may thus easily be distinguished from the sulphur, which, peradventure, may have separated. My personal experience has convinced me of the infallibility of these tests for the detection of arsenic.

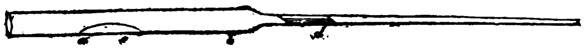
b. The limb *e* (vide sketch of the apparatus) is turned into an horizontal position, and the gas kindled and made to burn in a small glass receiver, having a capacity of about twelve ounces. This receiver is placed in a beaker glass filled with cold water, and constantly turned and moved, so as to prevent its becoming hot. After some time, when the oxygen in the receiver becomes exhausted, and the flame grows feeble, another is substituted for the first, and several are filled in this manner. They contain, 1st, arsenious acid alone, or, 2d, oxide of antimony alone, or, 3d, both together. If the first be the case, the white sublimate obtained will completely dissolve in hot water, and the solution may then be further tested for arsenic. In the second case, nothing will dissolve, nor in the third, if the oxide of antimony is present in sufficient quantity, as this gives rise to the formation of arsenite of antimony. The arsenic in this last case may be detected by dissolving the sublimate in slightly dilute solution of potash, and adding sulphuretted hydrogen first, and then bicarbonate of ammonia in excess. All the antimony will precipitate as sulphuret of antimony, whilst the sulphuret of arsenic remains dissolved in the excess of bicarbonate of ammonia.

The sulphuret of arsenic precipitates on the addition of hydrochloric acid to the solution, till an acid reaction becomes manifest. Marsh was the first who suggested the method of detecting arsenic by the production of arseniuretted hydrogen.

8. If arsenious acid or an arsenite be mixed with *carbonate of soda and charcoal*, and the mixture (which must be perfectly dry) be then heated over a spirit-lamp to redness, in a well-dried glass tube, closed at one end, and drawn out into a point at the other, the charcoal will oxidize at the expense of the oxygen of the arsenious acid, and arsenic will become liberated, which volatilizes and condenses above the heated part of the tube, forming a more or less dark brown metallic mirror of great lustre. This crust may be further driven on in the tube by gradually heating the latter to redness towards its emission aperture, and may thus finally be expelled, when the characteristic odour of arsenic (on volatilizing in the air) will afford a further proof of its presence. For the reduction of the free arsenious acid, a mere fragment of charcoal is used, instead of carbonate of soda and charcoal; the arsenious acid is introduced into the drawn-out point of the tube, the fragment of charcoal is placed over it and heated to redness; heat is then applied to the point of the tube. This process has the advantage over the former of not soiling the tube, which is done when operating with carbonate of soda and charcoal. The non-appearance of the metallic crust is not always a sure sign that no arsenic is present, when testing a supposed arsenite by means of carbonate of soda and charcoal, as there are several compounds of arsenious acid, especially of those with heavy metallic oxides, as e. g. oxide of iron, which do not yield metallic mirrors.

9. If arsenites, or arsenious acid, or a sulphuret of arsenic, be fused together with a mixture of dry carbonate of soda and cyanide of potassium, all the arsenic contained in the test specimen will become reduced, under all circumstances, and sometimes the bases also, if their properties admit of this reduction; in this process the oxygen which these substances lose, converts a portion of the cyanide of potassium into cyanate of potash. The opera-

tion is conducted in the following manner:—the arsenic compound, which must be perfectly dry, is put into a small glass tube, expanded into a bulb at one end, and covered with six times its quantity of the mixture of perfectly dry carbonate of soda and cyanide of potassium. The quantity of the whole mass must not fill more than half of the bulb, or else the cyanide of potassium, when in fusion, will get into the tube. The heat of a spirit-lamp is then applied to the bulb, and continued, as the arsenic often requires some time for its complete sublimation. The mirrors which are obtained in this process are of exceeding purity. These crusts are produced from all arsenites, the bases of which remain either altogether unreduced, or are converted into such arseniurets as partly or totally lose their arsenic on the simple application of heat. This method may be especially recommended on account of its simplicity, neatness, and cleanness, as well as for the certainty of its results, even though but minute quantities of arsenic be present. It is especially adapted for the direct production of arsenic from sulphuret of arsenic, and is, in this respect, superior to all other methods suggested. The most exact results are obtained by placing the sulphuret of arsenic, rubbed together with twelve times its amount of a mixture consisting of three parts of dry carbonate of potash, and one part of cyanide of potassium, into a glass tube, open at its anterior extremity.



The mixture is best introduced into the tube by means of a slip of paper, folded into the shape of a gutter. This paper containing the mixture is inserted into the tube, and the latter then being turned half way round its axis, the powder falls into it (at the spot *a c*) without soiling any other part. The tube is then gently heated in its entire length, transmitting at the same time a very slow stream of dry carbonic acid gas (dried by means of sulphuric acid) through it, till all water is expelled. The spot *b* is then heated to a feeble degree of redness, when, as this point is attained, the mixture is heated from *a* towards *c*, by means of a second lamp. The arsenic condenses at *d*, forming a crust of admirable purity. In this manner the most distinct metallic mirrors may be obtained, from one 260th part of a grain of sulphuret of arsenic, and even less. Fresenius and Babo.

10. If to arsenious acid (either in solid form or in solution) some acetic acid, and then some potash in excess, be added, the mixture evaporated to dryness, and the residue heated to redness in a tube, alcarsin (Oxide of cacodyl. $C_4\ H_6\ As+O$) will be formed, which is immediately detected by its characteristic and insupportable odour. This odour immediately changes into that not less characteristic of chloride of cacodyl, when the contents of the tube are again exposed to heat, with the addition of a few drops of protochloride of tin. This property affords us also a means of further testing the metallic crusts obtained by Marsh's apparatus. They are for this purpose boiled with water containing atmospheric air, till completely dissolved; acetic acid, and potash in excess, are then added to the solution, which is evaporated to dryness, the residue heated to redness in a small tube, and the further operation conducted as just now stated. Bunsen has recently suggested this method of testing crusts of arsenic; these are, however, but slowly dissolved in boiling water containing air.

11. If arsenious acid or an arsenite be exposed on a charcoal support to the *reducing flame of a blow-pipe*, a highly characteristic odour of garlic will be perceived, especially if some carbonate of soda be added to the test specimen. This odour is owing to the reduction and reoxidation of the arsenic, and enables us to detect even minute quantities of this substance. This test, however, cannot be implicitly relied upon. The garlic odour belongs neither to the vapour of arsenious acid, nor to those of arsenic, but probably to a lower degree of oxidation of the latter substance. It is always perceived on exposing arsenic to heat, with the free access of air.

e. ARSENIC ACID. ($As\ O_5$.)

1. Arsenic acid and the arseniates are volatile only at a *very* high degree of heat. Nearly all the arseniates are colourless, and insoluble in water, with the exception of the alkaline arseniates.

2. *Sulphuretted hydrogen* does not precipitate alkaline and neutral solutions; in acid solutions it produces a yellow precipitate of SULPHARSENIC ACID, ($As\ S_5$.) In dilute solutions this precipitate is often formed after the lapse of a considerable time (twenty-four hours.) Heat promotes its separation. The sulpharsenic acid shows the same relations as the sulpharsenious acid to these solvents and means of decomposition which we have mentioned when treating of the latter substance. If to a solution of free arsenic acid or of an arseniate, sulphurous acid is added, this latter substance decomposes with the arsenic acid, giving rise to the formation of arsenious acid and sulphuric acid. If sulphuretted hydrogen, and if needed, an acid be then added, all the arsenic will immediately precipitate as sulpharsenious acid.

3. *Hydrosulphuret of ammonia* in neutral and alkaline solutions, converts arsenic acid into sulpharsenic acid, which remains in solution as sulpharsenico-sulphuret of ammonium. This compound is decomposed on the addition of an acid, and sulpharsenic acid precipitates. This precipitation is more rapid than that from acid solutions by means of sulphuretted hydrogen. It is promoted by heat.

4. *Nitrate of silver* produces in neutral solutions of the arseniates highly characteristic reddish-brown precipitates of ARSENIATE OF SILVER, ($3\ Ag\ O,\ As\ O_5$) which is soluble both in dilute nitric acid and in ammonia. *Ammonio-nitrate of silver* yields the same precipitate with solutions of arsenic acid or arseniates.

5. *Ammonia-sulphate of copper* produces under the same circumstances as the salts of silver, greenish blue precipitates of ARSENIATE OF COPPER. ($2\ Cu\ O,\ As\ O_5$.)

6. The arseniates present the same relations as the arsenites to *hydrogen, to carbonate of soda, and charcoal,* to *cyanide of potassium* and before the *blow-pipe.*

Recapitulation and remarks.—The separation and safe detection of the oxides belonging to the second section of the sixth group, and especially of oxide of tin, presents difficulties under certain circumstances. The protoxide of tin may be easily and safely detected by its reaction with perchloride of gold, even in the presence of other oxides. The separation of peroxide of tin from oxide of antimony succeeds pretty well in the humid way by means of a hot solution of bitartrate of potash, or of a solution of free tartaric acid; but it succeeds only when the peroxide of tin is present in the form of the modification obtained by the action of nitric acid on metallic tin. To obtain this modification, it is necessary to reduce the substance under examination by means of zinc, if this substance is not an alloy; in this reduction the presence of nitric acid must be carefully avoided. The method of separating the sulphurets by means of ammonia gives rise to errors, as the higher degrees of sulphuration of the antimony are soluble in ammonia; and even the simple sulphuret of antimony is not absolutely insoluble in it, when mixed with a trace of free sulphur, which cannot easily be avoided. The presence of peroxide of tin is certain only when a ductile metallic grain of tin is obtained in the reducing flame; its ductility in this case enables us to distinguish it from antimony. This reduction is very easily effected before the blow-pipe by means of a mixture of equal parts of cyanide of potassium and carbonate of soda; but care should be taken that the peroxide of tin be not mixed with nitre, which causes it to deflagrate, &c. Peroxide of tin and oxide of antimony may be detected before the blow-pipe, even if combined, the antimony being distinguished by its characteristic oxidation crust, and the tin by its ductility after the volatilization of the antimony. Inexperienced students, however, generally fail in this method. Antimony may, moreover, be detected by the decomposition of chloride of antimony by means of water, and by the colour of its sulphuret. If the sulphuret of antimony is mixed with a large proportion of any of the sulphur-compounds of arsenic, this latter mark of detection is unsafe. In this case the mixed sulphurets may be heated to redness, which causes the sulphuret of arsenic to volatilize; and the residue may be dissolved in hydrochloric acid, and this solution again tested by means of sulphuretted hydrogen.

The detection of arsenic upon the whole can by no means be said to be difficult; but, nevertheless, frequent errors take place, especially if we content ourselves with drawing definite conclusions from individual reactions, such as the characteristic odour when heated on charcoal. We must, therefore, lay it down as a rule that the presence of arsenic can only be proved by a concurrence of the various reactions, and especially by the formation of metallic arsenic. It may be pretty completely separated from tin by deflagrating the sulphurets with carbonate of soda and nitre. The presence of tin does not, however, prevent the detection of arsenic. But the case is different with antimony, especially in testing by Marsh's method, which is now so generally followed. A metallic mirror obtained by Marsh's apparatus ought, therefore, never to be considered as a proof of the presence of arsenic, if further tests do not give the most certain conviction that the metallic crust is indeed produced by arsenic. And this conviction is sometimes very difficult to be obtained, when we operate upon very minute quantities, so that the formerly used methods of reduction are by far superior to Marsh's method, as far as *certainty* is concerned, although it cannot be denied that they do not equal it in delicacy, nor in rapidity and convenience. The complete separation of arsenic from antimony may be effected by means of bicarbonate of ammonia, the simple sulphuret of antimony being insoluble in this substance, whilst sulphuret of arsenic readily dissolves in it. But this method of distinction yields a positive and certain result only in a few cases, viz. in those where we are quite sure that the simple sulphuret of antimony cannot be mixed with a higher sulphuret of antimony, nor with free sulphur, whilst in all other cases it easily gives rise to mistakes. It is, therefore, exceedingly well adapted for the testing of the products of combustion obtained by means of Marsh's apparatus, (vide § 94, *d* 7, *b*,) but it cannot be used for the separation of the sulphurets obtained in the usual way. And even less complete are those separations of antimony from arsenic which are founded on the relations of their sulphurets to concentrated hydrochloric acid or to caustic ammonia. The separation of both metals from each other does not succeed even by dissolving the sulphuret in potash, and boiling the solution with oxide of copper. A far more certain result may be obtained by deflagrating the sulphurets with carbonate of soda and nitre, treating the mass obtained with water, filtering, and decomposing with nitric acid the basic alkaline antimoniates, which the filtrate contains in solution to a small extent. By means of this process almost all the antimony is obtained as an insoluble, and all the arsenic as a soluble compound.

The presence of antimony cannot easily give rise to any errors in the reduction of arsenites or arseniates, by means of carbonate of soda and charcoal, or cyanide of potassium and carbonate of soda. The reduction of sulphuret of arsenic by means of cyanide of potassium and carbonate of soda, in a stream of carbonic acid gas, does not admit even of the possibility of confounding arsenic with antimony, and is of all methods best adapted to yield a most conclusive proof of the presence of arsenic. Nitrate of silver is the safest test for distinguishing arsenious acid from arsenic acid, in their aqueous solutions. If extraneous substances be contained in the solution, they prevent its being directly tested for arsenious or arsenic acid; in that case the solution must be completely precipitated by means of sulphuretted hydrogen, and the sulphurets obtained dissolved in liquor of potash; this solution must then be boiled with pure oxide of bismuth, or with the carbonate or basic nitrate of bismuth; the liquid is then filtered off from the sulphuret of bismuth formed; one part of the filtered liquid is tested for arsenious acid by means of sulphate of copper, according to the method described § 94, *d* 6, and the other part for arsenic acid, by means of nitrate of silver, after neutralization with nitric acid.

B. RELATIONS OF THE ACIDS TO REAGENTS.

§ 95.

We divide the reagents which serve for the determination of acids, in like manner as those used for the determination of the bases into GENERAL REAGENTS, i. e. such as indicate the GROUP to which the acid under examination belongs; and SPECIAL REAGENTS, i. e. such as enable us to detect the INDIVIDUAL ACIDS. The determination and limitation of the groups can hardly be made with the same degree of exactness with the acids as with the bases.

The two principal groups into which acids are divided are that of INORGANIC and that of ORGANIC ACIDS. No characteristic distinction can, however, be selected which is applicable through the entire series; for we can neither select the ternary composition as a distinguishing mark of organic acids, nor can we define organic acids to be such as require for their formation the co-operation of the vital power, for this definition not only leaves us in doubt as to a great many acids, for instance, formic acid, uric acid, &c., but it is in itself altogether unscientific, since all the vital processes in the animal and vegetable body are, in fact, merely modified chemical processes. We shall, therefore, select, as the characteristic mark by which we divide organic from inorganic acids, the properties they exhibit at a high temperature, calling those organic acids, the salts of which—(especially those with alkaline bases or bases of the alkaline earths)—are decomposed at a red heat, with separation of carbon. This mark of distinction has the advantage of being easily perceived, and of enabling us by a very simple preliminary experiment immediately to decide upon the principal group to which an acid belongs.

1. INORGANIC ACIDS.

First Group.

ACIDS WHICH ARE PRECIPITATED FROM THEIR NEUTRAL SOLUTIONS BY CHLORIDE OF BARIUM: *Arsenic Acid, Arsenious Acid, Chromic Acid, Sulphuric Acid, Phosphoric Acid, Boracic Acid, Oxalic Acid, Hydrofluoric Acid, Carbonic Acid, Silicic Acid.*

We subdivide this group into four classes, as follow:

1. Acids which are decomposed, in their acid solutions, by sulphuretted hydrogen, and which we have, there-

fore, already remarked upon, when treating of the bases, viz. ARSENIOUS ACID, ARSENIC ACID, and CHROMIC ACID.

2. Acids which are not decomposed, in their acid solutions, by sulphuretted hydrogen, and the barytes compounds of which are insoluble in hydrochloric acid. SULPHURIC ACID alone belongs to this class.

3. Acids which are not decomposed, in their acid solutions, by sulphuretted hydrogen, and the barytes compounds of which are dissolved by hydrochloric acid, WITHOUT DECOMPOSITION: these are PHOSPHORIC ACID, BORACIC ACID, OXALIC ACID, and HYDROFLUORIC. (Although we intend to treat of oxalic acid also in the organic group, yet we must consider this acid, in the inorganic group too, since its salts have the property of being decomposed at a red heat, without *real* carbonization, and it might, therefore, easily be overlooked as an organic acid.)

4. Acids which are not decomposed, in their acid solutions, by sulphuretted hydrogen, and the barytes salts of which are soluble in hydrochloric acid, WITH DECOMPOSITION: CARBONIC ACID, SILICIC ACID.

First Section of the First Group of the Inorganic Acids.

§ 96.

a. The ARSENIOUS ACID and ARSENIC ACID, are, as we have stated, decomposed by sulphuretted hydrogen, so as to separate their corresponding sulphurets. On account of this property, we have considered them together with the bases, as it leads to confounding them with the metallic oxides rather than with other acids. (Vide § 93.)

b. CHROMIC ACID. ($Cr\,O_3$.)

1. The chromates are all red or yellow; most of them are insoluble in water. Some of them are decomposed at a red heat; those with an alkaline base are fixed, and soluble in water; the solutions of the neutral chromates are yellow, those of the acid chromates are red. These tints

are still visible in highly dilute solutions. The yellow colour of a neutral solution changes into red on the addition of a mineral acid, owing to the formation of an acid salt.

2. *Sulphuretted hydrogen* reduces the chromic acid, as well when free as combined in solution, so as to give rise to the formation of oxide of chromium, water, and sulphuric acid, with precipitation of sulphur. Heat promotes this decomposition. If no free acid is present, only a portion of the oxide of chromium formed is kept in solution by the sulphuric acid formed at the same time, and a greenish-gray precipitate is obtained, consisting of a mixture of hydrated oxide of chromium and sulphur. But if free acid is present, a far less considerable precipitate of pure sulphur is obtained. The salt of oxide of chromium formed imparts a green tint to the fluid, in either case.

3. Chromic acid may be reduced to chromic oxide by means of many other substances, especially by *sulphurous acid*, or by being heated with *hydrochloric acid*, particularly on the addition of alcohol, (whereupon hydrochloric ether and aldehyde escape,) or by *metallic zinc*, or by heating with *tartaric acid*, *oxalic acid*, &c. All these reactions are clearly characterized by the red or yellow colour of the solution changing into the green tint of the salt of oxide of chromium.

4. *Chloride of barium* produces a yellowish white precipitate of CHROMATE OF BARYTES ($Ba\ O,\ Cr\ O_3$) which is soluble in hydrochloric and in nitric acid.

5. *Nitrate of silver* produces a dark purple precipitate of CHROMATE OF SILVER ($Ag\ O,\ Cr\ O_8$.) which is soluble in nitric acid and in ammonia.

6. *Acetate of lead* produces a yellow precipitate of CHROMATE OF LEAD ($Pb\ O,\ Cr\ O_3$) which is soluble in potash, and sparingly soluble in dilute nitric acid. The yellow colour of this precipitate changes to red, on the addition of ammonia.

7. If insoluble chromates be fused with *carbonate of soda* and *nitre*, and the fused mass dissolved in water, a YELLOW coloured fluid will be obtained, the colour of which is owing to the dissolved alkaline chromate; on the addi-

tion of an acid, this colour changes to red. The oxides remain either in their pure state or as carbonates.

Remarks.—When testing for bases we always find the chromic acid as chromic oxide, since sulphuretted hydrogen converts the acid into the oxide. The colour of the solution is so characteristic, that a further testing for it is almost unnecessary. If we have any reason to suppose that chromic acid is present in a substance under examination, and if metallic oxides are at the same time in the solution, we prefer reducing the chromic acid by means of hydrochloric acid and alcohol, to effecting this reduction by sulphuretted hydrogen. The reactions with salts of silver and of lead afford a safe test in aqueous solutions.

Second Section of the First Group of the Inorganic Acids.

§ 97.

SULPHURIC ACID. (SO_3.)

1. The sulphates are, for the most part, soluble in water ; the insoluble sulphates are generally white, the soluble sulphates are for the most part colourless in their crystalline state. The sulphates of alkalies and of alkaline earths are not decomposed by a red heat.

2. *Chloride of barium* produces in solutions of sulphuric acid and sulphates, even when extremely dilute, a heavy white precipitate of SULPHATE OF BARYTES (BaO, SO_3) in the form of a fine powder ; this precipitate is insoluble in hydrochloric acid and in nitric acid.

3. *Acetate of lead* produces a heavy, white precipitate of SULPHATE OF LEAD (PbO, SO_3) which is sparingly soluble in dilute nitric acid, but completely so in hot and concentrated hydrochloric acid.

4. Those sulphates which are insoluble in water and acids, are converted into CARBONATES on being fused with *alkaline carbonates*, giving at the same time rise to the formation of an alkaline sulphate.

5. The sulphates of alkalies and alkaline earths, may be reduced to sulphurets by being exposed on charcoal to the *reducing flame of the blow-pipe* either by themselves

or (and with greater facility) mixed with carbonate of soda and charcoal. These sulphurets may be detected by the odour of sulphuretted hydrogen which they emit upon being moistened with a few drops of an acid. If this is done on a paper which has been previously dipped into a solution of lead, or on a clean silver plate, (such as a polished coin,) a black stain of sulphuret of lead or sulphuret of silver is immediately formed.

Remarks.—Of all acids, sulphuric acid is almost the easiest to be detected, by its characteristic and excessively sensible reaction with salts of barytes. It is only necessary to take care not to mistake for sulphate of barytes, precipitates of chloride of barium, and especially of nitrate of barytes, which are formed when aqueous solutions of these salts are mixed with fluids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from sulphate of barytes, as they immediately disappear again, on the acid fluid being diluted with water. It is, however, possible to be misled by this relation to barytes, so as to confound sulphuric acid with hydrofluosilicic acid. Although we have not treated of this acid, yet we may here as well point out, that should any doubt exist as to the nature of a precipitate of barytes, this may be easily set at rest by treating the precipitate before the blow-pipe, with carbonate of soda and charcoal. (Compare § 97, 5.)

Third Section of the First Group of the Inorganic Acids.

§ 98.

a. PHOSPHORIC ACID. (PO_5.)

We consider here only the tribasic phosphoric acid, since this and its salts alone are most frequently employed in pharmacy, &c.; we disregard altogether the monobasic and bibasic phosphoric acid.

1. The phosphates with a fixed base are not completely decomposed by heat, but they may thereby be converted, according to the higher or lower degree applied, into pyrophosphates or metaphosphates. Of the phosphates, only

those with an alkaline base are soluble in water, in their neutral state. The solutions have an alkaline reaction.

2. *Chloride of barium* produces in aqueous solutions of neutral or basic phosphates, a white precipitate of PHOSPHATE OF BARYTES ($2\ Ba\ O,\ PO_5$) which is soluble in hydrochloric acid and in nitric acid, and sparingly soluble in muriate of ammonia.

3. *Solution of gypsum* produces in neutral or alkaline solutions, a white precipitate of PHOSPHATE OF LIME ($2\ Ca\ O,\ PO_5$) which is easily soluble in acids, even in acetic acid.

4. *Chloride of magnesium* or *sulphate of magnesia* produce in neutral or alkaline solutions white precipitates of PHOSPHATE OF MAGNESIA ($2\ Mg\ O,\ PO_5$) which are, however, perceptible only in rather concentrated solutions, especially on the application of heat. But if *free ammonia* or *carbonate of ammonia* be added to a even highly dilute solution, a white crystalline and quickly subsiding precipitate of BASIC PHOSPHATE OF MAGNESIA AND AMMONIA ($2\ Mg\ O,\ NH_4\ O$) ($PO_5 + 2\ HO + 10$ aq.) is formed, which is insoluble both in ammonia and in muriate of ammonia, but is of easy solution in acids, even in acetic acid. This precipitate often becomes visible only after the lapse of some time ; agitation promotes its separation. (Vide § 86, *d* 5.)

5. *Nitrate of silver* throws down from the solution of the neutral and basic alkaline phosphates, a bright yellow precipitate of PHOSPHATE OF SILVER. ($3\ Ag\ O\ P,\ O_5$.) If the solution contained a basic phosphate, the fluid in which the precipitate is suspended, manifest a neutral reaction, whilst it has an acid reaction if the solution contained a neutral phosphate. This is owing to the nitric acid receiving for 3 eq. of oxide of silver which it yields to the phosphoric acid, only 2 eq. of alkali and 1 eq. of water, (for the water does not neutralize the characteristic properties of the acid.)

6. *Acetate of lead* produces in neutral and alkaline solutions a white precipitate of PHOSPHATE OF LEAD, ($2\ Pb\ O,\ P\ O_5$,) which is easily soluble in nitric acid, and almost insoluble in acetic acid. By its behaviour before the blow-pipe this precipitate affords us an excellent means of

detecting the presence of phosphoric acid. For, in the first place, it is not reduced, or at least, only with the greatest difficulty, on being exposed on charcoal, even to the reducing flame; and it is, in the second place, distinguished inasmuch as the transparent and colourless pearl which it presents in the oxidizing flame, crystallizes on cooling, becomes opaque, and generally shows quite distinct dodecahedrons.

7. If to a hydrochloric solution of a phosphated alkaline earth *perchloride of iron* be added in excess, and then *ammonia* till the solution manifest an alkaline reaction, a bulky, more or less dark, reddish-brown precipitate is obtained, consisting of a mixture of hydrated peroxide of iron and BASIC PERPHOSPHATE OF IRON. Ammonia withdraws from it but very little of its phosphoric acid, whilst hydrosulphuret of ammonia completely decomposes it into sulphuret of iron and phosphate of ammonia. If an insufficient quantity of perchloride of iron, is used, a white precipitate of neutral perphosphate of iron is formed, which redissolves on the addition of ammonia in excess.

b. BORACIC ACID. ($B\,O_3$.)

1. The aqueous solution of boracic acid reddens litmus paper, but it tinges tumeric paper brown. The borates are not decomposed by a red heat; only those with alkaline bases are easily soluble in water. The solutions are colourless, and all of them, even those of the acid salts manifest an alkaline reaction.

2. *Chloride of barium* produces in solutions of borates, when not too highly dilute, a white precipitate of BORATE OF BARYTES, ($Ba\,O.\ B\,O_3$,) which is soluble in acids and ammoniacal salts.

3. *Nitrate of silver* produces in rather concentrated solutions of borates, a white precipitate of BORATE OF SILVER, ($Ag\,O,\ B\,O_3$,) which is soluble in nitric acid and in ammonia.

4. If *Sulphuric acid* or *hydrochloric acid* be added to highly concentrated, hot solutions of borates, the BORACIC ACID will separate on cooling, in the form of shining crystalline scales.

5. If free boracic acid or a borate—(in which latter case the boracic acid must be liberated by the addition of sulphuric acid)—be ignited with *alcohol*, the flame will appear of a very distinct YELLOWISH-GREEN colour, especially on stirring the mixture, owing to the boracic acid evaporating together with the alcohol, and becoming incandescent in the flame. This reaction becomes most sensible, if the cup containing the mixture is first heated, the alcohol then ignited, allowed to burn for a short time, then extinguished and rekindled. At the first flickering of the flame its borders appear green in that case, even though the quantity of the boracic acid be so minute as to produce no perceptible colouring of the flame, when treated in the usual manner.

c. OXALIC ACID. $(\bar{O}=C_2\,O_3.)$

1. All the oxalates are decomposed at a red heat, owing to the oxalic acid decomposing into carbonic acid and carbonic oxide. Those which have an alkali or an alkaline earth for their base, are in this process converted into carbonates (without separation of carbon, when pure ;) those with a metallic base leave the metal behind either in its metallic state or as an oxide, according to the degree of reducibility of the metallic oxide. The alkaline oxalates are soluble in water, and so are some oxalates with metallic base.

2. *Chloride of barium* produces in the neutral solutions of oxalates, a white precipitate of OXALATE OF BARYTES, $(\mathrm{Ba\,O}, \bar{O} + \mathrm{aq.},)$ which is soluble in nitric acid and in hydrochloric acid, but is more sparingly soluble in ammoniacal salts than borate of barytes.

3. *Nitrate of silver* produces in neutral solutions of oxalates, a white precipitate of OXALATE OF SILVER, $(\mathrm{Ag\,O}\,\bar{O},)$ which is soluble in nitric acid and in ammonia.

4. *Lime-water*, and all the *soluble salts of lime*, and thus also *solution of gypsum*, produce in even highly dilute solutions of free oxalic acid or of oxalates, precipitates of OXALATE OF LIME, $(\mathrm{Ca\,O}, \bar{O}+2\,\mathrm{aq.})$ in the form of a fine white powder, which readily dissolve in hydrochloric acid and in nitric acid, but are almost insoluble in oxalic acid, and in acetic acid. The presence of ammoniacal salts does

not at all prevent the formation of these precipitates. The addition of ammonia considerably promotes the precipitation of the free oxalic acid, by salts of lime.

5. If oxalic acid or an oxalate in a dry state be heated with *concentrated sulphuric acid* in excess, the latter withdraws from the oxalic acid its necessary constitutional water, the oxalic acid is decomposed into CARBONIC ACID and CARBONIC OXIDE, and both these gases escape with effervescence. If the quantity operated upon is not too minute, the escaping carbonic oxide gas may be kindled; it burns with a blue flame. If in this reaction the sulphuric acid assumes a dark tinge, it is a sign that the oxalic acid contained an admixture of some organic substance.

d. HYDROFLUORIC ACID. (H Fl.)

1. Hydrofluoric acid is distinguished from all other acids by its property of dissolving the insoluble modification of silicic acid, as well as the silicates insoluble in hydrochloric acid, giving rise to the formation of fluoride of silicon, and of water. The hydrofluoric acid decomposes in the same manner with metallic oxides, giving rise to the formation of fluorides and of water. The fluorides of the alkaline metals are soluble in water; those corresponding with the alkaline earths are either not at all or but very sparingly soluble in water; floride of aluminum is easily soluble. Most of the fluorides corresponding with the oxides of the heavy metals are very sparingly soluble in water, such as, for instance, fluoride of copper, fluoride of lead, fluoride of zinc; many other fluorides are of easy solution in water, as, for instance, perfluoride of iron, fluoride of tin, perfluoride of mercury, &c. Of those compounds which are either insoluble or but sparingly soluble in water, many dissolve in free hydrofluoric acid, whilst others remain undissolved. Most of the fluorides do not undergo decomposition, when heated to redness in a crucible.

2. If to the aqueous solution of hydrofluoric acid or of a fluoride, *chloride of calcium* be added, FLUORIDE OF CALCIUM, (Ca Fl,) is obtained in the form of a gelatinous precipitate, which is so transparent, as at first to induce the belief, that the fluid has remained clear and unaltered. The addition of ammonia promotes the complete separation of

this precipitate, which is insoluble in hydrochloric acid and nitric acid, as well as in alkaline fluids when cold; a minute quantity is, however, dissolved on boiling with hydrochloric acid. It is scarcely more soluble in free hydrofluoric acid than in water.

3. If any fluoride, reduced to a fine powder, be mixed with pounded glass or sand, and the mixture be drenched in a test tube, with *concentrated sulphuric acid* and heat applied, FLUOSILICIC GAS ($Si\,Fl_3$) is evolved, giving rise to dense white fumes in the air when the latter contains moisture. If the gas be transmitted through water—(by means of a bent tube fitted to the test tube)—silicic acid separates in a gelatinous form, whilst the fluid becomes strongly acid, owing to the formation of hydrofluosilicic acid. (Compare § 43.)

4. If a plate of glass be covered with bees-wax, which can readily be done by heating it and allowing the wax to spread equally over the surface, and lines be traced on it with a point, (which should not be too hard, a point of wood answers best,) and the plate be then covered with the solution of a fluoride mixed with sulphuric acid, and allowed to dry, the lines exposed will be found, on removing the wax, to be etched upon the glass. If we have but very minute quantities to test, the acid solution of a fluoride mixed with sulphuric acid is, at a gentle heat, evaporated to dryness, in a watch glass; after washing off the salt mass remaining, the internal surface of the glass appears dimmed.

5. If a fluoride, reduced to a fine powder, no matter whether soluble or insoluble, is drenched, in a platinum crucible, with concentrated sulphuric acid, and the crucible, being covered with a glass plate, prepared as stated above, is exposed fifteen minutes or half-an-hour to a gentle heat, taking always care not to melt the wax, the exposed lines are found engraved after the removal of the wax. If the quantity of hydrofluoric acid evolved by means of the sulphuric acid was very minute, the etching frequently is not perceived, after the removal of the wax; but if the glass be breathed upon, the exposed lines become visible again, owing to the unequal capacity of condensing water, which the etched and untouched parts of the plate possess.

Remarks.—The third section contains, as we have stated, phosphoric acid, boracic acid, oxalic acid and hydrofluoric acid. The barytes compounds of these acids, as we have seen, are dissolved by hydrochloric acid, without decomposition; alkalies, therefore, precipitate them unaltered, by neutralizing the hydrochloric acid. The barytes compounds of arsenious acid, arsenic acid, and chromic acid, present the same property, and must, therefore, if present, be removed before any conclusion, as to the presence of phosphoric acid, boracic acid, oxalic acid, or hydrofluoric acid, can be drawn from this precipitation of a salt of barytes. But even without regard to this point, no great value can be placed on their reaction, not even for the detection of these acids, and far less for their separation from other acids, since the salts of barytes in question, and especially the borate of barytes, are not precipitated from their hydrochloric solutions, by ammonia, if the quantity of free acids present is to any extent, or if any ammoniacal salt in a certain quantity is present. Boracic acid may always be detected by the tint which it communicates to the flame of alcohol, if care is taken that the solution be sufficiently concentrated before the addition of the alcohol, and when the substance under examination is a borate, that it be mixed with a sufficient quantity of sulphuric acid (best concentrated). If the boracic acid is free, it should first be combined with an alkali when evaporating its solution, or else a large portion of it will volatilize with the vapours of the water. The phosphoric acid is sufficiently characterized by the yellow silver precipitate, by the characteristic properties of the basic phosphate of magnesia and ammonia, (especially the insolubility of this compound in sal ammoniac,) and finally, by the behaviour of phosphate of lead before the blow-pipe. Perchloride of iron is undoubtedly the best means of decomposing those phosphates which have an alkaline earth for their base, after they have been dissolved in hydrochloric acid. Oxalic acid may always easily be detected by solution of gypsum, if we only keep in view, that the precipitate thereby formed must not disappear on the addition of acetic acid, (herein it is distinguished from phosphoric acid,) and must readily dissolve in dilute hydrochloric acid, and be converted into carbonate of lime on the application of a red heat, (herein it differs from hydrochloric acid). The oxalates of the alkaline earths are completely decomposed by boiling with carbonate of soda. Lastly, the hydrofluoric acid cannot easily be confounded with other acids; since, under all circumstances, it is certainly detected by its property of etching glass. The most sensitive results are always obtained by treating solid fluorides with sulphuric acid.

Fourth Section of the First Group of Inorganic Acids.

§ 99.

a. CARBONIC ACID. ($C O_2$.)

1. The carbonates lose a part of their carbonic acid, at a red heat. All carbonates or colourless oxides appear white or colourless. Only those with an alkaline base are soluble in water, in their neutral state. Their solutions have a very strong alkaline reaction. Further, the bi-carbonates with alkaline bases, those also which have an alkaline earth for their base, and some with metallic bases, are soluble in water.

2. The carbonates are decomposed by all free acids soluble in water, with the exception of hydrocyanic acid and hydrosulphuric acid. In this process, the carbonic acid escapes with effervescence, as a colourless and almost inodorous gas, which imparts a transient reddish tint to litmus paper. It is necessary to use the decomposing acid in excess, especially when operating upon a salt with an alkaline base, since frequently no effervescence takes place, when adding the acid in too small a quantity, owing to the formation of acid carbonates.

3. *Lime-water* and *water of barytes* produce, when brought into contact with carbonic acid or soluble carbonates, white precipitates of NEUTRAL CARBONATE OF LIME OF BARYTES. When testing for free carbonic acid, the reagent ought always to be employed in excess, as the acid carbonates of the alkaline earths are soluble in water. The precipitates formed dissolve in acids, with efferves-

cence, and are not precipitated again by ammonia; after the complete expulsion of the carbonic acid, by boiling.

4. *Chloride of calcium* and *chloride of barium* yield with neutral alkaline carbonates immediately, and with bicarbonates only on boiling, precipitates of CARBONATE OF LIME or of BARYTES. These reagents yield no precipitate with free carbonic acid.

b. SILICIC ACID. ($Si O_3$.)

1. Silicic acid occurs in two modifications, the one is soluble in acids and water, the other is affected only by hydrofluoric acid. The soluble modification is converted by heat into the insoluble. If the insoluble modification is fused with pure alkalies or alkaline carbonates, a basic alkaline silicate is produced, which is soluble in water and from which acids separate the silicic acid in its soluble modification. The soluble modification readily dissolves when boiled with solution of potash, the insoluble modification dissolves only very slowly in the same menstruum. The silicates of the alkalies alone are soluble in water.

2. The solutions of the alkaline silicates are decomposed by all *acids ;* when the solutions are highly concentrated the SILICIC ACID precipitates in the form of gelatinous flakes, whilst it remains dissolved in more dilute solutions. If a solution of this kind, mixed with an acid, (hydrochloric acid or nitric acid,) is evaporated to dryness, the silicic acid is converted from its soluble into its insoluble modification, and remains, therefore, as a white gritty powder, on the residue being treated with water.

3. In the silicates which have an earth or a metal for their base, the silicic acid is also present either in its soluble or in its insoluble modification. The silicates with the soluble modification are decomposed by boiling hydrochloric or nitric acid, the silicic acid separating as a gelatinous hydrate, and the decomposing acid combining with the base. But on silicates with the insoluble modification, these acids have no action; in order to separate the silicic acid from its base, such silicates must be either treated in the humid way, with hydrofluoric acid, or fused with alkaline carbonates.

4. *Carbonate of soda* dissolves a large proportion of silicic acid in the flame of the blow-pipe, forming SILICATE OF SODA as a colourless glass, which remains transparent on cooling; the carbonic acid escapes with effervescence. Inexperienced students often fail in obtaining a clear glass, because they use too much carbonate of soda in proportion to the quantity of the test specimen.

5. *Phosphate of soda and ammonia* leave silicic acid almost entirely undissolved. The silicic acid floats about as an opaque mass in the transparent glass, and may, therefore, be perceived with greater facility in the glass when red hot than after cooling. The silicates present the same property; the phosphate of soda and ammonia withdraws their base from them, and separate silicic acid. The bases are dissolved, whilst the silicic acid remains undissolved.

Recapitulation and Remarks.—Carbonic acid is generally very easily detected by its salts evolving an almost inodorous gas when treated with acids. We transmit the gas through lime-water or water of barytes, when operating upon compounds which evolve other gases at the same time. Silicic acid in its soluble modification, (into which it must always be converted first,) is detected, under all circumstances, by supersaturating its compounds with hydrochloric acid, evaporating to dryness, treating the residue with water, and testing the undissolved part before the blow-pipe.

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, Hydrosulphuric Acid.*

§ 100.

All the silver compounds of the oxides belonging to this group are insoluble in dilute nitric acid. The acids of this group decompose with metallic oxides, so as to give rise to the combination of the metals with [illegible] metalloïds, whilst the oxygen of the oxide at the same [illegible] with the hydrogen of the acid forming water.

a. HYDROCHLORIC ACID. ($Cl\ H$.)

1. The chlorides are easily soluble in water, with the exception of chloride of lead, chloride of silver, and protochloride of mercury; most of the chlorides are white or colourless. Many of them volatilize at a high temperature, without decomposition; many chlorides are decomposed at a red heat, and but few of them are fixed.

2. Hydrochloric acid, and solutions of chlorides, yield with *nitrate of silver*, even when highly dilute, white precipitates of CHLORIDE OF SILVER, ($Ag\ Cl$,) which, when exposed to light, change first into a violet colour and then into a black; these are readily soluble in ammonia, insoluble in nitric acid, and fuse without decomposition when heated. (Vide § 90, *a* 4.)

3. *Protonitrate of mercury* and *acetate of lead* produce in solution, containing free hydrochloric acid or chloride, precipitates of CHLORURET OF MERCURY ($Hg_2\ Cl$) and CHLORIDE OF LEAD ($Pb\ Cl$.) For the properties of these precipitates, vide § 90, *b* 4, and § 90, *c* 4.

4. When chlorides are heated with *manganese* and *sulphuric acid*, chlorine is evolved, which is easily detected by its YELLOWISH-GREEN colour, and its odour.

5. If a chloride be rubbed together with *chromate of potash*, and the mixture be drenched with *concentrated sulphuric acid*, in a tubular retort, and gentle heat applied, a deep brownish-red gas will be copiously evolved; (CHROMATE OF PERCHLORIDE OF CHROMIUM, $Cr\ Cl + 2\ Cr\ O_3$;) this gas condenses into a fluid of the same colour, and passes over into the receiver. If this chromate of perchloride of chromium is mixed with ammonia in excess, a yellow-coloured liquid is obtained, owing to the formation of chromate of ammonia; this yellow colour changes into a reddish yellow, on the addition of an acid, owing to the formation of acid chromate of ammonia.

b. HYD[illegible]ROMIC ACID. ($Br\ H$.)

1. The b[illegible]des have, in general, a great analogy with th[illegible] in insolubility and in their relations when e[illegible] to heat.

2. *Nitrate of silver* produces in aqueous solution of hydrobromic acid and bromides a yellowish-white precipitate of BROMIDE OF SILVER, (Ag Br,) which is insoluble in dilute nitric acid, and somewhat sparingly soluble in ammonia.

3. *Nitric acid* decomposes hydrobromic acid and the bromides, with the application of heat, liberating bromine, by oxidizing the hydrogen or the metal. The liberated bromine colours the solution yellowish-red; but if we operate upon a bromide in a solid form, yellowish red vapours of bromine gas escape, with the odour of chlorine; these vapours, when present in sufficient quantity, condense in the cold part of the test-tube into small drops.

4. *Chlorine*, or *solution of chlorine*, also liberates bromine in solutions of its compounds; the fluid assuming a yellowish-red tint, if the quantity of the bromine present is not too minute. If a yellow-coloured solution of this kind be agitated with ether, it becomes colourless; all the bromine dissolves in the ether, which appears distinctly yellow, even though but a very minute quantity of bromine be present. If the etherial solution of bromine be agitated with some solution of potash, the yellow tint vanishes, and we have bromide of potassium and bromate of potash in solution. If the solution be then evaporated, and the residue heated to redness, the bromate of potash is converted into bromide of potassium. This substance may be further tested as follows:

5. If bromides are heated with *manganese* and *sulphuric acid*, YELLOWISH-RED VAPOURS OF BROMINE are evolved. If the bromine is present only in very minute quantity, the colour of their vapours may not be visible. The experiment, in that case, must be conducted in a small retort, and the vapours passing over transmitted through a long condensing glass tube into small test-tubes, containing some starch, for if

6. Moist *starch* is brought into contact with free bromine, no matter whether in solution or in gaseous form, YELLOW BROMIDE OF STARCH is formed. The colouring does not always take place immediately. The reaction is rendered most delicate by closing the test-tube which contains the starch drenched with the fluid under examination, before a spirit-lamp, and then inverting it, so that

the moist starch becomes placed above the liquid. The slightest trace of bromine will then, after twelve to twenty-four hours, impart a yellow tinge to the starch. This colour vanishes again on the tube-being allowed to stand for a longer time.

7. If a mixture of a bromide and of *chromate of potash* be drenched with sulphuric acid, and heat applied, a brownish-red gas is evolved, just as is the case with the chlorides. But this gas consists of pure BROMINE, and the fluid passing on, therefore, becomes not yellow, but colourless, when supersaturated with ammonia.

c. HYDRIODIC ACID. (I H.)

1. The iodides also correspond, in many respects, with the chlorides. Of those, however, which contain heavy metals, by far more are insoluble in water than is the case with the chlorides. Many iodides present characteristic tints.

2. Nitrate of silver produces in aqueous solutions of hydriodic acid and of iodides, yellowish white precipitates of IODIDE OF SILVER, ($Ag\ I$,) which blacken when exposed to light, are insoluble in dilute nitric acid, and very sparingly soluble in ammonia.

3. A solution of one part of *sulphate of copper*, and two and a quarter parts of *sulphate of iron*, precipitates from aqueous neutral solutions of the iodides, PROTIODIDE OF COPPER, ($Cu_2\ I$,) in the form of a dirty-white precipitate. The addition of some ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent.

4. *Nitric acid* decomposes the hydriodic acid and the iodides in the same manner as the bromides. Colourless solutions of hydriodic acid or of the iodides are, therefore, immediately coloured BROWNISH-YELLOW by nitric acid, even at a low temperature; and from concentrated solutions the IODINE separates as a BLACK PRECIPITATE, whilst nitric oxide gas escapes with effervescence. Solid iodides, when heated with nitric acid, evolve, besides the nitric acid gas VIOLET vapours of iodine, which condense on the colder parts of the vessel into a blackish sublimate.

5. *Chlorine* and *solution of chlorine*, liberate iodine from

its combinations, but the liberated iodine combines with these reagents when they are added in excess, forming a colourless CHLORIDE OF IODINE.

6. If iodides are heated with concentrated *sulphuric acid*, or with *sulphuric acid* and *manganese*, IODINE becomes liberated, and may be easily detected by the violet colour of its gas. If concentrated sulphuric acid alone has been used, sulphurous acid is evolved at the same time. If the quantity of the iodine present is very minute, it can no longer be detected by the colour of its gas, and we have recourse to the test with starch, as follows:

7. If to a solution of iodine or of hydriodic acid, or of an iodide, (the iodine in the latter must first be liberated by means of nitric acid,) thin *starch paste* be added, a more or less blackish-blue tint or precipitate of IODIDE OF STARCH is formed, even though but the most minute traces of iodine be present. When solution of chlorine is employed for the liberation of the iodine, it ought to be added very cautiously, as, owing to the formation of chloride of iodine, the blue tint does not appear, or at least manifests itself only after the addition of sulphuretted hydrogen, protochloride of tin, or some other means of reduction. Even the most minute traces of iodine in dry compounds of any description, may be detected most safely by means of starch, in the following manner. The substance under examination is drenched in a retort, with concentrated nitric acid, and the retort loosely closed with a stopper, to which a moistened slip of paper, or, better still, a moistened strip of white cotton cloth, imbued with starch, is attached; after a few hours this will appear blue, even though but the most minute trace of iodine be present.

8. The iodides present the same relation to chromate of potash and sulphuric acid combined, as to sulphuric acid alone. (Compare § 100, *a* 5.)

d. HYDROCYANIC ACID. (Cy H.)

1. Those cyanides which have an alkali or alkaline earth for their base, are soluble in water, as hydrocyanates. They are easily decomposed by acids, even by carbonic acid, but are not decomposed by heat when the access of air is prevented. When fused with the oxide of lead, of copper, of

antimony, of tin, and many other oxides, they reduce these oxides, and are converted into cyanates. Only a few of those cyanides which contain heavy metals are soluble in water; all of them are decomposed at a red heat, giving rise either to the formation of cyanogen and metals, as the cyanides of the noble metals, or of nitrogen gas and carbonates, as the cyanides of the other heavy metals. Many combinations of cyanogen with heavy metals are not decomposed by dilute oxygen acids, and with difficulty by concentrated nitric acid. Hydrochloric acid and sulphuretted hydrogen decompose most of them easily and completely. Cyanogen combines with several metals, (iron, manganese, cobalt, chromium,) forming compound radicals, in which these metals cannot be detected by many of the usual methods.

2. *Nitrate of silver* produces, in solutions of free hydrocyanic acid and of alkaline hydrocyanates, white precipitates of CYANIDE OF SILVER, ($Ag\,Cy$,) which are easily soluble in cyanide of potassium, somewhat difficult of solution in ammonia, and insoluble in dilute nitric acid; these precipitates are decomposed at a red heat, leaving the pure metallic silver behind.

3. If to the solution of an alkaline hydrocyanate, solution of *sulphate of iron*, which has been for some time in contact with the air, (*magnetic oxide of iron*,) is added, a precipitate or tint of PRUSSIAN BLUE is formed. (Compare § 88, *f* 5.) Free hydrocyanic acid, to be detected in this manner, must, therefore, first be combined with an alkali. If the alkali is present in excess, hydrated magnetic oxide of iron is precipitated beside the Prussian blue; in that case this latter precipitate must first be redissolved by hydrochloric acid, before the blue colour of the precipitate can appear clearly and distinctly.

3. If to a solution of hydrocyanic acid, potash be added in excess, and then finely pounded *peroxide of mercury*, the latter substance readily dissolves just as well as in free hydrocyanic acid. As peroxide of mercury is soluble in an alkaline fluid only in presence of hydrocyanic acid, it follows that by means of this reaction we can safely detect the presence of hydrocyanic acid.

4. The cyanogen cannot be detected in cyanide of mer-

cury by any of these methods. To detect it in this combination, we add hydrochloric acid and metallic iron to a solution of cyanide of mercury. Metallic mercury is separated in this process, and hydrocyanic acid and protochloride of iron formed, (which latter substance is partly converted into perchloride of iron, on exposure to the air.) If an alkali is then added to the fluid, Prussian blue is formed, the colour of which, however, becomes distinct only after having removed, by the addition of hydrochloric acid, the excess of the hydrated magnetic oxide of iron present. Cyanide of mercury may also be easily decomposed by sulphuretted hydrogen, giving rise to the formation of sulphuret of mercury and hydrocyanic acid. When heated, the cyanide of mercury decomposes, as we have already stated, (1,) into metallic mercury and cyanogen, which latter substance may be detected by its characteristic effect on the olfactory organs.

5. In the ferrocyanides and ferricyanides with alkaline bases, the presence of these compound radicals may be easily detected, in the former by *solutions of protoxide of iron*, or *solution of copper*, and in the latter by solution of peroxide of iron. Free hydrocyanic acid may be obtained from these cyanides by distilling them with sulphuric acid. The insoluble ferrocyanides and ferricyanides are decomposed by being heated with caustic potash or carbonate of potash, giving rise to the formation of ferrocyanide of potassium, and the separation of the metals either as carbonates or as pure oxides.

e. HYDROSULPHURIC ACID. (H S.)

Sulphuretted Hydrogen Gas.

1. Only those sulphurets are soluble in water which have an alkali or an alkaline earth for their base. These as well as those which contain metals of the fourth group, (such as iron, manganese, &c.,) are decomposed by dilute mineral acids, with evolution of sulphuretted hydrogen gas, which may easily be detected by its odour, and by its action on solution of lead. (Vide infra 2.) If the sulphuret is of a higher degree of sulphuration, a white precipitate of minutely divided sulphur is formed at the same time, which can easily be distinguished from similar pre-

cipitates by its inflammability. Part of the sulphurets of the fifth and sixth group are decomposed by concentrated and boiling *hydrochloric* acid, with evolution of sulphuretted hydrogen gas, whilst others are not dissolved by hydrochloric acid, but by concentrated and boiling *nitric* acid. The combinations of sulphur with mercury resist both these acids, but dissolve readily in aqua regia. On the solution of sulphurets in nitric acid, and in aqua regia, sulphuric acid is formed; and in most cases, moreover, sulphur separates, which is easily detected by its colour and behaviour when heated.

2. If sulphuretted hydrogen in solution, or in a gaseous form, is brought into contact with *nitrate of silver* or *acetate of lead*, black precipitates of SULPHURET OF SILVER and SULPHURET OF LEAD are formed. (Vide supra, § 89, *a*, and § 89 *c*.) If the odour of sulphuretted hydrogen is, therefore, not sufficient for its detection, these reagents will afford the surest proof of its presence. When the sulphuretted hydrogen is in a gaseous form, a small slip of paper, moistened with solution of lead, is placed in the air to be tested; if sulphuretted hydrogen is present, this paper will become covered with a thin, brownish-black and lustrous film of sulphuret of lead.

3. If sulphurets are exposed to the *oxidizing flame of the blow-pipe*, their sulphur burns with a blue flame, emitting at the same time the well-known odour of sulphurous acid.

Recapitulation and remarks.—Most of the acids of the first group are precipitated by nitrate of silver; but these precipitates will not 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* in that fluid. The presence of hydrosulphuric acid prevents us more or less from testing for the other acids of the second group; this acid must, therefore, if present, first be removed previous to testing for the other acids. This removal may be effected by mere boiling, if the hydrosulphuric acid is free, but, if combined with an alkali, by the addition of a metallic salt, which does not precipitate the other acids, or at least not from acid solutions. Hydriodic and hydrocyanic acid may be detected even in the presence of hydrochloric or hydrobromic acid, by the reactions with starch and magnetic oxide of iron, which are as characteristic as they are delicate. But the detection of chlorine and bromine is more or less difficult in presence of iodine and cyanogen. These latter substances, if present, must, therefore, be removed first, before we can test for chlorine and bromine. The separation of cyanogen is easily effected by heating to redness the silver compounds of the group. Cyanide of silver decomposes at a red heat, whilst chloride, bromide, and iodide of silver undergo no decomposition. Iodine may be separated from bromine and chlorine, by treating the silver compounds with ammonia, as the iodide of silver is almost insoluble in this substance. But the separation is more perfect by precipitating the iodine as protiodide of copper, whilst chlorine and bromine remain in solution. Bromine may be detected and distinguished from chlorine, by mixing the compound containing both substances with hydrochloric acid and chloride of lime, or with solution of chlorine, and absorbing the liberated bromine by ether. Chlorine may be detected when present with bromine, by the reaction with carbonate of potash and sulphuric acid.

Third Group of the inorganic Acids.

ACIDS WHICH ARE PRECIPITATED NEITHER BY SALTS OF BARYTES NOR SALTS OF SILVER: *Nitric Acid, Chloric Acid.*

§ 101.

a. NITRIC ACID. (NO_5)

1. All the neutral salts of nitric acid are soluble in water; only a few basic nitrates are insoluble in water. All nitrates are decomposed at a strong red heat. Those with alkaline bases yield oxygen and nitrogen: the other salts, oxygen and nitrous acid.

2. If a nitrate is thrown upon *red-hot charcoal*, or if charcoal or some organic substance, paper, for instance, is brought into contract with a nitrate in fusion, DEFLAGRATION takes place, i. e. the charcoal burns at the expense of the oxygen of the nitric acid, with vivid scintillations.

3. If a nitrate is mixed with *cyanide of potassium* in powder and the mixture heated on a platinum plate, a vivid DEFLAGRATION takes place combined with distinct ignition and feeble detonation. Even very minute quantities of nitrates may be detected by this reaction.

4. If the solution of a nitrate be mixed with one-fourth part of its quantity of concentrated sulphuric acid, and a chrystal of *protosulphate of iron* be thrown into the mixture, the fluid immediately surrounding this crystal will assume a DEEP BROWN TINT. This tint generally vanishes by merely agitating the fluid, and always after the application of heat for some time. In this process, the nitric acid is decomposed by the protoxide of iron, three-fifths of its oxygen combine with the protoxide, and convert a portion of it into peroxide, and the remaining nitric oxide combines with the remaining protoxide of iron, forming a characteristic compound, which dissolves in water producing a brownish-black colour.

5. If to the solution of a nitrate some sulphuric acid be added, and as much *solution of sulphate of indigo* as to make the fluid appear of a feeble light-blue colour, and the mixture be then heated to boiling, this blue tint will disappear, owing to the indigo becoming oxidized at the expense of the oxygen of the nitric acid liberated by the sulphuric acid; the fluid becomes colourless, or assumes a feeble yellowish tint. Several other substances, especially free chlorine, cause the same discoloration, which ought to be especially borne in mind.

6. If a nitrate is mixed with *copper filings*, and the mixture drenched with concentrated sulphuric acid, in a text tube, the air in the tube assumes a yellowish red tint, owing to the nitric oxide gas which becomes free on the oxidation of the copper by the nitric acid, combining with the oxygen of the air, and forming nitrous acid.

b. CHLORIC ACID. ($Cl O_5$.)

1. All chlorates are soluble in water. When heated to redness, their oxygen escapes completely, leaving chlorides behind.

2. When heated with *charcoal* or some organic sub-

stance, the chlorates DEFLAGRATE, and this with by far greater violence than the nitrates.

3. If the chlorate is mixed with CYANIDE OF POTASSIUM, and the mixture heated on a platinum plate, DEFLAGRATION takes place, with strong detonation and the appearance of flame, even though the chlorate be present only in a very minute quantity.

4. Free chloric acid oxidizes and discolours *indigo* in the same manner as nitric acid; if, therefore, the solution of a chlorate is mixed with sulphuric acid and solution of indigo, the phenomena manifest themselves, which we have described when treating of nitric acid, (vide supra, *a* 5.)

5. If chlorates be heated with *hydrochloric acid*, the constituents of both acids are mutually decomposed, giving rise to the formation of water, chlorous acid and chlorine, which latter substances may easily be detected by their odour and their greenish colour. ($Cl\ H+Cl\ O_5=Cl\ O_4+Cl+HO$.)

6. If a chlorate be drenched with *concentrated sulphuric acid*, two-thirds of the metallic oxide are converted into a sulphate, and the other third into a hyperchlorate, whilst chlorous acid escapes, which is characterized by its odour and greenish colour. [$3\ (KO, Cl\ O_5)+2\ SO_3=2\ (KO, 2\ SO_3)+KO, Cl\ O^7+2\ (Cl\ O_4.)$] The application of heat must be avoided in this experiment, and small quantities only operated upon, or else the decomposition might take place with great violence, so as to occasion an explosion.

Recapitulation and remarks.—Of the reactions which have been suggested for the detection of nitric acid, those with sulphate of iron and sulphuric acid, and with copper filings and sulphuric acid, give the safest results, for deflagration with charcoal, detonation with cyanide of potassium, and discolouration of solution of indigo take place, as we have stated also when chlorates are present instead of nitrates. These latter reactions, therefore, are decisive only when no chloric acid is present. The best test to ascertain whether chloric acid be present or not, is to heat the test specimen to redness, dissolving it and then testing its solution with nitrate of silver.

If a chlorate be present, it is converted into a chloride, on being heated to redness, and a precipitate of chloride of silver is obtained, on testing the solution with nitrate of silver. But this test is thus simple only when no chloride is present at the same time. But if the latter is the case, nitrate of silver must be added as long as any precipitate is formed; the supernatant liquid is then filtered from this precipitate, evaporated to dryness, and the residue heated to redness. The results obtained by the fusion of chlorates with cyanide of potassium are less certain. The violence and detonation, with which the deflagration takes place, render it, however, scarcely possible to confound the chlorates with nitrates.

II. ORGANIC ACIDS.

First Group.

ACIDS WHICH ARE PRECIPITATED BY CHLORIDE OF CALCIUM: *Oxalic Acid, Tartaric Acid, Paratartaric Acid, Citric Acid, Malic Acid.*

§ 102.

None of these acids volatilize without decomposition.

a. OXALIC ACID.

For the reactions of oxalic acid we refer to § 98 *c.*

b. TARTARIC ACID. ($\bar{T} = (C_8 H_4 O_{10}.)$)

1. The combinations of tartaric acid with alkalies, as well as with those metallic oxides which are weak bases, are soluble in water. All tartrates insoluble in water are dissolved by hydrochloric acid.

2. The tartaric acid and the tartrates carbonise when heated to redness, emitting a perfectly characteristic odour. The salts which have an alkali or alkaline earth for their base, are in this process converted into carbonates.

3. If to a solution of tartaric acid, or to that of a tartrate, solution of *peroxide of iron, protoxide of manganese,* or

alumina, and then ammonia or potash be added, no precipitation takes place of peroxide of iron, protoxide of manganese or alumina, since the new-formed double tartrates are not decomposed by alkalies. Tartaric acid prevents also the precipitation of several other oxides by alkalies.

4. Free tartaric acid yields, with a *salt of potash*, and best with acetate of potash, a sparingly soluble precipitate of BITARTRATE OF POTASH ($KO, HO, \bar{T}$). The same precipitate is formed, if acetate of potash and free acetic acid, or bisulphate of potash, be added to a neutral tartrate. When using bisulphate of potash, we must be careful not to add it in excess. The acid tartrate of potash readily dissolves in alkalies and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. Violent agitation greatly promotes the precipitation of tartar.

5. *Chloride of calcium* throws down from the solutions of neutral tartrates, TARTRATE OF LIME as a white precipitate. The presence of ammoniacal salts prevents the formation of this precipitate more or less. The precipitate of tartrate of lime dissolves to a clear fluid, in cold and dilute solution of caustic potash. If this solution is boiled, the dissolved tartrate of lime separates in the form of a gelatinous precipitate. On cooling, the solution becomes clear again.

6. *Lime-water* produces in solutions of neutral tartrates, or even in solutions of free tartaric acid, when added till an alkaline reaction manifests itself, white precipitates of TARTRATE OF LIME ($\bar{T}$, 2 Ca O 8 aq.) which readily dissolve in tartaric acid. This precipitate of tartrate of lime dissolves with the greatest facility in solution of sal ammoniac, and separates from this solution only after the lapse of several hours, in the form of small crystals, deposited on the sides of the vessel.

7. *Solution of gypsum* does not produce any precipitate in a solution of tartaric acid, and causes only a minute precipitate after the lapse of some time in the solution of a neutral tartrate.

c. PARATARTARIC ACID. (RACEMIC ACID.) $\bar{R}=(C_4\ H_2\ O_5.)$

1. The relations which paratartrates present to solvents, and their behaviour when heated, are very analogous to

those of the tartrates, prevent, like the latter, the precipitation by alkalies of protoxide of manganese, peroxide of iron, alumina, &c.

2. Paratartaric acid has the same relations to *salts of potash*, as tartaric acid. The precipitate of acid paratartrate of potash is as difficult of solution as tartar.

3. *Chloride of calcium* precipitates from the solutions of free as well as of combined paratartaric acid, PARATARTRATE OF LIME, as a shining white powder. This precipitate is not soluble in sal ammoniac. Cold and concentrated solution of potash dissolves it completely, dilute solution of potash only partly; this solution becomes turbid and gelatinous, on boiling, and clear again on cooling.

4. *Lime-water* produces in the solutions of neutral paratartrates, instantaneously, white precipitates of PARATARTRATE OF LIME. ($\bar{R}$, Ca O + 4 aq.) It yields the same precipitate with a solution of paratartaric acid, when added, till an alkaline reaction becomes manifest. When added in a smaller proportion, so that the solution still remains acid, this precipitate is formed only after the lapse of a few moments. Paratartrate of lime is insoluble in paratartaric acid as well as in tartaric acid; when it is dissolved in hydrochloric acid, and ammonia added in excess, it precipitates again instantaneously, or at least after the lapse of a few moments.

6. *Solution of gypsum* does not instantaneously produce a precipitate in a solution of paratartaric acid; after ten or fifteen minutes, however, paratartrate of lime precipitates; in solutions of neutral paratartrates the precipitation is instantaneous.

7. If crystallized paratartaric acid, or a paratartrate is heated with concentrated sulphuric acid, the latter assumes a black tinge, owing to the evolution of sulphurous acid and carbonic oxide gas. Tartaric acid has the same property.

d. CITRIC ACID. ($Ci = (C_{12}\,H\,O_{11}.)$)

1. The citrates with alkaline bases are easly soluble in water, as well in their neutral as in their acid state; the same is the case with the combinations of citric acid with such of the metallic oxides as are weak bases. Citric acid prevents the precipitation of peroxide of iron, protoxide of

manganese, alumina, &c., in the same manner as tartaric acid.

2. Citric acid and the citrates carbonize when *heated to redness*, emitting pungent acid vapour, which may be easily distinguished by their odour from those caused by the combustion of tartaric acid.

3. *Chloride of calcium* produces no precipitate in a solution of citric acid, not even on boiling. But if the free acid be saturated with potash or soda, a precipitate of NEUTRAL CITRATE OF LIME ($\bar{C}i$, 3 Ca O, 4 aq.) is formed instantaneously. This precipitate is insoluble in potash, but readily dissolves in solution of sal ammoniac. If this solution in sal ammoniac is boiled, a white and heavy precipitate of BASIC CITRATE OF LIME ($\bar{C}i$, 3 Ca O$+$Ca O$+$aq.) separates immediately. If a solution of citric acid, mixed with chloride of calcium, be saturated with ammonia, no precipitate will be formed at a low temperature, (if the solution was not highly concentrated.) But if the clear fluid be then boiled, a white, heavy precipitate of basic citrate of lime separates suddenly.

4. *Lime-water* produces no precipitate in a cold solution of citric acid or of a citrate. But on heating the solution to boiling with excess of lime-water, a white precipitate of BASIC CITRATE OF LIME is formed, which disappears again on cooling.

5. If to a solution of citric acid, *acetate of lead* be added in excess, a white precipitate of CITRATE OF LEAD ($\bar{C}i$, 3 Pb O, aq.) is formed, which is very sparingly soluble in ammonia, but easy of solution in citrate of ammonia. A precipitate of citrate of lead is equally formed, on adding citric acid in excess to a solution of neutral acetate of lead. This precipitate readily redissolves on the addition of ammonia. We have just now seen that the citrate of lead is very sparingly soluble in ammonia; this solution therefore is not caused by the ammonia, but by the new citrate of ammonia.

6. If citric acid or a citrate is heated with concentrated sulphuric acid, carbonic oxide gas and carbonic acid escape first, without simultaneous blackening of the sulphuric acid; but after boiling for some time, the solution becomes dark coloured, and sulphurous acid escapes.

e. MALIC ACID. $(\bar{M} = (C_8 H_4 O_8.)$

1. Malic acid forms with most bases, salts soluble in water. The acid malate of potash is not of difficult solution in water. Malic acid prevents the precipitation of the peroxide of iron, &c. by alkalies, in the same manner as tartaric acid.

2. When heated to 200° Reaumur, malic acid is decomposed into MALEIC ACID and HUMARIC ACID. This property is highly characteristic. If the experiment is made in a spoon, pungent acid vapours of maleic acid are evolved with froth, but if conducted in a tube, these vapours condense in the cold part of the tube, forming crystals. The fumaric acid remains behind.

3. *Chloride of calcium* produces no precipitates, neither in solutions of free malic acid, nor in those of the malates. But if after the addition of chloride of calcium, alcohol is added to the solution of a malate, MALATE OF LIME, $(\bar{M}, 2CaO)$ immediately precipitates as a white powder.

4. *Lime-water* precipitates neither the free nor the combined malic acid.

5. *Acetate of lead* throws down from solutions of malic acid and of malates, a white precipitate of MALATE OF LEAD $(\bar{M}, 2PbO, 6\ aq.)$ This precipitate is distinguished, 1st, by losing its curdiness, and changing into concentrically-grouped needles, with the lustre of mother-o'-pearl, when the fluid is allowed to stand for some time; and, 2d, by its melting point being lower than the boiling point of water. On heating, therefore, the fluid wherein this precipitate is suspended to the boiling point, the precipitate fuses and resembles resin which has been melted under water.

6. On heating malic acid with concentrated sulphuric acid, the latter substances become black with evolution of sulphurous acid.

Recapitulation and remarks.—Of the organic acids of this group, the tartaric acid and paratartaric acid are sufficiently characterized by the sparing solubility of their acid salts of potash, by the relation of their lime salts to solution of potash, and by the characteristic odour which they emit during their combustion. Tartaric acid may be distinguished from paratartaric acid best by means of its combination with lime, since tartrate of lime is soluble in free tartaric acid, and also in solution of sal ammoniac, and thus presents two properties, which are wanting in paratartrate of lime. The paratartaric acid, moreover, differs from tartaric acid in its relation to solution of gypsum. This relation to a certain extent assimilates paratartaric acid to oxalic acid; it does not, however, give rise to any mistake when operating upon the free acids, since the precipitate which solution of gypsum produces in solutions of paratartaric acid, is never formed instantaneously. The oxalates, moreover, are easily to be distinguished from the paratartrates by the properties they exhibit when heated either by themselves or with sulphuric acid. Citric acid is best detected by its relations to lime-water, or to chloride of calcium and ammonia.

The sparing solubility of the washed citrate of lead in ammonia, distinguishes citric acid from tartaric and paratartaric acid. The other re-agents which produce precipitates or other alterations in its solutions, such as chloride of gold, and salts of silver and mercury, &c., show the same or similar relations to tartaric and paratartaric acid, and, therefore, do not afford us safe means of distinguishing citric acid from the two latter substances. Malic acid would be sufficiently characterized by the properties which malate of lead presents when heated under water, if this re-action were of greater sensibility, and if it were not prevented so easily by the presence of other acids. The precipitation of malate of lime by alcohol can only be of value for the detection of malic acid, when we have previously convinced ourselves of the absence of all other acids, the lime salts of which are sparingly soluble in water, and quite insoluble in alcohol, such, for instance, as sulphuric acid or boracic acid. It is, however, always necessary further to test the precipitate produced by alcohol. The heating of malic acid in a glass tube leads to the most certain result; this test is, however, not applicable under all circumstances.

Second Group of the Organic Acids.

ACIDS, WHICH ARE UNDER NO CONDITION WHATEVER PRECIPITATED BY CHLORIDE OF CALCIUM, BUT ARE PRECIPITATED FROM THEIR NEUTRAL SOLUTIONS BY PERCHLORIDE OF IRON: *Succinic acid, Benzoic acid.*

§ 103.

a. SUCCINIC ACID. $\bar{S}=(C_4\ H_2\ O_3.)$

1. Pure succinic acid is inodorous, dissolves readily in water, and volatilizes completely when heated. The officinal acid, which has an empyreumatic odour, leaves a small carbonaceous residue. The succinates are decomposed at a red heat, with the exception of succinate of ammonia; those which have an alkali or alkaline earth for their base, are converted into carbonates in this process. Most of the succinates are soluble in water; succinic acid enters into insoluble or sparingly soluble combinations only with the metallic oxides which are weak bases.

2. *Perchloride of iron* produces, in a solution of succinic acid brownish pale red, bulky precipitate of PERSUCCINATE OF IRON ($Fe^2\ O_3,\ 3\bar{S}$). To render this precipitation complete, the free acid must first be neutralized with ammonia. Persuccinate of iron readily dissolves in acids, and is decomposed by ammonia; the hydrated peroxide of iron separates, in this process of decomposition, and succinic acid dissolves as succinate of ammonia.

3. *Acetate of lead* yields with succinic acid a white precipitate of SUCCINATE OF LEAD ($Pb\ O,\ \bar{S}$) which is soluble in succinic acid in excess, in solution of acetate of lead, and in acetic acid.

4. *Protonitrate of mercury* and *nitrate of silver* also precipitate the succinates; these precipitates, however, are by no means characteristic.

5. The alkaline succinates are insoluble in alcohol.

b. BENZOIC ACID. $(\bar{B}e=Bz\ O\ =C_{14}\ H_5\ O_3.)$

1. Pure benzoic acid appears in the form of white scales or needles, or merely as a crystalline powder. It volatilizes completely when heated. Its vapours cause a peculiar

irritating sensation in the throat, and provoke coughing. The common officinal benzoic acid has the odour of benzoin, and on being heated, leaves a small carbonaceous residue. The benzoates of the alkalies and alkaline earths, are converted into carbonates by heat. Benzoic acid is very sparingly soluble in cold water, but of pretty easy solution in hot water and in alcohol. It forms with most oxides salts soluble in water, and enters into insoluble or sparingly soluble combinations only with those oxides which are weak bases.

2. Benzoic acid shows the same relation to *chloride of iron* as succinic acid. The PERBENZOATE OF IRON, (Fe_2, O_3, $3\overline{\mathrm{Be}}$,) is however by far brighter and more yellow than the succinate. Ammonia decomposes it in like manner as the succinate. When treated with stronger acids, the latter combine with the peroxide of iron, and the benzoic acid, on account of its sparing solubility, separates as a white precipitate.

2. If to the solution of a benzoate a *strong acid* be added, the benzoic acid is expelled, and separates in the form of a shining white, sparingly soluble powder. The benzoic acid separates in the same manner from its soluble salts, as already stated, 2,) if some stronger acid is added to these salts which forms soluble salts with the bases with which the benzoic acid was combined.

Acetate of lead does not, or at least not immediately, precipitate the free benzoic acid nor the benzoate of ammonia, but it precipitates benzoates with fixed alkaline bases, in the form of white flakes.

5. The alkaline benzoates are soluble in alcohol.

Recapitulation and Remarks.—Succinic and benzoic acid are distinguished from all other acids by their ready volatility and their relation to perchloride of iron. They differ from each other in the colour of their persalts of iron, but especially in their solubility, succinic acid being readily soluble, whilst benzoic acid is very difficult of solution. Benzoic acid may, moreover, be detected by its irritating and cough-provoking vapours. Succinic acid is generally not quite pure, and may, therefore, also be detected by its odour of oil of amber.

A separation of these acids from each other may be effected by decomposing their persalts of iron by ammonia, and treating the new-formed compounds with alcohol, after previous evaporation to dryness. The separation of these acids is, of course, even more simple, if we can combine them with alkalies in a more direct way. The benzoate in that case dissolves, whilst the succinate remains.

Third Group of the Organic Acids.

ACIDS WHICH ARE NOT PRECIPITATED, UNDER ANY CONDITION, BY CHLORIDE OF CALCIUM OR PERCHLORIDE OF IRON: *Acetic Acid, Formic Acid.*

§ 104.

a. ACETIC ACID. ($\bar{A} = C_4\ H_3\ O_3$.)

1. Acetic acid is completely volatilized by heat, forming vapours of a pungent odour, which in their concentrated state are inflammable and burn with a blue flame. The acetates are decomposed at a red heat. Among the products of their decomposition we usually find acetic acid, and invariably acetone. The acetates which have an alkali or alkaline earth for their base are converted into carbonates, in this process. Many of those with a metallic base leave the metal behind in its metallic state, others as oxide. All the residues are carbonaceous. Almost all acetates are soluble in water and alcohol; most of them readily dissolve in water, but a few are difficult of solution.

2. If *perchloride of iron* is added to acetic acid, no alteration takes place, but if the acid is previously saturated with ammonia, or if a neutral acetate is mixed with perchloride of iron, the solution assumes a deep and dark red tint, owing to the formation of PERACETATE OF IRON. Ammonia precipitates all the peroxide of iron from such a solution.

3. Neutral acetates (but not free acetic acid) yield with *nitrate of silver*, white crystalline precipitates of ACETATE OF SILVER, ($Ag\ O,\ \bar{A}$) which are very sparingly soluble in cold water. They dissolve more readily in hot water, but they separate again from the solution, on cooling, in the

form of very fine crystals. Ammonia dissolves them readily; free acetic acid does not increase their solubility in water.

4. *Protonitrate of mercury* produces in solutions of acetic acid, and even with greater facility in solutions of acetates, white scaly crystalline precipitates of PROTACETATE OF MERCURY, (Hg_2 O, $\bar{A}$,) which are sparingly soluble in water and acetic acid, at a low temperature, but easily soluble in an excess of the precipitant. Protacetate of mercury dissolves in water on the application of heat, but separates again, on cooling, in the form of small crystals; it becomes partly decomposed in this process, metallic mercury separates and imparts a gray colour to the precipitate. If protonitrate of mercury is boiled with dilute acetic acid instead of water, the quantity of the metallic mercury separating is exceedingly minute.

5. If acetates are heated with *dilute sulphuric acid*, ACETIC ACID is evolved, which may be detected by its pungent odour. And if the acetates are heated with about equal weights of *concentrated sulphuric acid* and *alcohol*, ACETIC ETHER is evolved; the odour of this ether is highly characteristic and agreeable; it becomes particularly perceptible on agitating the mixture when somewhat cooled down, and scarcely admits of any mistake, and certainly far less than the pungent odour of free acetic acid.

6. If acetates are distilled with dilute sulphuric acid, and the distillate digested with oxide of lead in excess, part of this oxide will be dissolved as a basic acetate of lead, which may easily be detected by its alkaline reaction.

b. FORMIC ACID. (Fo $O_3 = C_2HO_3$.)

1. Formic acid has a characteristic pungent odour; it volatilizes completely on heating; the vapours of the concentrated acid are inflammable and burn with a blue flame. The formiates, like the corresponding acetates, when heated to redness, leave either carbonates or oxides, or metals behind; with simultaneous separation of carbon, carburetted hydrogen, and escape of carbonic acid and of water. All combinations of formic acid with bases are soluble in water; alcohol does not dissolve all of them.

2. Formic acid presents the same relation to *perchloride of iron* as acetic acid.

3. *Nitrate of silver* does not precipitate free formic acid, and precipitates alkaline formiates only from concentrated solution. The white, sparingly soluble, crystalline precipitate of FORMIATE OF SILVER ($Fo\ O_3\ Ag\,O$) soon assumes a deeper tint owing to the separation of metallic silver. This reduction to metallic silver takes place, even at a low temperature, after the solution containing the formiate of silver has been allowed to stand for some time, but it follows instantaneously upon the fluid being heated with the precipitate. The same reduction of the oxide of silver ensues even if the solution of the formate was so dilute, that no precipitate had been formed, or if we have to operate upon free formic acid. In this process, the formic acid, which may be considered a compound of carbonic oxide and water, deprives the oxide of silver of its oxygen, giving rise to the formation of carbonic acid, which escapes, and of water; the metal is precipitated in its metallic state.

4. *Protonitrate of mercury* does not produce precipitation in free formic acid; but in concentrated solutions of alkaline formiates it causes a white, sparingly soluble precipitate of PROTOFORMIATE OF MERCURY, ($Fo\ O_3\ Hg_2\ O$,) which after a very short time turns gray, owing to the separation of metallic mercury; complete reduction takes place, sometimes even at a low temperature, but instantaneously on heating. In this process, also, carbonic acid and water are formed. This reduction, in the same manner, as is the case with the nitrate of silver, takes place, even if the fluid is so dilute, that the protoformiate of mercury remains in solution, or if we have free formic acid to operate upon.

5. If formic acid or an alkaline formiate be heated with *perchloride of mercury* to 60–70° Reaumur, a precipitate of PROTOCHLORIDE OF MERCURY is obtained. When heated to the boiling point of water, metallic mercury separates besides the protochloride.

6. If formic acid or a formiate is heated with concentrated sulphuric acid, it becomes decomposed without blackening the fluid, giving rise to the formation of water and carbonic oxide gas, which escapes with effervesence,

and when ignited, burns with a blue flame. The sulphuric acid withdraws from the formic acid, the water or oxide necessary to the existence of this substance, and thus causes a transposition of its atoms to take place ($C_2 H O_3 = 2 CO + HO$.) If a formiate is heated with dilute nitric acid, formic acid escapes, which may easily be detected by its odour. If a formiate is drenched with a mixture of sulphuric acid and alcohol, formic ether is evolved, which is characterized by its peculiar arrack smell.

Recapitulation and remarks.—As the reactions of acetic acid and formic acid are not so characteristic as those of many other acids, their safe detection can only be based on the concurrence of all the reactions we have stated. Acetic acid is most easily detected by its odour or by that of acetic ether, but most safely by its behaviour with oxide of lead. Formic acid may best be detected by its behaviour with sulphuric acid and with the salts of the noble metals. The separation of acetic acid from formic acid is effected by heating both acids with peroxide of mercury in excess, or with oxide of silver. The formic acid reduces the oxides, and becomes decomposed at the same time; the acetic acid combines with them and remains in solution.

PART II.

SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.

PART II.

PRELIMINARY REMARKS

ON THE

COURSE OF QUALITATIVE ANALYSIS IN GENERAL,

AND ON THE

PLAN OF THIS SECOND PART OF THE PRESENT WORK

IN PARTICULAR.

When we are once acquainted with the reagents and the relation of other bodies to them, we are immediately able to determine, whether some simple compound or other, the physical qualities of which admit of drawing an inference as to its nature, is in reality what we take it to be. Thus, for instance, a few simple reactions convince us that a body which we suppose to be calcareous spar, is really carbonate of lime; and another substance, which we deem gypsum, is really sulphate of lime. This knowledge is usually equally sufficient to ascertain, whether a certain body be present or not in some compound substance or other; for instance, whether a white powder contains protochloride of mercury or not. 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 a chemical combination—if we intend to prove that, besides certain bodies we have detected in a mixture or compound, no other substance can be present with it, and, consequently, if a COMPLETE qualitative analysis is our object, the mere knowledge of reagents and reactions is no longer sufficient; we must of necessity know besides how to proceed systematically in our analysis; i. e. we must know in what *order* we have to apply solvents, and general and especial reagents, so as to be enabled with celerity and certainty to determine that all those substances which a compound or mixture does NOT contain, ARE REALLY NOT contained in it; and on the other hand, quickly and safely to detect those bodies which ARE PRESENT in the substance under examination. If we do not possess the knowledge of this systematic course, or if, in the hope of more rapidly attaining our object, we adhere to no method whatever in our investigations and experiments, analysis becomes (at least in the hand of a novice) mere guessing, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which sometimes may prove lucky hits, and at others total failures.

A definite method, therefore, must form the basis of every analytical investigation. But it is not by any means necessary that this method should be in all cases one and the same. Practice, reflection, and a due attention to circumstances, will, on the contrary, in most cases direct us to various and different methods. But all analytical methods agree in this, that the substances existing, or supposed to exist, must first be divided into certain groups, and the bodies belonging to these groups be further distinguished from each other, so as at last to admit of their individual detection. The diversity of analytical methods depends partly on the order in which reagents are applied, and partly on their selection.

Before we can venture upon inventing methods of our own for individual cases, we must first make ourselves thoroughly conversant with a certain definite course or system of chemical analysis in general. This system must have passed through the ordeal of experience, and must be adapted to every case imaginable, so as to enable us afterwards, when we have acquired some practice in analysis, to determine which modification of the general method will, in certain given cases, most easily and rapidly lead to the attainment of the object in view.

The exposition of such a systematic course, adapted to all cases, tested by experience, and combining the greatest possible simplicity with the greatest possible security, is the object of the second part of this work.

The elements and combinations comprised in it are the same which we have enumerated in our preliminary remarks.

Since it is necessary in the formation of such a systematic course to provide for every possible circumstance which may occur, it follows, as a matter of course, that we are obliged to suppose those substances which we treat of—(however mixed and intermixed with each other we may admit them to be) free from extraneous organic matters, since the presence of such matters prevents the manifestation of many reactions, and causes various modifications in others. We by no means intend to assert here that the proposed systematic course may not be exactly followed even in presence of many organic substances, especially of those which dissolve in water, forming colourless transparent fluids. Experience and reflection in every individual case will best instruct us how to act in cases where dark colouring slimy matters are present. For the most important rules, and the method in general, we refer to § 129.

This second part is divided into two sections; the first contains PRACTICAL INSTRUCTIONS IN ANALYSIS, wherein we have pointed out a way which must lead to the end in view, if systematically followed. At first sight, many parts of it may, perhaps, be deemed rather prolix; I think, however, that it would have scarcely been possible to abbreviate it, except at the expense of clearness and perspicuity for beginners. I hope, moreover, that my readers will soon become convinced by experience that this prolixity, after all, does not prove any bar to the celerity with which the systematic course may be gone through, as I have always divided the phenomena which may occur, into clearly characterized instances; and thus a given object being the only one to be considered, and one number always referring to the other, the student may save himself the trouble of reading through those parts which are not adapted for the especial case engaging his attention.

The subdivisions of this practical course are, 1, Preliminary examination; 2, Solution; 3, Real examination; 4, Confirmatory experiments. The third subdivision (the real examination) is again subdivided into, 1, Examination of compounds in which we suppose but one basis and but one acid present; and, 2, Examination of mixtures or compounds in which we suppose that all those substances which we have taken into consideration may be present. With respect to the latter, it must be observed that where the preliminary examination has not afforded us the most certain conviction of the absence of certain groups of substances, we cannot safely disregard any paragraph to which we refer, in consequence of the phenomena that manifest themselves. In cases where we merely intend to test a combination or mixture for certain substances, and not for all its constituents, it will be easy to find those numbers which we have to take into consideration.

The second section contains an EXPLANATION OF THE PRACTICAL PROCESS, an exposition and explanation of the grounds whereon the separation, and the causes, whereon the detection of substances depend; and, moreover, various additions to the first section. Students would do well to make themselves early acquainted with this section, which may be advantageously studied, concurrently with the practical process.

As an appendix, we give A GENERAL SCHEME OF THE ORDER IN WHICH THOSE SUBSTANCES WHICH ARE TO BE ANALYZED FOR THE SAKE OF PRACTICE MAY MOST JUDICIOUSLY BE SUCCESSIVELY TAKEN; and ALSO A TABULAR ARRANGEMENT OF THE MORE FREQUENTLY OCCURRING FORMS AND COMBINATIONS OF THE SUBSTANCES ENUMERATED IN OUR PRELIMINARY REMARKS, ACCORDING TO THEIR VARIOUS DEGREES OF SOLUBILITY IN WATER AND ACIDS. The first is intended to serve the pupil as a guide to the rapid and certain attainment of his object; i. e. a sound and complete acquisition of qualitative analysis; and the second will, undoubtedly, prove useful to many who are not yet quite conversant with the various degrees of solubility of compound bodies, especially in cases where they have to draw conclusions as to how the detected acids, bases, &c., have been combined, or what particular acids cannot possibly be present in aqueous or acid solutions, when the latter contain certain bases.

FIRST SECTION.

PRACTICAL PROCESS.

I. PRELIMINARY EXAMINATION.

§ 105.

In the first place, the external and sensible properties of the substance under examination should be considered, such as its colour, shape, hardness, gravity, odour, &c., as many conclusions may often be drawn therefrom. Before proceeding any further, we ought to consider well how much of the substance to be examined we have at command, since it is necessary at this early period of the examination to determine the quantity which we may use in the preliminary investigation. A reasonable economy is in all cases advisable, though we may possess the substance in large quantities; and it must be laid down as a fixed rule, never to use at once all we possess of a substance, but always to keep at least a small portion of it for unforeseen accidents, and for confirmatory experiments.

A. THE BODY UNDER EXAMINATION IS SOLID.

I. IT IS NEITHER A PURE METAL NOR AN ALLOY.

1. The substance is fit for examination when in powder or in small crystals; but when in larger crystals or in solid pieces, a portion of it, if possible, must first be reduced to powder.

2. The powder is heated over the spirit-lamp, in a small iron spoon. The phenomena resulting admit of many safe inferences as to the nature of the substance, and allow us to draw many probable conclusions.

a. THE SUBSTANCE REMAINS UNALTERED: no organic substances, no salts containing water of crystallization, no easily fusible matter, no volatile bodies.

b. IT FUSES EASILY, AND BECOMES SOLID AGAIN WITH THE EXPULSION OF AQUEOUS VAPOUR; salts which contain water of crystallization. If the solidified residue fuses again upon the application of an increased heat, c must be referred to.

c. IT FUSES WITHOUT EXPULSION OF AQUEOUS VAPOUR. A small piece of paper is added to the melting mass; if deflagration takes place, it indicates NITRATES, or more rarely, CHLORATES.

d. IT VOLATILIZES COMPLETELY OR PARTLY. In the first case, no fixed bases are present; in the latter, the substance contains a volatile body in admixture.

α. No odour is emitted. In this case we must especially have regard to compounds of AMMONIA, MERCURY, and ARSENIC.

β. An odour is emitted at the same time. If it is that of sulphurous acid, SULPHUR is present; if that of iodine, and if the vapours are violet, the presence of free IODINE is certain. With equal certainty free BENZOIC ACID, and many other substances, may be detected by the odour of their vapours.

e. THE SUBSTANCE IS A WHITE POWDER TURNING TO YELLOW ON HEATING; this indicates OXIDE OF ZINC or OXIDE OF LEAD; the latter substance remains yellow on cooling, whilst the oxide of zinc resumes its white colour.

f. CARBONIZATION TAKES PLACE: organic substances. If the residue effervesces when drenched with acids, whilst the original substance does not present that property, it indicates the presence of ORGANIC ACIDS, combined with alkalies or alkaline matter. If the odour of cyanogen is perceptible, it indicates the presence of a CYANIDE.

Many substances, moreover, swell up considerably, as for instance, borax, sulphate of alumina; others decrepitate, e. g. chloride of sodium, and chloride of potassium, &c.; these phenomena, however, less admit of general and certain conclusions than those stated above.

3. A small portion of the substance is put on a charcoal support, and exposed to the reducing flame of the blowpipe. Since most of the phenomena just now described (2) are equally obtained by this process, we will here mention only those which particularly belong to the latter.

a. THE SUBSTANCE VOLATILIZES PARTLY OR COMPLETELY. This indicates besides the substances mentioned in § 105, 2, *d*, also OXIDE OF ANTIMONY, and several other oxides. (Compare § 105, 6, *d*, *β*.) Oxide of antimony fuses previous to its volatilization, in the form of a white vapour. It must, moreover, be remarked, that when ARSENIOUS or ARSENIC ACID are present, a characteristic odour of garlic is perceptible, which is stronger if soda has previously been added to the test specimen.

b. THE BODY FUSES, AND IS IMBIBED BY THE CHARCOAL; this indicates the presence of ALKALIES. This process is conducted by putting a portion of the substance reduced to powder on the moistened loop of a platinum wire, and applying the heat of the reducing blow-pipe flame to it. If the oxidizing flame assumes a violet tint, it indicates the presence of POTASH alone; if a yellow tint, the presence of SODA, which may, however, be mixed with potash, even in a considerable proportion, since the flame always appears yellow when both these alkalies are present.

c. AN INFUSIBLE WHITE RESIDUE REMAINS ON THE CHARCOAL, EITHER IMMEDIATELY, OR AFTER PREVIOUS MELTING IN THE WATER OF CRYSTALLIZATION; this indicates especially the presence of barytes, strontian, lime, magnesia, alumina, zinc, and silicic acid. Of these substances STRONTIAN, LIME, MAGNESIA, and ZINC, are distinguished by being very luminous in the blow pipe flame. A drop of solution of nitrate of cobalt is added to the white residue, and the latter then again strongly heated. ALUMINA presents a fine blue tint, MAGNESIA a reddish, and ZINC a green colour. When SILICIC ACID is present, the flame assumes also a feeble bluish tint, which should not be confounded with that produced by alumina. Silicic acid is moreover distinguished by forming a clear glass, with effervescence, when mixed with carbonate of soda, and exposed to a strong blow-pipe flame. (§ 99, *b.*)

d. AN INFUSIBLE RESIDUE OF A DIFFERENT COLOUR REMAINS, OR A METALLIC REDUCTION TAKES

PLACE, WITH OR WITHOUT INCRUSTATION OF THE CHARCOAL SUPPORT. A portion of the powder is mixed with carbonate of soda, and heated in the reducing flame on charcoal.

α. A metallic grain is obtained, without simultaneous incrustation of the charcoal; this indicates the presence of GOLD, SILVER, TIN, OR COPPER. Platinum, iron, cobalt, and nickel, equally become reduced, but yield no metallic grains.

β. The charcoal support is coated over with an incrustation, either with or without simultaneous formation of a metallic grain: this indicates the presence of bismuth, lead, cadmium, antimony, or zinc.

aa. If the incrustation is white, ANTIMONY or ZINC may be supposed present. The incrustation produced by zinc appears yellow as long as it remains hot. The pure metallic grain of antimony evolves white vapour, even for a long time after all application of heat has been withdrawn; and at last, on cooling, becomes generally surrounded with crystals of oxide of antimony. It is brittle under the stroke of a hammer.

bb. The incrustation is more or less yellow or brown; this indicates the presence of BISMUTH, LEAD, OR CADMIUM. The yellow incrustation of oxide of cadmium has a shade of orange colour in it; the brownish-yellow incrustations of oxide of lead and oxides of bismuth change into a light yellow on cooling. Cadmium immediately volatilizes on becoming reduced. The grains of lead are very ductile, whilst the grains of bismuth are brittle under the stroke of the hammer.

The student must be prepared, of course, to meet with combinations of bodies giving rise to mixed phenomena, and must deduce his conclusions accordingly, since we cannot give strictly defined cases in these general rules.

II. THE SUBSTANCE IS A METAL OR AN ALLOY.

1. The test-specimen is drenched and heated with water, mixed with some acetic acid.

a. HYDROGEN IS EVOLVED; this indicates the presence of a light metal. The presence of alkalies and of alkaline earths must be had regard to in the real examination.

b. NO HYDROGEN IS EVOLVED; this indicates the absence of light metals. Alkalies and alkaline earths need not be considered in the course of the special investigation.

2. The test-specimen is heated on charcoal, in the reducing blow-pipe flame, and the phenomena observed, such as, for instance, whether the substance fuses, whether an incrustation is formed, whether any odour is emitted, &c.

a. THE SUBSTANCE REMAINS UNALTERED; this is pretty conclusive of the absence of antimony, zinc, lead, bismuth, cadmium, tin, mercury, and arsenic; the absence of gold, silver, and copper, is also probable; it indicates the presence of PLATINUM, IRON, MANGANESE, NIKEL, or COBALT.

b. THE SUBSTANCE FUSES WITHOUT SIMULTANEOUS INCRUSTATION, AND WITHOUT EMISSION OF ODOUR; this indicates the absence of antimony, zinc, lead, bismuth, cadmium, and arsenic, and the presence of GOLD, SILVER, COPPER, or TIN.

c. THE SUBSTANCE FUSES WITH THE FORMATION OF A CRUST, BUT WITHOUT EMITTING ANY ODOUR; this indicates the absence of arsenic, and the presence of ANTIMONY, ZINC, BISMUTH, LEAD, or CADMIUM. (Compare § 105 A. I., 3 *d*, *β*.)

d. THE SUBSTANCE EMITS A GARLIC ODOUR; this indicates the presence of ARSENIC. For the other phenomena which may manifest themselves, we refer to *a*, *b*, or *c*.

3. The substance is heated before the blow-pipe in a glass tube, closed at one end.

a. NO SUBLIMATE IS FORMED IN THE COLDER PART OFTHE TUBE; this indicates the absence of mercury.

b. A SUBLIMATE IS FORMED; this indicates the presence of **MERCURY**, **CADMIUM**, or **ARSENIC**. The sublimate of mercury, which consists of small globules, cannot be confounded with the sublimate of cadmium or arsenic.

B. THE SUBSTANCE UNDER EXAMINATION IS A FLUID.

1. A small portion of the fluid is evaporated in a platinum spoon, or in a small porcelain crucible, to enable us to determine whether the fluid contains any substance in solution, and what is the nature of the residue. (§ 105 A.)

2. The fluid is tested by litmus papers.

a. **BLUE LITMUS PAPER BECOMES RED.** This reaction may be caused either by a free acid, or an acid salt, or by a soluble metallic salt. In order to distinguish these two cases from each other, a small quantity of the liquid is poured into a watch-glass, and a little rod placed into it, the extreme point of which has previously been dipped into dilute solution of carbonate of potash; if the fluid remains clear, or if the precipitate which may form is redissolved on stirring the liquid, it indicates the presence of a free acid or an acid salt; but if the fluid becomes turbid, it proves the presence of a soluble metallic salt, at least generally. As a matter of course, with the presence of a free acid or acid salt, the solution cannot be considered as a mere aqueous one, and consequently we must look carefully to all those phenomena which may indicate the presence of bodies insoluble in water, and soluble only in acids.

b. **REDDENED LITMUS PAPER BECOMES BLUE**; this indicates the presence of free alkalies, or alkaline carbonates, free alkaline earths, or alkaline sulphurets, and also of a series of other salts of which this reaction is characteristic. With the presence of a free alkali, a body dissolved in the fluid may as well belong to those soluble as to those insoluble in water. We refer to § 114 I., 2, for further information on this subject.

3. We test by smelling and tasting, or should this not yield any safe results, by distillation, whether the simple

solvent present is water, alcohol, ether, &c. If it is found not to be water, the solution is evaporated to dryness, and the residue treated according to § 106 A.

4. If the solution is aqueous, and manifests an acid reaction, a portion of it is highly diluted with water. If it becomes milky, the presence of ANTIMONY, BISMUTH, or TIN, may be supposed. If the precipitate disappears on the addition of tartaric acid, we may conclude that antimony is present, whilst its disappearance on the addition of acetic acid, but not of tartaric acid, indicates the presence of bismuth. The original fluid is then treated either as § 107 directs, or § 114, according to whether we have reason to suppose it to be the solution of a simple or of a compound or mixed substance.

II. SOLUTION OF BODIES OR CLASSIFICATION OF SUBSTANCES ACCORDING TO THEIR RELATIONS TO CERTAIN SOLVENTS.

§ 106.

Water and hydrochloric acid, or in certain cases acetic acid, are the solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. We divide substances into three classes, according to their relations to these solvents.

First class.—SUBSTANCES SOLUBLE IN WATER.

Second class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC OR NITRIC ACID.

Third class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE, BOTH IN WATER, AND ALSO IN HYDROCHLORIC OR IN NITRIC ACID.

A special method for the solution of alloys is given in § 106 B, as it is advisable to dissolve them in a manner somewhat different from that employed by other bodies.

The process of solution or separation is conducted in the following manner.

A. THE SUBSTANCE UNDER EXAMINATION IS NEITHER A METAL NOR AN ALLOY.

1. About fifteen or twenty grains of the substance to

be examined, reduced to powder, are covered in a test-tube with ten or twelve times as much water, and heated to the boiling point over a spirit-lamp.

a. THE SUBSTANCE IS COMPLETELY DISSOLVED. In this case it belongs to the first class; regard must be had to what we have stated in § 105 B, 2, concerning reactions. The solution is treated either as stated at § 107, and at § 114, according as to whether one or several acids and bases are supposed to be present.

b. A RESIDUE REMAINS, EVEN AFTER BOILING THE SOLUTION FOR A LONG TIME. The solution is allowed to settle, and filtered, so that the residue remains in the test-tube if possible; a few drops of the clear filtrate are then evaporated on a clean platinum plate; if no residue remains, the substance is completely insoluble in water, and is then further tested, as stated in § 106, 2. But if a residue remains, the substance is at least partly soluble. It is then again boiled with water, filtered, and the filtrate added to the original solution. This fluid is treated, according to circumstances, either as § 107 directs, or as stated § 114. The residue is washed, and treated according to § 106, 2.

2. This residue is drenched with dilute hydrochloric acid. If it does not dissolve, it is heated to the boiling point, and if even then no complete solution takes place, the fluid is decanted, and the residue boiled with concentrated hydrochloric acid.

The phenomena which may manifest themselves in this operation, and which ought to be carefully observed, are, α, Effervescence, which indicates the presence of carbonic acid, or sulphuretted hydrogen, vide § 108, 2. β. Evolution of chlorine, which indicates the presence of hyperoxides, chromates, &c. γ. Emission of the odour of hydrocyanic acid, which indicates the presence of insoluble cyanides. Since it is advisable to decompose the latter in a different manner, a special paragraph will be devoted to them. (Vide § 128.)

a. The RESIDUE IS COMPLETELY DISSOLVED BY THE HYDROCHLORIC ACID; the solution is treated according to circumstances, either as directed § 110, or as stated § 114. The substance belongs to the second class.

The separation of undissolved sulphur, which is easily detected by its colour and specific gravity, belong also to this category.

b. A RESIDUE REMAINS. In this case the test-tube containing the specimen boiled with hydrochloric acid, is put aside pro tempore, and another specimen of the substance under examination is boiled with nitric acid, with the subsequent addition of water.

α. The specimen is completely dissolved, or undissolved sulphur alone remains; the body in these cases also belongs to the second class; the solution is further tested for bases, according to circumstances, either as directed § 110, or as stated § 114, iii.

β. A residue remains.

aa. WE HAVE REASON TO SUPPOSE THAT THE SUBSTANCE UNDER EXAMINATION CONTAINS BUT ONE BASE AND ONE ACID. The substance is drenched with aqua regia, and then heated.

αα. The substance dissolves. The solution is treated according to § 110.

ββ. The substance does not dissolve. In that case we proceed according to § 113.

bb. WE HAVE REASON TO SUPPOSE THAT THE SUBSTANCE UNDER EXAMINATION IS A COMBINATION OR MIXTURE OF SEVERAL COMPOUNDS. In this case the reserved hydrochloric solution (§ 106 A. 2, *b*,) is used to test for the bases. It is for this purpose heated to boiling with the insoluble residue—(which latter must then be treated as stated, § 106, 3)—and filtered hot into a tube containing some water, the residue is then boiled with some water, filtered hot, and the filtrate added to the hydrochloric solution.

αα. The filtrate becomes turbid and milky; this indicates ANTIMONY OR BISMUTH; or it deposits fine crystals; this indicates the presence of LEAD. The filtrate is heated again (if needed, with the addition of some hydrochloric acid) till it appears clear, and then treated, according to § 114. II.

ββ. *The filtrate remains clear.* A few drops of it are evaporated to satisfy ourselves whether the hydrochloric acid has dissolved anything. If any residue remains, the filtrate is treated according to § 114, II.

3. If boiling concentrated hydrochloric acid has left a residue, it is washed with water, and treated as directed, § 127.

B. THE SUBSTANCE UNDER EXAMINATION IS A METAL OR AN ALLOY.

The metals are best divided according to their behaviour with nitric acid.

I. METALS WHICH ARE NOT AFFECTED BY NITRIC ACID: gold, platinum.

II. METALS WHICH ARE OXIDIZED BY NITRIC ACID, BUT THE OXIDES OF WHICH DO NOT DISSOLVE IN AN EXCESS OF THE ACID: antimony tin.

III. METALS WHICH ARE OXIDIZED BY NITRIC ACID, AND THE OXIDES OF WHICH DISSOLVE IN AN EXCESS OF THE ACID, FORMING NITRATES: all other metals.

A specimen of the substance is drenched with nitric acid of 1·25 sp. gr., and heated.

1. COMPLETE SOLUTION TAKES PLACE, OR IS EFFECTED BY THE ADDITION OF WATER; this indicates the absence of platinum, gold, antimony, and tin; a small specimen of the solution is diluted with much water.

a. The solution remains clear; some hydrochloric acid is added; if this produces a white precipitate, which does not dissolve, on heating the fluid, but is dissolved by ammonia, after having been rinsed previously, SILVER is present. The original solution is treated as directed § 115.

b. The solution becomes turbid and milky; this indicates the presence of BISMUTH. The solution is filtered, and the filtrate tested for silver, as stated, § 106, B, 1, *a*. The original solution is treated according to § 115.

2. A RESIDUE REMAINS.

a. A metallic residue remains. The solution is filtered, and the filtrate treated as directed § 106, B, 1, after having examined whether anything has been dissolved. The residue is by rinsing freed from all dissolved metallic particles, dissolved in aqua regia, and divided into two portions; chloride of potassium is added to one portion: if a yellow precipitate is formed, it indicates the presence of PLATINUM. Protosulphate of iron is added to the other portion: if a black precipitate is formed, it indicates the presence of GOLD.

b. A white pulverulent residue remains; this indicates the presence of ANTIMONY OR TIN. The solution is filtered, and the filtrate treated as directed § 106, B, 1, after having examined whether anything has been dissolved. The residue is carefully rinsed, and heated with a hot saturated solution of bitartrate of potash or a solution of tartaric acid.

α. Complete solution takes place; this indicates the presence of oxide of ANTIMONY alone; the solution is tested with solution of sulphuretted hydrogen.

β. A white precipitate remains, even after boiling with a fresh portion of solution of bitartrate of potash or of tartaric acid; this indicates the probable presence of tin. The solution is filtered and mixed with solution of sulphuretted hydrogen. If an orange-red precipitate is formed, oxide of antimony is present. The presence of oxide of tin is ascertained by mixing the residue with cyanide of potassium and carbonate of soda, and reducing it before the blow-pipe. (Compare § 94, *c*, 7.)

III. REAL EXAMINATION.

Compounds supposed to consist simply of one base and one acid; or one metal and one metalloid.

A. Substances soluble in water.

Detection of the base.[*]

§ 107.

1. Some Hydrochloric acid is added to a portion of the aqueous solution.

a. No precipitate is formed; this indicates the absence of silver and protoxide of mercury with certainty, and is also a probable indication of the absence of lead. For further examination, vide § 107, 2.

b. A precipitate is formed. Divide the fluid, in which the precipitate is suspended, into two portions, and add ammonia in excess to the one.

α. *The precipitate vanishes, and the fluid becomes clear;* the precipitate in this case consists of chloride of silver, and is, therefore, indicative of the presence of SILVER. To obtain a conviction on this point the original solution must be tested with chromate of potash, and with sulphuretted hydrogen. (Vide § 90, *a*, 2, and 96, *b*, 5.)

β. *The precipitate becomes black;* it consists in this case of protochloride of mercury, which has been converted by the ammonia into protoxide of mercury, and is, consequently, indicative of the presence of PROTOXIDE OF MERCURY. To set all doubt at rest as to this point, test the original solution with protochloride of tin and with metallic copper. (Vide § 90, *b*.)

γ. *The precipitate remains unaltered;* it consists in this case of chloride of lead, which is neither decomposed nor dissolved by ammonia; this reaction is, therefore, indicative of the presence of LEAD. We assure ourselves of the presence of this substance; 1st, by diluting the second portion of the fluid in which the precipitate produced by

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[*] We include here arsenious and arsenic acid.

hydrochloric is suspended, with much water and applying heat. The precipitate must dissolve if it really is chloride of lead; 2d, by adding dilute sulphuric acid to the original solution, (§ 90, *c.*)

2. Solution of sulphuretted hydrogen is added to the fluid acidified with hydrochloric acid, till it has imparted its characteristic odour to this fluid, which the latter must still retain even after stirring and shaking; the liquid is then heated.

a. THE FLUID REMAINS CLEAR. Pass over to 3, for lead, bismuth, copper, cadmium, peroxide of mercury, gold, platinum, tin, antimony, arsenic, and peroxide of iron, are not present.

b. A PRECIPITATE IS FORMED.

α. THIS PRECIPITATE IS WHITE; it is in this case produced by the separation of sulphur, and is indicative of the presence of PEROXIDE OF IRON. (§ 88, *f.*) The original solution is then further tested with ammonia and with ferrocyanide of potassium, in order to ascertain whether the substance present is really peroxide of iron.

β. THE PRECIPITATE IS YELLOW; in this case it may consist either of sulphuret of cadmium, or a sulphuret of arsenic, or bisulphuret of tin, and indicates therefore the presence either of cadmium, or of arsenic, or of peroxide of tin. To distinguish them, ammonia in excess is added to the fluid, wherein the precipitate is suspended.

aa. The precipitate does not disappear; CADMIUM is present, sulphuret of cadmium being soluble in ammonia. The blow-pipe is resorted to for further proof. (§ 91, *d.*)

bb. The precipitate disappears. It consists either of peroxide of tin or of arsenic. Ammonia is added to a portion of the original solution.

αα. A white precipitate is formed. PEROXIDE OF TIN is the substance present. As a conclusive proof, the precipitate is then mixed with cyanide of potassium and carbonate of soda, and reduced before the blowpipe. (§ 94, *b.*)

ββ. *No precipitate is formed.* This indicates the presence of ARSENIC. The real presence of the arsenic may then be ascertained by the production of a metallic crust, either from the original substance, or from the precipitated sulphuret of arsenic, mixed with cyanide of potassium and carbonate of soda, or in some other way, and also by mixing the original substance with carbonate of soda, and exposing it to the reducing flame of the blowpipe. (§ 94, *d.*)

γ. THE PRECIPITATE IS ORANGE COLOURED; in this case it consists of sulphuret of antimony, and indicates the presence of OXIDE OF ANTIMONY. The blow-pipe is resorted to for further proof. (§ 94, *a.*)

δ. THE PRECIPITATE IS BROWN. It consists of sulphuret of tin, and indicates the presence of PROTOXIDE OF TIN. For conclusive proof, one portion of the original solution is tested with solution of perchloride of mercury, and another with solution of gold. (§ 94, *b.*)

ε. THE PRECIPITATE IS BLACK. It may in this case consist of sulphuret of lead, or sulphuret of copper, or sulphuret of bismuth, or sulphuret of gold, or sulphuret of platinum, or bisulphuret of mercury. To distinguish these from each other, the following experiments are made with the original solution.

aa. Dilute sulphuric acid is added to a portion of it; a white precipitate is formed; this indicates the presence of LEAD. Chromate of potash is employed as a conclusive test. (§ 90, *c.*)

bb. Ammonia in excess is added to a portion of it. A blue precipitate is formed which redissolves in the excess of the precipitant, imparting an azure colour to the solution; this indicates COPPER. Ferrocyanide of potassium is resorted to as a conclusive test. (§ 91, *b.*)

cc. Potash is added to a portion of it. A yellow precipitate is formed; this indicates the presence of PEROXIDE OF MERCURY. Protochloride of tin and metallic copper are employed as conclusive tests. (§ 91, *a.*) The presence of peroxide of mercury may generally also be detected by the precipitate which it yields with sulphuretted hydrogen, not appearing black from the beginning, but on the addition of an excess of the precipitant, passing through white, yellow, and orange, and then at last changing its colour into black. (§ 91, *a*, 2.)

dd. A portion of the original solution is evaporated nearly to dryness, in a porcelain crucible, and the residue put into a test tube, half filled with water. If the solution becomes milky, a basic salt of bismuth is present; this reaction, therefore, indicates BISMUTH. The blow-pipe is resorted to, as a conclusive test. (§ 91, *c.*)

ee. Solution of sulphate of iron is added to a portion of the original solution. A fine black precipitate is indicative of the presence of GOLD. The blow-pipe is resorted to as a conclusive test; or the original solution is tested with protochloride of tin. (§ 93, *a.*)

ff. Chloride of potassium is added to a portion of the original solution; the formation of a yellow crystalline precipitate is indicative of the presence of PLATINUM. For further proof this precipitate is heated to redness. (§ 93, *b.*)

3. To the fluid in which sulphuretted hydrogen has not produced any precipitate, or—should this have become too dilute—to a portion of the original solution, ammonia is added, till the solution has an alkaline reaction; hydrosulphuret of ammonia is then added. (If the solution was not acid, and thus no ammoniacal salt has been formed on the addition of ammonia, the addition of the hydrosulphuret of ammonia is preceded by that of sal ammoniac.)

a. NO PRECIPITATE IS FORMED; pass over to § 107, 4; for iron, cobalt, nickel, manganese, zinc, chromium, and alumina are not present.

b. A PRECIPITATE IS FORMED.

α. The precipitate is black; protoxide of iron, nickel, or cobalt. A portion of the original solution is treated with caustic potash.

aa. A dirty greenish white precipitate is obtained, which soon changes into a reddish-brown, when exposed to the air: PROTOXIDE OF IRON. Ferricyanide of potassium is resorted to as a conclusive test. (§ 88, *e.*)

bb. A precipitate of a light greenish tint is produced, which does not change its colour: NICKEL. Ammonia and addition of potash are resorted to as conclusive tests. (§ 88, *c.*)

cc. A sky-blue precipitate is formed, which changes its tint into red, on boiling: COBALT. The blow-pipe is resorted to as a conclusive test. § 88, *d.*)

β. The precipitate is not black.

aa. If the precipitate is of a clear flesh colour, it consists of sulphuret of manganese, and is, therefore, indicative of the presence of PROTOXIDE OF MANGANESE. The addition of potash to the original solution, or the blow-pipe, are resorted to as conclusive tests. (§ 88, *b.*)

bb. If the precipitate is bluish-green, it consists of hydrated OXIDE OF CHROMIUM. The addition of potash to the original solution, and the blow-pipe are resorted to as conclusive tests. (§ 87, *b.*)

cc. If the precipitate is white, it may consist either of hydrate of alumina, or of sulphuret of zinc, and thus be indicative of the presence either of alumina or of oxide of zinc. To distinguish these, solution of potash is gradually dropped into a portion of the original solution, till the precipitate is redissolved, and then

αα. Solution of sulphuretted hydrogen is added to a portion of it; the formation of a white precipitate is indicative of the presence of zinc. For further proof, the reaction with solution of cobalt before the blow-pipe is selected. (§ 88, *a.*)

ββ. Muriate of ammonia is added to another portion of the alkaline solution. The formation of a white precipitate is indicative of the presence of ALUMINA. The test with solution of cobalt before the blow-pipe is selected as a conclusive proof. (§ 87. *a.*).

Note to § 107. 3. β.

As very slight contaminations may impair the distinctness of the tints which the precipitates considered under § 107. 3. *b*. β present, it is advisable where such are suspected to adopt the following method for the detection of manganese, chromium, zinc, and alumina.

Potash in excess is added to a portion of the original solution.

aa. A whitish precipitate is formed, which is not redissolved in an excess of the precipitant, and soon changes its colour to a blackish brown when exposed to the air: MANGANESE. The blow-pipe is resorted to as a conclusive test. (§ 88, *b*.)

bb. A precipitate is formed which redissolves in an excess of the precipitant: oxide of chromium, alumina, zinc.

αα. Sulphuretted hydrogen is added to a portion of the solution with potass. The formation of a white precipitate indicates the presence of ZINC.

ββ. If the original or solution with potass appear green, and the precipitate, first produced by potash and then redissolved in the excess of the precipitant, was bluish, OXIDE OF CHROMIUM is present. For further proof, the solution with potass may be boiled, or the blow-pipe resorted to. (§ 87, *b*.)

γγ. Muriate of ammonia is added to the solution with potass. The formation of a white precipitate indicates the presence of ALUMINA. The test with solution of cobalt before the blow-pipe is selected as a further proof, (§ 87, *a*.)

4. Muriate of ammonia and carbonate of ammonia, mixed with a small quantity of caustic ammonia, are added to a portion of the original solution, which is then BOILED.

a. NO PRECIPITATE IS FORMED: absence of barytes, strontian, or lime. Pass over to § 107, 5.

b. A PRECIPITATE IS FORMED. Presence of barytes, strontian, or lime. Solution of gypsum is added to a portion of the original solution, and heat applied.

α. *The solution does not become turbid even after the lapse of five to ten minutes:* LIME. The test with oxalic acid is selected for further proof. (§ 86, *c.*)

β. *The solution does not become turbid at first, but after the lapse of some time:* STRONTIAN. The alcohol flame is resorted to as a conclusive test. (§ 86, *b.*).

γ. *A precipitate is immediately formed:* BARYTES. For further proof, test with hydrofluosilicic acid. (§ 86, *a.*)

5. Phosphate of soda is added to the solution of (4) in which carbonate of ammonia, after the addition of muriate of ammonia has produced no precipitate.

a. NO PRECIPITATE IS FORMED, not even after agitating the solution: absence of magnesia. Pass over to § 107, 6.

b. A FINE CRYSTALLINE PRECIPITATE IS FORMED: MAGNESIA.

6. A drop of the original solution is evaporated on a platinum plate and the residue heated to redness.

a. NO FIXED RESIDUE REMAINS. The original solution is tested for AMMONIA, by adding potash to it, and examining the odour, the vapours formed with acetic acid, and the reaction of the escaping gas. (§ 85, *c.*)

b. A FIXED RESIDUE REMAINS. Potash or soda. Tartaric acid is added to a portion of the original solution, and the latter well shaken.

α. *No precipitate is formed, not even after the lapse of ten to fifteen minutes:* SODA. The blowpipe flame and alcohol flame, and especially the reaction with antimoniate of potash, are selected as conclusive tests. (§ 85, *b.*)

β. *A crystalline granular precipitate is formed:* POTASH. Chloride of platinum, the blow-pipe flame, and alcohol flame, are selected as conclusive tests. (§ 85, *a.*)

Compounds which are supposed to contain but one acid and one base, &c.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

I. *Detection of inorganic acids.*

§ 108.

We must in the first place consider what acids form combinations soluble in water, with the base detected, and bear it in mind in the subsequent examination.

1. We have already spoken of the detection of the ARSENIOUS and ARSENIC ACID in treating of the detection of the bases. They are distinguished from each other by their behaviour with nitrate of silver, or with potash and sulphate of copper. (§ 94, *d* and *e.*)

2. The detection of CARBONIC ACID, HYDROSULPHURIC ACID and CHROMIC ACID, has also already been pointed out, when treating of the detection of the bases. The two former betray their presence by effervescing on the addition of hydrochloric acid; they may be distinguished from each other by their odour, and if needed, the presence of carbonic acid may be proved by its reaction with lime-water, (§ 99, *a*,) and that of sulphuretted hydrogen by the reaction with solution of lead. (§ 100, *e*.) Chromic acid may, in most cases, be detected by the yellow or red tint of its solution, and also by its solution changing colour and yielding a precipitate of sulphur, on the addition of sulphuretted hydrogen. We may assure ourselves of the presence of chromic acid by the reaction with solution of lead, and solution of silver. (§ 96, *b.*)

3. Chloride of barium is added to a portion of the solution; should the latter have an acid reaction, it must first be neutralized or rendered feebly alkaline, by the addition of ammonia.

a. THE FLUID REMAINS CLEAR. (Pass over to § 108, 4.) The absence of sulphuric acid, phosphoric acid, and silicic acid is certain, that of oxalic acid and boracic acid, probable. For the barytes compounds of these two latter acids are kept in solution by ammoniacal salts, and borate of barytes does not at all precipitate from dilute solutions.

b. A PRECIPITATE IS FORMED. Hydrochloric acid is added in excess.

α. The precipitate redissolves. Absence of sulphuric acid. Pass over to 4.

β. The precipitate remains and does not dissolve even in a large proportion of water: SULPHURIC ACID.

4. Solution of gypsum is added to a portion of the original solution, which, should it have an acid reaction, must first be rendered neutral or feebly alkaline, by the addition of ammonia.

a. NO PRECIPITATE IS FORMED: absence of oxalic acid and phosphoric acid. Pass over to § 108, 5.

b. A PRECIPITATE IS FORMED. Acetic acid is added in excess.

α. The precipitate is redissolved: PHOSPHORIC ACID. The reactions with sulphate of magnesia and ammonia, with solution of silver, and before the blow-pipe, are selected as conclusive tests. (§ 98, *a.*)

β. The precipitate remains undissolved, but dissolves readily in hydrochloric acid: OXALIC ACID. The reaction with concentrated sulphuric acid is selected as a conclusive test. (§ 98, *c.*)

5. A fresh portion of the original solution is acidified with nitric acid, and solution of nitrate of silver is then added.

a. THE FLUID REMAINS CLEAR. This is a certain indication of the absence of chlorine and iodine. The absence of cyanogen is also probable. For cyanide of mercury is not precipitated by nitrate of silver; and from the detected base we may conclude whether we have to look for the presence of this substance or not; for the manner in which the presence of the cyanogen in it is proved, we refer to § 100, *d.* Pass over to § 108, 6.

b. A PRECIPITATE IS FORMED. Ammonia is added in excess.

α. The precipitate does not dissolve IODINE. As a conclusive test, we select the reaction with starch. (§ 100, *c.*)

β. *The precipitate is redissolved.* If it redissolves readily, we have reason to suppose that CHLORINE is present; if it dissolves with difficulty and only on the addition of much ammonia, we may suppose that CYANOGEN is present. We assure ourselves of the presence of chlorine, by testing the original solution with protonitrate of mercury, and by the behaviour of the silver precipitate formed when exposed to a high temperature. (§ 100, *a.*) The presence of cyanogen may be further proved by adding potash, solution of magnetic oxide of iron and hydrochloric acid to the original solution. (§ 100, *d.*)

6. A portion of the solid substance—(or if we have a fluid to operate upon, the residue obtained by evaporation).—is drenched with some sulphuric acid, alcohol added, and then kindled. BORACIC ACID is present if the flame appears green on stirring.

7. The preliminary examination generally enables us to detect nitric acid. (§ 105, A, I, 2, *c.*) The reactions with sulphate of iron and sulphuric acid, or solution of indigo, are selected as conclusive proofs. (§ 101, *a.*)

8. We refer to § 123 for the detection of chloric acid, hydrofluoric acid, cilicic acid, and bromine.

Compounds which we suppose to contain only one acid and one base, &c.

A. SUBSTANCES SOLUBLE IN WATER. DETECTION OF THE ACID.

II. DETECTION OF ORGANIC ACIDS.

§ 109.

1. To a portion of the aqueous solution, ammonia is added till a feeble alkaline reaction becomes manifest, and then chloride of calcium. If we have to operate upon a neutral solution, some muriate of ammonia is added to it, previous to the addition of the chloride of calcium.

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER AGI-

TATING THE SOLUTION, NOR AFTER THE LAPSE OF A FEW MINUTES: absence of oxalic acid and tartaric acid. Pass over to § 109, 2.

b. A PRECIPITATE IS FORMED. Lime-water is added in excess to a portion of the original solution, and the precipitate formed treated with solution of sal ammoniac.

α. *The precipitate vanishes:* TARTARIC ACID. The reaction with acetate of potash may be resorted to for further proof; but the safest test is the behaviour of the precipitate produced by chloride of calcium, with caustic potash. (§ 102, *b.*)

β. *The precipitate does not vanish:* OXALIC ACID.

2. The fluid of 1, *a*, is heated to boiling, kept at the boiling point for some time, and some ammonia added whilst boiling.)

a. IT REMAINS TRANSPARENT; no citric acid. Pass over to § 109, 3.

b. IT BECOMES TURBID, AND DEPOSITS A PRECIPITATE: CITRIC ACID.

3. The fluid of 2, *a*, is mixed with alcohol.

a. IT REMAINS TRANSPARENT: no malic acid. Pass over to § 109, 4.

b. A PRECIPITATE IS FORMED: MALIC ACID. The re-action with acetate of lead is selected as a conclusive test. (§ 102, *e.*)

4. A portion of the original solution is rendered perfectly neutral—(if it is not already so)—by ammonia or hydrochloric acid, and solution of perchloride of iron added.

a. A CINNAMON-COLOURED OR DIRTY YELLOW BULKY PRECIPITATE IS FORMED. This precipitate is treated with dilute hydrochloric acid.

α. *It dissolves transparent;* SUCCINIC ACID.

β. *It dissolves, with the separation of a white precipitate:* BENZOIC ACID. We assure ourselves of the real presence of this substance, by heating the precipitate. It must manifest the properties of free benzoic acid. (Vide § 103, *b.*)

b. THE LIQUID ASSUMES AN INTENSE RED TINT, AND UPON BOILING FOR SOME TIME, A LIGHT REDDISH-BROWN PRECIPITATE SEPARATES: acetic acid or formic acid. A portion of the solid salt under examination, or the residue obtained by evaporating the liquid—(if the liquid is acid, it must be neutralized with potash, previous to the evaporation)—is heated with sulphuric acid and alcohol, (§ 104, *a.*) The characteristic odour of acetic ether, indicates the presence of ACETIC ACID.

If we do not detect acetic acid in the fluid, we must conclude that the substance under examination contains FORMIC ACID: the certain presence of this latter substance may be proved by its behaviour with nitrate of silver and protoxide of mercury. (§ 104, *b.*)

Compounds which are supposed to consist of but one acid and one base.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

*Detection of the base.**

§ 110.

A portion of the solution in hydrochloric acid, nitric acid, or aqua regia, is diluted with water,† and the further operations conducted exactly as directed § 107, beginning at 1, when the substance is dissolved in nitric acid, and at 2, when it contains already hydrochloric acid. The following circumstances must be well attended to: we have seen that if in cases where we have A SUBSTANCE SOLUBLE IN WATER before us, we obtain in the course of the examination, a white precipitate on testing with hydrosulphuret of ammonia—(after having neutralized with ammonia the free acid either originally contained in or previously added to the solution under examination) this precipitate can consist only either of sulphuret of zinc, or of alumina. But the case is different, when the substance is INSOLUBLE IN

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* Regard has here been had also to several salts, since this course of examination directly leads to their detection.

† If, on the addition of the water, the liquid becomes turbid or is precipitated, it indicates the presence of antimony, bismuth, or tin. (Compare § 105, B 4.)

WATER, but dissolved by hydrochloric acid; for in that case the white precipitate produced by hydrosulphuret of ammonia, with the presence of sal ammoniac, may also consist of a phosphate of the alkaline earths as well as of oxalate of lime, (barytes and strontian.) If, therefore, we obtain a white precipitate when testing an acid solution, under the circumstances stated, and as directed § 107, at 3 *β. cc*, the following method must be employed. Caustic potash in excess is added to a small portion of the original hydrochloric solution.

1. THE PRECIPITATE AT FIRST FORMED, REDISSOLVES IN EXCESS OF THE PRECIPITANT; absence of the salts of the alkaline earths; presence of zinc or of alumina: to distinguish these from each other, the solution with potass is tested with sulphuretted hydrogen and muriate of ammonia. (Vide supra § 107, 3 *b. β cc.*) Alumina may have been present and precipitated as phosphate of alumina. This is ascertained by dissolving the precipitate in hydrochloric acid, adding tartaric acid, supersaturating with ammonia and mixing with sulphate of magnesia. If phosphoric acid is present, a precipitate of basic phosphate of ammonia and magnesia is formed.

2. THE PRECIPITATE FORMED DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT. Presence of a phosphate or oxalate with an alkaline earth for its base. In this case a portion of the original substance is heated to redness, in order to ascertain whether we have an oxalate or a phosphate before us. If the substance is converted by this process into a carbonate—(slightly blackening or not at all)—which is easily detected by the heated mass effervescing when treated with acids, whilst previous to the heating it did not present this property, we may conclude that the salt is an OXALATE; if, on the contrary, no alteration takes place, on the application of a red heat, we have a PHOSPHATE before us.

a. THIS PRELIMINARY EXAMINATION DENOTED THE PRESENCE OF A PHOSPHATE.

A certain, not too inconsiderable quantity, of perchloride of iron is added to a portion of the hydrochloric solution, which is then brought to alkaline reaction by the addition of ammonia, and the liquid filtered off from the bulky precipitate formed, which should present a reddish-brown tint. In this operation the phosphoric acid is separated from its base, and, combined with peroxide of iron, precipitated together with free hydrate peroxide of iron, whilst the alkaline earth base is contained in the filtered liquid as a chloride. The further process of the detection of this base is conducted as directed § 107, 4.

In order to determine the presence of the phosphoric acid also, the iron precipitate is rinsed, and digested with hydrosulphuret of ammonia. We obtain in this process sulphuret of iron and phosphate of ammonia. These are separated from each other by filtration, and sal ammoniac and sulphate of magnesia is then added to the filtered liquid; the precipitate which forms, of basic phosphate of ammonia and magnesia, is a safe indication of the presence of phosphoric acid. In more minute examinations, the excess present of hydrosulphuret of ammonia is first decomposed by the addition of hydrochloric acid, the solution heated to boiling, and the precipitated sulphur filtered off; the filtered solutions, if needed, concentrated by evaporation, supersaturated with ammonia, and sulphate of magnesia then added.

b. THE PRELIMINARY EXAMINATION INDICATED THE PRESENCE OF AN OXALATE.

Two methods may be pursued, with certainty, to determine the base and the acid.

1. A portion of the compound is heated to redness, the residue dissolved in hydrochloric acid, and the alkaline earth which forms the base, detected in the usual manner in this solution. Of the presence of the oxalic acid, we assure ourselves by testing another portion of the substance with concentrated sulphuric acid. (§ 98, *c.*)

2. A portion of the compound is boiled for some time in a concentrated solution of carbonate of potash, and the fluid filtered from the residue. In this manner we obtain in the residue the alkaline earth which forms the base of the substance under examination, combined with carbonic acid, whilst

we have the oxalic acid combined with potash in the filtered solution; to assure ourselves of the real presence of this acid, the solution is first acidified with acetic acid, and then treated with solution of gypsum. (§ 98, c.). The residue is rinsed and dissolved in hydrochloric acid, and the solution treated as directed § 107, 4.

Compounds which are supposed to consist of but one acid and one base, &c.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

DETECTION OF THE ACID.

1. *Detection of inorganic acids.*

§ 111.

1. **CHLORIC ACID** cannot be present, for all chlorates are soluble in water; the nitrates also, with the exception of a few, being soluble in water, we may generally disregard the presence of **NITRIC ACID**. The basic [illegible] of bismuth forms the most frequently occurring [illegible] to the general rule of solubility of the nitrates in water. The presence of nitric acid in such insoluble compounds may be immediately detected by deflagration taking place when the substance under examination is thrown upon red-hot charcoal. The deflagration which ensues on fusing a nitrate together with cyanide of potassium, is a safer test of the presence of nitric acid. (Vide § 101, *a*.) For the **CYANIDES** insoluble in water, we refer to § 128.

2. The detection of **ARSENIOUS** and **ARSENIC ACID**, **CARBONIC ACID**, **HYDROSULPHURIC ACID**, and **CHROMIC ACID**, has already been pointed out, when treating of the detection of bases; as the best tests and indications of the presence of chromic acid, we have pointed out the yellow or red colour of the compound, the evolution of chlorine, upon a chromate being boiled with hydrochloric acid, and the subsequent detection of chromic oxide in the solution. But the safest method, and that which was applicable in all

cases, is to fuse the substance supposed to contain chromic acid, together with some carbonate of soda and nitre. (§ 96, *b.*)

3. A portion of the substance under examination is boiled with nitric acid.

a. If nitric oxide gas is evolved, which is easily detected by the red fumes of nitrous acid, formed on coming in contact with the air, it indicates the presence of a SULPHURET; if carbonic acid is evolved, that of a CARBONATE. Of the presence of a sulphuret we may easily assure ourselves, by testing the nitric solution with chloride of barium; it should yield with this reagent a precipitate of sulphate of barytes, which must remain undissolved even in a large quantity of water. Sulphurets may as safely be detected by their behaviour before the blow-pipe. (Vide § 100, *c.*)

b. If violet vapours escape, the compound may be supposed to be an IODIDE. A slip of paper, covered with starch, forms the best conclusive test of the presence of iodine. (§ 100, *c.*)

4. Nitrate of silver is added to a portion of the nitric solution, (this solution must previously be filtered, if upon treating the substance with nitric acid any insoluble residue has remained.) If a white precipitate is formed soluble in ammonia, and fusing without decomposition when heated, it indicates the presence of CHLORINE.

5. A portion of the substance is boiled with hydrochloric acid, filtered, if needed, and nitrate of barytes added. The formation of a white precipitate, which does not disappear, even on the addition of a large proportion of water, indicates the presence of sulphuric acid.

6. For BORACIC ACID, test as stated supra, § 108.

7. If none of all these acids is present, we have reason to suppose the presence of either PHOSPHORIC ACID or OXALIC ACID, or the absence of all acids. If the phosphoric acid had been combined with an alkaline earth, and the oxalic acid with lime, (barytes, or strontian,) either of them would have already been detected when testing for these bases. (§ 110.) We may therefore disregard the presence of these two acids, except when other bases than those enumerated are present. In the latter case the fluid is prepared for further examination by precipitating and sepa-

rating the heavy metals from it—(this is effected in acid solutions by means of sulphuretted hydrogen, and in alkaline solutions by hydrosulphuret of ammonia)—and is then tested for phosphoric acid or oxalic acid, as directed § 108, 4.

8. For the detection of SILICIC ACID, BROMINE, AND FLUORINE, vide § 123, at the end.

Compounds which are supposed to consist of but one base and one acid, &c.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

DETECTION OF THE ACID.

II. *Detection of organic acids.*

§ 112.

1. A portion of the substance under examination is dissolved in the smallest possible quantity of hydrochloric acid. If a residue remains, this must be tested for BENZOIC ACID by heating. Carbonate of potash in excess is then added to the hydrochloric solution, and the latter boiled for some time and filtered. The alkaline filtrate contains the organic acid, under all circumstances. This filtered solution is therefore exactly saturated with hydrochloric acid, and the fluid tested, as directed § 109. No regard need be had to formic acid, all the formiates being soluble in water.

2. ACETIC ACID is most readily detected in such compounds by means of sulphuric acid and alcohol. (§ 104, *a.*)

Compounds which are supposed to consist of but one acid and one base, &c.

C. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, HYDROCHLORIC ACID, NITRIC ACID, AND AQUA REGIA.

DETECTION OF THE BASE AND THE ACID.

§ 113.

Under this head we propose to consider SULPHATE OF BARYTES, SULPHATE OF STRONTIAN, SULPHATE OF LIME,

SILICA, SULPHATE OF LEAD, CHLORIDE OF LEAD, and CHLORIDE OF SILVER, as the most frequently occurring compounds belonging to this class. For the less frequently occurring compounds of this kind, we refer to § 127.

Sulphate of lime and chloride of lead are not altogether insoluble in water, and sulphate of lead may be dissolved in hydrochloric acid. As these compounds are, however, so sparingly soluble that we seldom can effect their complete solution, we mention them here once more, in order that they may be detected by the method laid down in this section, should they have escaped detection in the examination of their aqueous or acid solutions.

1. A very minute quantity of the substance under examination is treated with hydrosulphuret of ammonia.

a. IT BECOMES BLACK; this indicates the presence of a SALT OF LEAD or CHLORIDE OF SILVER. A somewhat larger portion of the substance is then digested for some time with hydrosulphuret of ammonia. In this process the metallic salt becomes decomposed, and a sulphuret is formed, which remains undissolved, whilst we have in solution the acid of the metallic salt combined with the ammonia of the hydrosulphuret of ammonia. The solution is then filtered, the undissolved sulphuret washed and dissolved in nitric acid, and this nitric solution tested, with sulphuric acid, for lead; and with hydrochloric acid, and subsequent addition of ammonia, for SILVER. One portion of the filtered liquid is tested for SULPHURIC ACID, with chloride of barium, after having previously decomposed the excess of the hydrosulphuret of ammonia, by the addition of hydrochloric acid and boiling up; another portion is tested for HYDROCHLORIC ACID, with solution of silver; after having previously acidified the liquid with nitric acid, and then boiled it.

b. IT BECOMES WHITE. Absence of a heavy metallic oxide. A small portion of the substance under examination is reduced to a very fine powder, and then mixed with four times its quantity of carbonate of soda and potash, put into a small platinum crucible, and fused over a Berzelius spirit-lamp. The fused mass is boiled with water.

α. *Complete solution takes place:* SILICA. We assure ourselves of the presence of this substance by supersaturating the solution with hydrochloric acid, and evaporating to dryness. In this operation, silicic acid is converted from its soluble into its insoluble modification. It remains, therefore, undissolved on treating the residue with water. When mixed with carbonate of soda, and exposed to a strong blow-pipe flame, a transparent glass is produced. (§ 99, *b*.)

β. *A white residue remains;* this indicates one of the SULPHATES OF THE ALKALINE EARTHS. The solution is filtered, and the filtered liquid acidified with hydrochloric acid, and then tested for SULPHURIC ACID, with chloride of barium. The white residue (which contains the alkaline earth as a carbonate) is carefully washed, dissolved in a small quantity of dilute sulphuric acid, and the solution tested for BARYTES, STRONTIAN, or LIME, as directed § 107, 4.

Compounds in which all the more frequently occurring Bases, Acids, Metals, and Metalloids, are supposed to be present.

A. SUBSTANCES BOTH SOLUBLE AND INSOLUBLE IN WATER, AND SOLUBLE IN HYDROCHLORIC ACID OR NITRIC ACID.

Detection of the bases.[*]

§ 114.

In this scheme for the testing of the bases we have united the compounds belonging to classes I. and II., (vide § 106,) since the method of detection is in most cases the same for both classes. Those parts which refer only to substances insoluble in water, and soluble in hydrochloric acid and nitric acid, are enclosed between inverted

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[*] The arsenious and arsenic acid, and several salts, have here been had regard to, since we are, in this course of examination, led to their detection.

commas, ("——"), and may, therefore, be passed over unnoticed, when examining substances soluble in water.

I. THE SOLUTION IS AQUEOUS.

A small quantity of hydrochloric acid is added.

1. THE SOLUTION HAD AN ACID OR NEUTRAL REACTION PREVIOUS TO THE ADDITION OF THE HYDROCHLORIC ACID.

a. NO PRECIPITATE IS FORMED: this indicates the absence of silver and protoxide of mercury. Pass over to § 115.

b. A PRECIPITATE IS FORMED; hydrochloric acid is added to the solution drop by drop, as long as the quantity of the precipitate increases. This precipitate may consist of chloride of silver, protochloride of mercury, chloride of lead, or a basic salt of antimony, or, possibly, also of benzoic acid. The fluid is agitated, and a portion of it, together with the therein suspended particles of the precipitate, mixed with a large quantity of water, and heated to boiling. If compounds of antimony, bismuth, or tin are present, the dilution with water may render the liquid turbid, which phenomenon is usually distinctly perceived, notwithstanding the precipitate which the fluid already contained previous to the addition of the water. In order to judge with certainty, whether the precipitate produced by hydrochloric acid redissolves in the water on boiling or not, and, therefore, whether the further operation is to be conducted according to α or β, hydrochloric acid is added to the dilute solution—(previous to heating)—till the milkiness has completely vanished.

α *The precipitate vanishes;* this indicates the absence of silver and protoxide of mercury. The original solution, together with the precipitate produced in it by hydrochloric acid is heated to boiling and filtered hot. Should the precipitate not completely redissolve, the residue is once more boiled with water, and the solution filtered hot into the first filtrate. The filtered solution is treated as directed § 115. Should it have deposited a precipitate, or small crystals (chloride of lead) have formed on cooling, it must be previously heated, till it appears transparent again.

β. The precipitate does not vanish, at least not completely; this indicates the presence of SILVER or PROTOXIDE OF MERCURY.

The original solution (with the hydrochloric acid) is treated as directed § 114, I. 1, b, α The residuary insoluble precipitate is washed and tested as follows: it is, if possible, removed from the filter and treated with ammonia, in a small tube. If it dissolves in this substance, it consists exclusively of SILVER; if it becomes black, PROTOXIDE OF MERCURY is present. In this case, or whenever a residue insoluble in ammonia remains, this must be filtered off, and nitric acid in excess added to the filtered liquid; the formation of a white, curdy precipitate indicates SILVER.

2. THE AQUEOUS SOLUTION HAD AN ALKALINE REACTION.

a. NO EVOLUTION OF GAS TAKES PLACE AND NO PRECIPITATE IS FORMED, ON THE ADDITION OF HYDROCHLORIC ACID, OR, A PRECIPITATE IS AT FIRST FORMED, BUT REDISSOLVES ON THE FURTHER ADDITION OF HYDROCHLORIC ACID; pass over to § 115. For all that relates to substances belonging to the second class—(i. e. those insoluble in water, and soluble in hydrochloric acid or nitric acid)—enclosed between inverted commas, look to the passages upon phosphate of alumina, but, if an ammoniacal salt is present, also to those upon the oxalates of the alkaline earths, since the solution of these compounds in a fluid with alkaline reaction is not impossible.

b. A PRECIPITATE IS FORMED, ON THE ADDITION OF HYDROCHLORIC ACID, WHICH DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT.

α. The precipitate is formed without simultaneous evolution of sulphuretted hydrogen gas. A portion of the fluid with the precipitate suspended therein, is diluted with a large proportion of water, and heated. The solution of the precipitate is indicative of LEAD, or possibly also of benzoic acid. The original solution is then heated to boiling, together with the precipitate produced by hydrochloric acid, filtered hot, and the residue (if any remain) boiled with water and filtered hot into the hydrochloric solution. The filtrate is treated according to § 115; should it become turbid on cooling, it must be heated again previous to being further tested. If the precipitate does not redissolve on heating the fluid diluted with water, but is dissolved by ammonia, SILVER is present. The original solution is treated in the same manner as if the precipitate had been redissolved.

β. The precipitate is formed with simultaneous evolutions of sulphuretted hydrogen gas.

aa. The precipitate is of a pure white colour, and consists of sulphur. In this case an alkaline bisulphuret is present. Filter the solution and pass over to § 118, bearing in mind that of the substances considered § 118, oxide of chromium and alumina alone can be present.

bb. The precipitate is coloured. In this case we must suppose that a metallic sulphur salt is present, i. e. a combination of an alkaline sulphur base with an electro-negative sulphuret. The solution is heated to boiling and filtered; the filtrate is further tested as stated under *aa.* The precipitate is treated as § 116 directs; it may consist of SULPHURET OF GOLD, SULPHURET OF PLATINUM, SULPHURET OF TIN, SULPHURET OF ARSENIC, OR SULPHURET OF ANTIMONY.

c. NO LASTING PRECIPITATE IS FORMED, ON THE ADDITION OF HYDROCHLORIC ACID, BUT EVOLUTION OF GAS TAKES PLACE.

α. The escaping gas has the odour of sulphuretted hydrogen; this indicates a simple alkaline sulphur compound. The further operations are conducted as directed *aa.*

β. The escaping gas emits no odour; in this case it is carbonic acid which was combined with an alkali. Pass over to § 115, bearing in mind, that mercury, bismuth, insoluble salts of magnesia, and (if the reaction is strongly alkaline) barytes, strontian, and lime cannot be present, or at least only under very peculiar circumstances, (e. g. mercury as a cyanide.)

II. The solution is hydrochloric.

It is treated as § 115 directs.

III. The solution is nitric.

A small portion of it is diluted with much water.

1. It remains transparent; add hydrochloric acid.

a. No precipitate is formed. Absence of silver. The original solution is treated according to § 115.

b. A precipitate is formed. If it does not redissolve on heating the fluid, but is dissolved by ammonia, after washing, SILVER is present. The original solution is treated as stated § 115.

2. The solution becomes turbid and milky: BISMUTH or ANTIMONY. The fluid is filtered, and the filtrate tested for silver according to § 114, III. 1; the original solution is tested as § 115 directs.

§ 115.

Solution of sulphuretted hydrogen is added to a SMALL PORTION of the transparent acid solution, till the fluid, after agitation, and application of heat, emits a clearly perceptible odour of sulphuretted hydrogen.

a. No precipitate is formed, not even after the lapse of some time. Pass over to § 118, for neither lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, nor arsenic,* are present; the absence of peroxide of iron and of chromic acid is also indicated by this negative reaction.

b. A precipitate is formed.

aa. It is of a pure white colour, thin, in the form of a fine powder, and does not vanish on the addition of hydrochloric acid. It consists of sulphur, and indicates PEROXIDE OF IRON.† None of the

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* To assure ourselves of the certain absence of arsenic acid, we must allow the test solution to stand for some time, or add sulphurous acid, previous to the addition of the sulphuretted hydrogen. (Compare § 93, *e.*)

† Sulphur is also precipitated in presence of sulphurous acid, iodic acid, bromic acid,—which substances we do not treat of in the present work,—and also when chromic acid, chloric acid, or free chlorine are present.

other metals, enumerated at § 115, *a*, can be present. The original solution is treated as § 118 directs.

bb. The precipitate is coloured.

Solution of sulphuretted hydrogen is added to the larger portion of the acid or acidified solution, till the latter has acquired the distinct odour of sulphuretted hydrogen, and the precipitate no longer increases on the continued addition of the reagent; the solution is then heated to boiling, and strongly agitated for some time.

In many cases, and especially when there is any reason to suppose arsenic to be present, it is better to transmit sulphuretted hydrogen gas through the solution.

1. THE PRECIPITATE IS OF A PURE YELLOW COLOUR. In this case it can consist only of ARSENIOUS OR ARSENIC ACID, of PEROXIDE OF TIN, or of OXIDE OF CADMIUM. The fluid—(which is then further to be tested according to § 118)—is separated from the precipitate,* and the latter washed and drenched with ammonia.

a. The precipitate is completely redissolved: absence of cadmium. Acetic acid is added slightly in excess to the solution, and the precipitate formed is tested for TIN and ARSENIC, as § 116, 1, directs.

b. A yellow residue remains, even after a further addition of ammonia and the application of a moderate heat: CADMIUM. The solution is filtered, and acetic acid, slightly in excess, added to the filtrate. If no precipitate is formed, the first precipitate consisted exclusively of sulphuret of cadmium; but if a precipitate is formed, it denotes the presence of PEROXIDE OF TIN, OR ARSENIC; this precipitate is tested as directed § 116, 1.

2. THE PRECIPITATE IS ORANGE-RED, OR YELLOW, WITH A SHADE OF ORANGE-COLOUR. It indicates ANTIMONY, but may, morover, contain TIN—(should it have

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* The best method of separating a precipitate from a fluid, is to allow the precipitate to settle—(this is facilitated by heating and agitating)—the fluid may then be decanted and the precipitate washed.

been present as a peroxide)—ARSENIC or CADMIUM; the precipitate is separated from the fluid—(which is tested as § 118 directs)—washed, and a small portion of it digested with hydrosulphuret of ammonia, which contains sulphur in excess.

a. It redissolves completely: absence of cadmium. The rest of the precipitate is treated as directed § 116, 2.

b. A yellow residue remains, even after a more protracted digestion, with a larger quantity of hydrosulphuret of ammonia: CADMIUM. The entire precipitate is then treated in the same manner as the specimen, the fluid filtered off from the sulphuret of cadmium, and acetic acid in a slight excess added to the filtrate; the precipitate formed is treated as § 116, 2, directs.

3. THE PRECIPITATE IS OF A DARK BROWN OR BLACK COLOUR. The precipitate is separated from the fluid—(which is then tested as § 118 directs)—washed with water, drenched and digested for some time, with hydrosulphuret of ammonia, containing sulphur in excess.*

a. The precipitate is completely redissolved in hydrosulphuret of ammonia, or in sulphuret of potassium; absence of cadmium, lead, bismuth, copper, and mercury: § 117 may, therefore, be passed over unnoticed. The solution is diluted, and acetic acid added, till an acid reaction becomes manifest; it is then heated to boiling, and the precipitate formed, treated as § 116 directs.

b. It does not dissolve, or at least not completely. The fluid is filtered off from the precipitate, and the latter is washed, (in case § 115, 3 *b* α,) or (in case β) once more digested with hydrosulphuret of ammonia, filtered into the first solution, and then washed. The residue is reserved for further examination, as directed § 117. A small portion of the filtrate contain-

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* If the solution contains copper, which may generally be detected by its colour, but with certainty by testing with a clean iron rod, (vide § 91, *b*, 6,) solution of sulphuret of potassium must be substituted for hydrosulphuret of ammonia, and the sulphur precipitate be boiled in it, (i. e. in the sulphuret of potassium,) vide § 91, *b*, 2.

ing hydrosulphuret of ammonia is diluted with from three to four parts of water, acetic acid added, till an acid reaction becomes manifest, and the liquid heated to boiling.

α. *The fluid simply becomes milky, owing to the separation of sulphur.* Absence of gold, platinum, tin, antimony, and arsenic. Pass over to § 117.

β. *A coloured precipitate is formed.* The colour of the precipitate is minutely inspected; the entire solution containing the hydrosulphuret of ammonia is then slightly diluted, acetic acid added, till an acid reaction becomes manifest, and the fluid heated to boiling.

§ 116.

The precipitate which acetic acid has produced in the solution containing hydrosulphuret of ammonia or sulphuret of potassium, is

1. OF A PURE YELLOW COLOUR, WITHOUT THE SLIGHTEST SHADE OF ORANGE: ARSENIC OR TIN. The solution is filtered off from the precipitate, the latter well washed, and together with the filter placed between some sheets of blotting-paper; when the paper has imbibed the greater part of the water, the still moist precipitate is removed from the filter, and mixed in a small porcelain crucible with about half its amount of pure anhydrous carbonate of soda, and one and a-half its amount of pure nitre; the mass is then gently heated, and stirred, till it has become completely dry, when a stronger heat is applied—(beginning at the edge of the crucible)—till the entire mass fuses, and every particle of the sulphuret is decomposed. (If after drying the mass a very high degree of heat is suddenly applied and allowed to act upon the whole crucible at once, slight explosions take place, whereby more or less of the mass is thrown out of the crucible.)

a. *The melting mass is transparent.* Absence of tin. The mass, after cooling, is boiled with water, the solution divided into two portions, and very dilute nitric acid very cautiously added to the one, till a feebly acid reaction becomes manifest; heat is then applied. (If there is really no tin present, no white pulverulent residue must remain, on boiling the deflagrated mass with water, neither must any precipitate be formed, on acidulating the solution with nitric acid, not even after standing at rest for some time.) Nitrate of silver is added to the acidified solution, after cooling, and the fluid filtered; if any traces of chloride of silver should still separate, which is frequently the case if the reagents are not absolutely pure, or the precipitate not completely washed. The filtrate is then slowly and cautiously covered in a test-tube with very dilute ammonia—(one part of ammonia to twenty parts of water—and allowed to stand for some time, without agitating. The formation of a reddish brown precipitate, which appears like a cloud between the two layers (of the test specimen and the dilute ammonia,) indicates ARSENIC; (this precipitate is more clearly seen, on the light falling upon than through it.) As a further proof, the second portion of the solution of the deflagrated mass is precipitated by solution of neutral acetate of lead, the precipitate filtered off, dried between some sheets of blotting-paper, and then, on charcoal, exposed to the reducing flame of the blow-pipe. If arsenic is really present, a grain of metallic lead containing arsenic will be obtained, which emits the garlic odour of arsenic very long and continuously; as often as it is exposed to the reducing blow-pipe flame. For further confirmation, the arsenic must be obtained in its metallic state. (Compare § 94, *d* and (*e*.) Whether the arsenic was present in the compound under examination as arsenic acid, or as arsenious acid, may be ascertained according to the method described at the end of § 94.

b. The melting mass is milky and turbid. This is a probable indication of the presence of tin. The mass is digested with cold water, and rubbed with it in a mortar; the solution is then filtered, and the precipitate which remains, if tin is really present, very carefully washed, and then tested for tin, by reducing it before the blow-pipe mixed with cyanide of potassium and carbonate of soda, and strongly rubbing the specimen in a mortar, with the addition of water; vide § 94, *b*. The liquid filtered off from this precipitate is divided into two portions and tested for arsenic as § 116, 1, *a*, directs. A slight precipitate generally separates on acidifying the solution with nitric acid. This may be filtered off and tested for tin in the same manner as the undissolved residue, (vide supra.) But if the tin has already been detected, this precipitate may be left in the solution, nitrate of silver added, filtered, and the fluid tested for arsenic acid, as directed above. Whether the tin was present as protoxide, is ascertained, by mixing a portion of the original solution in water or hydrochloric acid, with a drop of nitric acid and some chloride of gold. (§ 94, *b*, 5.)

2. ORANGE-RED, OR YELLOW, WITH A SHADE OF ORANGE; ANTIMONY; and besides TIN and ARSENIC may be present. The precipitate is washed and fused with nitre and carbonate of soda, in short, tested for arsenic and protoxide of tin, exactly as § 116, 1, *b*, directs. The residue remaining on treating the deflagrated mass with cold water, as well as the precipitate which may perchance be formed on acidifying the solution with nitric acid, may be tested in three different ways.

a. The residue (or precipitate) is most carefully washed, mixed with cyanide of potassium and carbonate of soda, and exposed on charcoal, to the reducing flame of the blow-pipe.

α. Metallic globules appear, which at last completely volatilize, with the emission of white fumes and the formation of a white crust. This is confirmatory of the presence of ANTIMONY, and of the absence of tin.

β. White metallic globules remain, after long blowing: TIN. Their presence and nature may best be ascertained by rubbing the particles of the charcoal surrounding the test-specimen, together with the latter, in a mortar with some water. (§ 94, *b*.)

b. The residue (or precipitate) is very carefully washed with water, dried, and fused for some time in a small porcelain crucible, together with from four to five times its amount of cyanide of potassium. The mass, after cooling, is drenched with water heated to boiling, and thus the dross is separated from the metallic globules. These are treated with nitric acid, and the operation for the detection of tin and antimony conducted exactly as § 106 B, 2, *b*, directs.

c. The residue (or precipitate) is well washed, dissolved in hydrochloric acid, the solution diluted, and a small zinc rod placed into it. When the action of the latter has ceased, and the reduction is complete, the reduced metals (which can be easily separated from the compact piece of zinc,) are boiled with nitric acid, and the operation is carried on exactly as § 106 B, 2, *b*, directs.

The two latter methods of distinguishing tin and antimony from each other, when together in the same substance, are for beginners at least, far safer than the first.

3. BROWNISH-BLACK; GOLD OF PLATINUM; besides, perhaps, also ANTIMONY, ARSENIC, TIN. Add to the original solution of the substance.

a. Protochloride of tin; the formation of a reddish-brown or purple red precipitate denotes GOLD. We assure ourselves of the presence of this metal by testing the original solution with protosulphate of iron, whereby metallic gold is precipitated as a black powder.

b. Muriate of ammonia; the formation of a yellow precipitate is indicative of the presence of PLATINUM. The solution, if highly dilute, should be concentrated by evaporation, previous to adding this reagent.

A portion of the precipitate is tested for ARSENIC, as directed § 116, 1. The rest is boiled with hydrochloric acid and filtered off; the filtrate is tested for ANTIMONY by dropping one drop of it into water; (after having previously removed, as much as possible, the excess of acid by evaporation; if the water becomes turbid and milky, antimony is present. Or a small portion of the filtrate is mixed with solution of sulphuretted hydrogen; the formation of an orange-coloured precipitate indicates antimony. The rest of the hydrochloric solution is evaporated to dryness, mixed with carbonate of soda and cyanide of potassium, and tested for peroxide of tin, as § 116, 2, directs. Antimony and tin may, however, more safely be detected by precipitating them from the hydrochloric filtrate, by means of zinc; in fact, by treating exactly as § 116, 2, *c*, directs.

§ 117.

The precipitate which has not been dissolved by hydrosulphuret of ammonia, is washed, and then boiled with nitric acid. This may best be done in a small porcelain basin, constantly stirring with a glass rod.

1. THE PRECIPITATE DISSOLVES, AND NOTHING REMAINS FLOATING IN THE FLUID EXCEPT THE SEPARATED LIGHT, FLOCCULENT YELLOW SULPHUR; this indicates the absence of mercury. CADMIUM, COPPER, LEAD, and BISMUTH, may be present. If the precipitate was of a pure yellow colour, it consisted of CADMIUM alone; if it was brown or black, it must be filtered off from the separated sulphur, and the filtrate tested as follows.

a. Ammonia in excess is added to one portion of the filtrate.

α. *No precipitate is formed, or the precipitate formed at first, redissolves completely in an excess of the precipitant.* Absence of lead and bismuth. The solution is treated as § 117, 1, *b*, directs, bearing in mind § 117, 1, *a*, γ.

β. *A lasting precipitate is formed:* LEAD or BISMUTH. The liquid is filtered off, and the filtrate treated according to § 117, 1, *b*, bearing in mind § 117, 1, *a*, γ.

γ. *The fluid is blue-coloured;* no matter whether a precipitate is formed or not; COPPER.

b. Hydrochloric acid is added to the ammoniacal solution till a slightly acid reaction becomes manifest; carbonate of ammonia is then added in excess.

α. *The fluid remains clear;* absence of cadmium.

β. *A white precipitate is formed immediately, or after applying heat to the solution:* CADMIUM. We assure ourselves of the presence of this substance by filtering the fluid off from the precipitate, washing the latter, dissolving it in hydrochloric acid, and adding solution of sulphuretted hydrogen. A yellow precipitate must appear, if cadmium is present.

Should copper not yet have been indicated by a blue colouring of the ammoniacal solution, the fluid in which carbonate of ammonia has produced no precipitate, (§ 117, 1, *b*, *α*,) or the filtrate of § 117, 1, *b*, *β*, must be further and more minutely examined, by slightly acidifying the one or the other with acetic acid, and adding ferrocyanide of potassium. If copper is present, a brownish-red precipitate or tint will be produced.

c. In the case of § 117, 1, *a*, *β*, a not too inconsiderable quantity of sulphuric acid is added to a second portion of the solution of the sulphurets in nitric acid: the formation of a precipitate is indicative of the presence of LEAD. This reaction may be rendered more obvious and distinct by expelling the greater part of the free nitric acid by evaporation.

d. The rest of the solution (in the case of § 117, 1, *a*, *β*,) is evaporated to dryness, a few drops of water added, and, in proportion to the quantity, one or two drops of hydrochloric acid, and the fluid heated. The solution is then poured into a test-tube containing water; if the water becomes turbid and milky, BISMUTH is present.*

2. THE PRECIPITATE OF THE SULPHURETS DOES NOT COMPLETELY REDISSOLVE IN THE BOILING NITRIC ACID, AND A PRECIPITATE REMAINS, BESIDES THE LIGHT FLOCCULENT SULPHUR. This indicates PEROXIDE OF MERCURY, with a certain degree of probability, (and almost with certainty, if the precipitate is heavy and black.) The precipitate is allowed to settle, and the fluid filtered off from it; this filtrate must be tested for CADMIUM, COPPER, LEAD, and BISMUTH, by mixing a small portion of it with a large volume of solution of sulphuretted hydrogen, and if a

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* We refer to chapter II. (additions and remarks to § 117) for another method of distinguishing cadmium, copper, lead, and bismuth, from each other

precipitate is formed, treating the rest of the filtrate as § 117, 1, directs. The residuary precipitate is washed, dissolved by the addition of a few drops of aqua regia, ammonia added, till the solution retains only a feeble acid reaction, and a drop of it placed upon a clean copper plate. If **MERCURY** is really present, a white stain will appear after some time upon the copper surface, which presents a metallic lustre when rubbed, and disappears on heating. Or the solution in aqua regia is, with addition of hydrochloric acid, evaporated till nearly dry, diluted with some water, and protochloride of tin added. The formation of a precipitate, white at first, but changing into gray on the protochloride of tin being added in excess, is a safe indication of the presence of mercury.

§ 118.

A portion of the fluid in which solution of sulphuretted hydrogen has produced no precipitate, (§ 115, *a*,) or of the fluid which has been filtered off from the precipitate formed, is mixed with ammonia, till an alkaline reaction becomes manifest, and hydrosulphuret of ammonia is then added.

In cases where but a minute quantity of hydrochloric acid is present, and where, therefore, but little muriate of ammonia has been formed, a not too inconsiderable measure of a solution of this latter salt must be added, previous to the addition of the hydrosulphuret of ammonia.

a. **NO PRECIPITATE IS FORMED.** Pass over to § 119, for neither iron, manganese, cobalt, zinc, nickel, oxide of chromium, nor alumina, are present ; neither are the phosphates of the alkaline earths, nor oxalate of lime (barytes, strontian).

b. **A PRECIPITATE IS FORMED.** The whole fluid is treated in the same manner as the first portion.

1. The precipitate is white. Absence of iron, cobalt, nickel. We must look for the presence of all the other metals and compounds enumerated at § 118, *a*, since the faint tints of sulphuret of manganese and oxide of chromium vanish altogether if the quantity of white precipitate is considerable. The precipitate is filtered off—(the filtrate is

treated according to § 119)—washed, dissolved in hydrochloric acid,* boiled up, the solution filtered, and potash in excess added.

a. THE PRECIPITATE FORMED AT FIRST ON THE ADDITION OF POTASH, REDISSOLVES COMPLETELY IN THE EXCESS OF THE PRECIPITANT. Absence of the phosphates and oxalates of the alkaline earths, and manganese. The solution with potash is divided into two portions; one portion is slightly acidified with hydrochloric acid, ammonia in excess added, and the fluid boiled for a short time.

α. *No lasting precipitate is formed.* Absence of alumina and of oxide of chromium. Solution of sulphuretted hydrogen is added to the other portion of the solution with potash. The formation of a white precipitate indicates ZINC.

β. *A lasting precipitate is formed.* It is filtered off, and, (should a green tint of the solution with potash, or a green, yellow, or red tint of the original solution make us conclude that OXIDE OF CHROMIUM is present,) a small portion of it tested for this substance, with phosphate of soda and ammonia, (§ 87, *b*, 5,)† solution of sulphuretted hydrogen is added to the filtrate. The formation of a white precipitate indicates ZINC. For alumina we test as follows.

aa. No oxide of chromium has been detected. This is sufficient to prove the presence of ALUMINA. To assure ourselves of it we test the precipitate produced by ammonia, before the blow-pipe. (Vide § 87, *a*, 4.)

bb. Oxide of chromium has been detected.

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* If the precipitate is inconsiderable, this may best be done by forcing it to the lower part of the filter, by means of a syringe bottle, allowing the water to run off, and adding hydrochloric acid drop by drop. If sulphuret of zinc is present, the solution effected by hydrochloric acid is but incomplete; some nitric acid is added in that case, and heat applied.

† For even if chromic acid is present, a precipitate of oxide of chromium is produced by hydrosulphuret of ammonia, the chromic acid being reduced by sulphuretted hydrogen. In such cases, the yellow or red colour of the solution changes into a green tint, on the addition of the sulphuretted hydrogen, and sulphur separates at the same time.

In this case, the second portion of the solution with potash is boiled, until the oxide of chromium has completely precipitated; the fluid is then slightly diluted, filtered off from the oxide of chromium, slightly acidified with hydrochloric acid, and ammonia in excess added. The formation of a precipitate indicates ALUMINA. The blow-pipe, as in *aa*, is resorted to as a conclusive test. Should the separation of the oxide of chromium from the solution with potash not succeed by boiling, as may be the case under certain circumstances, the precipitate produced by ammonia must be fused with nitre and carbonate of soda, to remove the chromium. (Vide § 87, *b*, 4.) "Alumina may have been present as a PHOSPHATE, and may have precipitated as such. For the way in which this may be ascertained, we refer to § 110, 1."

b. A PRECIPITATE INSOLUBLE IN POTASH HAS REMAINED. The solution is filtered off and the filtrate treated as § 118, 1, *a*, directs. The residuary precipitate may consist of MANGANESE, "of the phosphates and oxalates of the alkaline earths." The presence of MANGANESE is indicated by the precipitate assuming a brown colour when exposed to the air. The test with carbonate of soda before the blow-pipe is resorted to as a conclusive proof. (§ 88, *b*, 5.) If manganese is present, the precipitate is dissolved in hydrochloric acid, some tartaric acid mixed with it, and then ammonia in excess added. If no precipitate is formed, neither phosphates nor oxalates of the alkaline earths are present; the formation of a precipitate indicates the presence of these compounds. This precipitate, (or, if no manganese was present, the residuary precipitate undissolved by potash), is washed and subjected to the following preliminary examination, in order to ascertain, whether it consists of phosphates of the alkaline earths alone or of oxalates of the alkaline earths alone, or whether it is a mixture of both. A small portion of the precipitate is gently heated upon a platinum plate, and the residue treated with hydrochloric acid.

α. *It dissolves without effervescence:* absence of oxalates. The rest of the precipitate is then dissolved in hydrochloric acid, perchloride of iron added in excess, and then ammonia, and the further operations, for the detection of the bases and of the phosphoric acid, conducted as directed § 110, 2, *a*.

β. *It dissolves with effervescence:* presence of an oxalate. In this case a preliminary examination for phosphates becomes necessary. For this purpose the hydrochloric solution is boiled, to expel the carbonic acid, and ammonia added.

aa. No precipitate is formed. Absence of phosphates: oxalates alone can be present. For the detection of the bases, and the confirmatory examination for oxalic acid, vide § 110, 2, *b*.

bb. A precipitate is formed: presence of a phosphate and an oxalate. The rest of the precipitate is then heated to redness and dissolved in very slightly diluted hydrochloric acid; the solution is boiled to expel the carbonic acid; ammonia in excess is added, and the solution filtered. The earths which were combined with the oxalic acid, are detected in the filtrate, as § 119 directs. The precipitate is treated as stated § 118, 1, *b*.

2. THE PRECIPITATE PRODUCED BY HYDROSULPHURET OF AMMONIA IS NOT WHITE; this indicates chromium, manganese, iron, cobalt, or nickel. If the precipitate is black or has a shade of black, one of the three latter metals is certainly present. But, under all circumstances, we must look for *all* the metals and compounds enumerated § 118, *a*. The precipitate is filtered off from the solution—(the filtrate is treated as § 119 directs)—carefully washed and treated with dilute hydrochloric acid.

a. NO SOLUTION TAKES PLACE, OR THE SOLUTION IS INCOMPLETE INASMUCH AS THE BLACK COLOUR OF THE PRECIPITATE DOES NOT DISAPPEAR; COBALT, NICKEL. Some nitric acid is then added to the hydrochloric acid, and the solution boiled and treated as follows. The fluid is filtered off from the separated sulphur, and a small portion of it mixed with solution of sal ammoniac, ammonia in excess added, and heat applied.

a. No LASTING PRECIPITATE IS FORMED BY AMMONIA: absence of peroxide of iron, oxide of chromium, alumina, phosphates and oxalates of the alkaline earths. The rest of the acid solution of the sulphurets is mixed with caustic potash in excess, heated, and the fluid filtered off from the precipitate formed. The filtrate is tested for zinc with solution of sulphuretted hydrogen. (Compare § 118, 1, *a*, *α*.) The precipitate is washed and drenched, heated and agitated for some time with a somewhat considerable quantity of solution of carbonate of ammonia, mixed with half its measure of caustic ammonia.

aa. The precipitate is completely redissolved. Absence of manganese. The ammoniacal solution is evaporated to dryness, the residue dissolved in a few drops of hydrochloric acid, once more slightly evaporated, and a portion of a residue—(which should still be moist)—tested for COBALT, with borax, (§ 88, *d*, 7.) The rest of the moist residue is then dissolved in some water, and solution of cyanide of potassium added, till the precipitate formed at first, is redissolved in an excess of cyanide of potassium; dilute sulphuric acid is then added and heat applied; the solution is allowed to stand for some time. The formation of a greenish white precipitate, immediately or after the lapse of some time, indicates NICKEL. (§ 88, *c*. 6, and Recapitulation and Remarks, § 88.)

bb. An insoluble residue remains, on treating the precipitate produced by caustic potash, with carbonate of ammonia and caustic ammonia. This is tested for MANGANESE, with carbonate of soda. (§ 88, *b*, 5.) If the precipitate really consists of protoxide of manganese, it may almost always safely be detected by its assuming a brown tint, when exposed to the air. The ammoniacal solution is tested for cobalt and nickel, as directed § 118, 2, *a*, α, *aa*.

β. AMMONIA PRODUCES A LASTING PRECIPITATE. The entire solution of the sulphurets in aqua regia is then treated in the same manner as the first portion, the precipitate produced by ammonia, in presence of sal ammoniac, is filtered off from the solution and washed; the further operations for testing both the filtrate and precipitate are conducted as follow.

1. Hydrosulphuret of ammonia is added to the FILTRATE, till it causes no longer any precipitation; the precipitate obtained is filtered off from thesolution, carefully was hed, dissolved in aqua regia, mixed with caustic potash in excess and tested for cobalt, nickel, manganese, and zinc, exactly as § 118, 2, *a*, α, directs.

2. The PRECIPITATE is digested with dilute solution of potash. (If we have obtained only a very minute precipitate, this should be dissolved, on the filter, by means of hydrochloric acid, and caustic potash in excess added to the solution.)

aa. The precipitate redissolves completely in the caustic potash: absence of peroxide of iron, and of the phosphates, and oxalates of the alkaline earths. The solution with potash is tested for alumina and oxide of chromium, exactly as § 118, 1, *a*, directs.

bb. The precipitate does not redissolve, or at least not completely. The solution is filtered and the filtrate tested for oxide of chromium and alumina, as stated at *aa*. The residue is dissolved in dilute hydrochloric acid, and a small portion of the solution mixed with ferrocyanide of potassium. The immediate formation of a blue precipitate or even a blue tint in the solution indicates IRON. If iron is present, the rest of the hydrochloric solution is mixed with some tartaric acid, and ammonia in excess added. Should no iron be present, the solution is simply supersaturated with ammonia. If no precipitate is formed, neither phosphates nor oxalates of the alkaline earths are present; if a precipitate is formed, this is treated as § 118, 1, *b*, directs. To ascertain whether the iron was present as peroxide or protoxide, the original solution in water or in hydrochloric acid (but not in nitric acid) is tested with ferrocyanide of potassium and with ferricyanide of potassium. The formation of a dark blue precipitate with the former reagent, indicates PEROXIDE; with the latter, PROTOXIDE.

b. THE PRECIPITATE PRODUCED BY HYDROSULPHURET OF AMMONIA REDISSOLVES READILY AND COMPLETELY UPON BEING TREATED WITH HYDROCHLORIC ACID, OR, AT LEAST, ITS BLACK COLOUR DISAPPEARS IMMEDIATELY: absence of cobalt and nickel. The solution is boiled with some nitric acid, filtered off from the sulphur which precipitates in this operation, and a small portion of the filtrate mixed with sal ammoniac; ammonia in excess is then added and heat applied.

α. No lasting precipitate is formed upon the addition of ammonia: absence of iron, oxide of chromium, alumina phosphates, and oxalates of the alkaline earths. The rest of the hydrochloric solution is mixed with potash in excess, and the precipitate formed tested for MANGANESE, with carbonate of soda; the alkaline filtrate is tested for ZINC, with sulphuretted hydrogen.

β. A lasting precipitate is formed upon the addition of ammonia. The entire solution of the sulphurets is treated in the same manner as the first portion. The precipitate is tested exactly as § 118, 2, *a*, *β*, 2 directs. The solution which has been filtered off from the precipitate, is mixed with hydrosulphuret of ammonia in excess.

aa. No precipitate is formed: absence of manganese and zinc.

bb. A precipitate is formed. This is well washed and dissolved in aqua regia, and potash in excess added to the solution.

αα. No lasting precipitate is formed: absence of manganese and consequently presence of ZINC. For further proof sulphuretted hydrogen is added to the solution with potash.

ββ. A precipitate is formed: MANGANESE. The blow-pipe is resorted to as a conclusive test. The fluid which has been filtered off from this precipitate is treated with sulphuretted hydrogen. The formation of a white precipitate indicates ZINC.

§ 119.

. A portion of the fluid in which hydrosulphuret of ammonia has produced no precipitate, or which has been filtered off from the precipitate formed, is mixed with phosphate of soda and with ammonia—(if it does not already contain free ammonia)—and strongly agitated.

a. NO PRECIPITATE IS FORMED; this indicates the absence of all the alkaline earths. A fresh portion of the fluid is evaporated to dryness and the residue heated to redness. If no residue remains, (on heating to redness,) neither potash nor soda are present: pass over to § 122. If a residue remains, the entire fluid is treated in the same manner as the first portion, and the further operations are conducted as § 121 directs.

b. A PRECIPITATE IS FORMED. The remainder of the fluid, if containing sulphuretted hydrogen or hydrosulphuret of ammonia—(in which latter case it must first be acidified with hydrochloric acid)—is heated, till it has lost all odour of sulphuretted hydrogen, and then filtered off from the sulphur, if any has been precipitated. To this filtrate a mixture of carbonate of ammonia and some caustic ammonia is added in excess—after having previously added muriate of ammonia, should this substance not already have been formed in the fluid in sufficient quantity during the course of examination. The solution is boiled for some time.

1. NO PRECIPITATE IS FORMED. Pass over to § 120, neither lime, nor barytes, nor strontian being present.

2. A PRECIPITATE IS FORMED: presence of LIME, BA-

RYTES, or STRONTIAN. The precipitate is filtered off—(the filtrate is tested as § 120 directs)—and dissolved in the least possible quantity of very dilute hydrochloric acid.

a. Solution of gypsum is added to a portion of the solution.

α. *No precipitate is formed*, NOT EVEN AFTER THE LAPSE OF SOME TIME. Pass over to § 119, 2, *b*, for barytes and strontian are not present.

β. *A precipitate is formed.*

aa. *It is formed immediately* upon the addition of the soluution of gypsum: this indicates BARYTES. Strontian may be present besides.

A portion of the hydrochloric solution (vide § 119, 2) is evaporated to dryness, and the residue digested with absolute alcohol—(at least, with very strong alcohol)—and the solution filtered. A few drops of the filtrate are evaporated upon a platinum plate.

αα. No residue remains. Pass over to § 120: for neither strontian nor lime are present.

ββ. A residue remains. The alcoholic solution is divided into two portions: one portion is heated in a small crucible and ignited; a carmine red tint of the flame indicates STRONTIAN. If the flame does not appear red, or if any doubt exists as to its exact tint, the second portion of the alcoholic solution is evaporated to dryness, the residue dissolved in a small proportion of water, and the solution tested with solution of gypsum. The formation of a precipitate after the lapse of some time, indicates STRONTIAN.

We can best assure ourselves of the presence of barytes by adding hydrofluosilicic acid to the solution in hydrochloric acid, and applying heat. The formation of a precipitate after the lapse of some time denotes the presence of BARYTES.

bb. *The precipitate is formed, only after the lapse of some time:* absence of barytes; presence of STRONTIAN.

b. Oxalic acid is added to a fresh portion of the hydrochloric solution, (vide § 119, 2,) after having previously made it alkaline by the addition of ammonia. Should (after § 119, 2, *a*, *β*,) barytes or strontian have been detected, these must be first precipitated with sulphate of potash, the solution filtered off, and the oxalic acid added to the filtrate, after the previous addition of ammonia. If a precipitate is formed, lime is present.

§ 120.

Two small portions are taken of the fluid, in which carbonate of ammonia has produced no precipitate, (§ 119, 1,) or of that which has been filtered off from the precipitate formed, and sulphate of potash is added to the one, oxalate of ammonia to the other.

1. BOTH THESE REAGENTS PRODUCE NO LONGER ANY PRECIPITATE. This is a certain proof that all barytes, strontian, and lime, have been completely precipitated by carbonate of ammonia. Phosphate of soda is added to a third portion of the fluid with carbonate of ammonia, and the mixture stirred with a glass rod. The formation of a crystalline precipitate, (vide § 86, *d*, 5,) indicates MAGNESIA. The rest of the fluid, a portion of which has been tested for magnesia, is evaporated to dryness, and heated till all the ammoniacal salts have been expelled. If no residue remains, pass over to § 122; if a residue remains, pass over § 121.

2. BOTH THE REAGENTS, OR AT LEAST ONE OF THEM, PRODUCE STILL A PRECIPITATE. In that case, barytes, strontian, and lime, have not yet been completely precipitated by carbonate of ammonia. This reagent, mixed with caustic ammonia, is, therefore, once more added to the rest of the fluid, and the mixture again boiled for some time. The precipitate formed is filtered off from the fluid, and again treated as § 120 directs.

§ 121.

We have now still to treat of the examination for fixed alkalies and for ammonia.

The combinations of the former are, with very few exceptions, soluble in water. It is, therefore, not necessary to look for them when testing compounds insoluble in water.

When we have to operate upon a substance insoluble in water, but soluble in hydrochloric acid, or in nitric acid, a portion of the fluid, in the specimen of which phosphate of soda did produce no precipitate, (§ 119, *a*,)—or of that in which carbonate of ammonia has occasioned none, (§ 119, 1,) or of that which has been filtered off from the precipitate formed, (§ 119, 2,)—is preserved and tested for phosphoric acid and oxalic acid, as § 125, 8, directs.

1. MAGNESIA IS NOT PRESENT. The roasted residue of § 119, *a*, is dissolved in a small proportion of water, and alcohol added to the solution; this is then heated to the boiling point and ignited.

a. THE FLAME HAS A VIOLET TINT. Absence of soda; probable presence of POTASH.

b. THE FLAME IS YELLOW: presence of SODA. The solution is evaporated to dryness, and the test with antimoniate of potash, and the blow-pipe flame, are resorted to as conclusive proofs of the presence of soda. (Vide § 85, *b*, 3.) We assure ourselves of the presence of potash, by dissolving this residue in water, or, better still, in alcohol, if possible, and heating one half of the solution with tartaric acid, and the other half with chloride of platinum. If potash be present, the tartaric acid will produce a colourless, granular, crystalline precipitate, after the lapse of some time, whilst the chloride of platinum will produce a yellow precipitate.

2. MAGNESIA IS PRESENT. The residue is dissolved in water, and water of barytes, or solution of sulphuret of barium (containing caustic barytes) added, as long as any precipitate is formed; the solution is then boiled, filtered, and dilute sulphuric acid dropped into the filtrate till the reaction has become acid. The fluid is then filtered off from the precipitated sulphate of barytes, the filtrate evaporated to dryness, and the residue which, perchance, may remain, tested for potash and soda, as directed § 121, 1. Or the residue containing magnesia (and perhaps alkalies

besides) is treated with sulphuric acid, the solution evaporated to dryness, and the residue heated to redness as long as any vapour escapes; the residuary mass is then dissolved in water, and the solution precipitated by acetate of barytes in excess, filtered off from the precipitate, and the filtrate again evaporated to dryness; the residue is exposed to a strong red heat, and then treated with a small proportion of water; the solution is filtered and further tested for potash and soda, as § 121, 1, directs. Should the filtrate manifest an alkaline reaction, it must first be neutralized with hydrochloric acid.

§ 122.

We have now still to consider the examination for ammonia. A portion of the substance under examination is treated with concentrated solution of potash, and heat applied. AMMONIA is present, if the escaping gas emits its characteristic odour, if it restores the blue colour of moist reddened litmus-paper, and if white fumes arise upon a small glass rod, moistened with hydrochloric acid, being dipped into the tube.

Compounds in which all the more frequently occurring acids and bases, metals and metalloids, are supposed to be present.

A. 1. SUBSTANCES SOLUBLE IN WATER. DETECTION OF ACIDS AND METALLOIDS.

I. *Absence of Organic Acids.*

§ 123.

1. Concerning the detection of ARSENIOUS and ARSENIC ACID, CARBONIC ACID, HYDROSULPHURIC ACID, and CHROMIC ACID, compare § 108, 1 and 2.

2. Nitrate of barytes is added to a portion of the solution; if the solution is acid, it must first be neutralized with ammonia.

a. NO PRECIPITATE IS FORMED. Absence of sulphuric acid, phosphoric acid, boracic acid, chromic acid, silicic acid, oxalic acid, arsenious and arsenic acid.[*] (Pass over to 3.)

b. A PRECIPITATE IS FORMED. The fluid is diluted, and hydrochloric acid added; if the precipitate does not redissolve, or, at least, not completely, SULPHURIC ACID is present.

3. Nitrate of silver is added to a portion of the solution; this is previously EXACTLY neutralized, if acid, by means of ammonia; if alkaline, by means of nitric acid.

a. NO PRECIPITATE IS FORMED. Pass over to 4; neither chlorine, nor iodine, cyanogen, phosphoric acid, silicic acid, oxalic acid, nor chromic acid are present, nor boracic acid, if the solution was not too dilute.

b. A PRECIPITATE IS FORMED. The colour of the precipitate is inspected, and the nitric acid then added.

α. *The precipitate redissolves completely.* Pass over to § 123, 4; for neither chlorine, iodine, nor cyanogen are present.

β. *A residue remains*: CHLORINE, IODINE, OR CYANOGEN. The residue is washed and digested with ammonia.

aa. A yellowish residue remains. This is caused by the presence of IODINE. We assure ourselves of the presence of this substance as § 100, *c*, directs. The solution is filtered off from the residue, and nitric acid in excess added to the filtrate; if a precipitate is formed, it indicates chlorine or cyanogen. For the further operation, vide *bb.*

bb. No residue remains, CHLORINE OR CYANOGEN; absence of iodine. For further examination, the solution is again precipitated with nitric acid. Previous to beginning the operation of distinguishing chloride of silver from cyanide of

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[*] If muriate of ammonia is present in the fluid under examination, the non-formation of a precipitate is not a conclusive proof of the absence of oxalic acid, arsenious and arsenic acid, and especially not of that of boracic acid, the barytes salts of these acids not being insoluble in water, in presence of ammoniacal salts.

silver, the fluid is tested for cyanogen, in order to see whether this operation is at all necessary. For this purpose solution of magnetic oxide of iron is added to a portion of the original solution, followed by the addition of hydrochloric acid. The formation of a blue precipitate indicates CYANOGEN.* If no precipitate is formed, and the fluid assumes no blue tint, the precipitate redissolved by ammonia consists of chloride of silver alone. If cyanogen has been detected, the precipitate to be examined is washed, taken from the filter when still moist, dried in a porcelain crucible, and heated to redness. Chloride of silver merely fuses, whilst cyanide of silver becomes reduced. The metallic silver may be separated from the chloride of silver by means of nitric acid.

4. The aqueous solution is tested for nitric acid, by mixing solution of indigo with it, till it has acquired a light blue tint, and then adding some sulphuric acid, and applying heat; and, moreover, by throwing a crystal of protosulphate of iron into the solution, previously mixed with the third part of its amount of concentrated sulphuric acid. If nitric acid is present, the blue solution loses its colour, and a brown-coloured halo forms round the crystal.

We have now still to speak of the examinations for phosphoric acid, boracic acid, silicic acid, oxalic acid, and chromic acid. It is necessary to make these examinations only in such cases where chloride of barium, as well as nitrate of silver, have caused the formation of precipitates in neutral solutions. Compare note to § 123, 2, *a*.

5. If the precipitate produced by nitrate of silver was of a yellowish colour, we must especially look for phosphoric acid. For this purpose, ammonia in excess is added to a portion of the fluid; if a precipitate is formed, the fluid is filtered, and muriate of ammonia added to the filtrate, and

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* Should the cyanogen be present as free hydrocyanic acid, which may easily be detected by its characteristic odour, this ought to be saturated with potash, previous to the addition of the solution of iron. We have already stated at § 100, *d*, that the cyanogen is not detected by nitrate of silver, in certain combinations, e. g. cyanide of mercury.

then sulphate of magnesia. The formation of a crystalline precipitate denotes PHOSPHORIC ACID.

6. A small portion of the substance under examination is drenched with alcohol, sulphuric acid added, and the mixture heated to boiling in a small crucible, and then ignited. If the flame has a green tint, BORACIC ACID is present. If copper is present, this must first be removed, either by means of sulphuretted hydrogen, or by boiling the fluid with potash in excess.

7. If the fluid was red, or yellow changing to red, on the addition of hydrochloric acid, and if the precipitate produced by nitrate of silver in the neutral solution had a purple red colour, the presence of CHROMIC ACID is confirmed.

8. For silicic acid, test as § 99, *b*, 2, directs.

9. For the detection of OXALIC ACID, solution of gypsum is added to a portion of the fluid under examination, which must first be neutralized with ammonia, if it manifests an acid reaction. The formation of a white precipitate, which does not vanish upon the addition of acetic acid, indicates the presence of oxalic acid.

CHLORATES, BROMIDES, and FLUORIDES, are of less frequent occurrence. Chlorates may be detected by their violent deflagration with charcoal, when in a state of fusion. (vide § 105, A. I. 2, *c*.) Chloric acid is best detected by heating a portion of the solid salt in a glass tube, closed at the lower end, and placing a wood-splinter which has been kindled and the *flame* extinguished, near the open end. If CHLORIC ACID be present, the flame of the wood-splinter will be rekindled. The residue dissolved in water yields in that case with nitrate of silver a copious precipitate of chloride of silver. Other tests are, to throw a few grains of the salt into fuming sulphuric acid, (§ 101, *b*. 6,) or fusing a portion of the salt with cyanide of potassium. (§ 101, *b*, 3.) The detection of BROMIDES is simple, if iodides are not present, at the same time. Vide § 100, for the safe detection of bromine in both cases. For the detection of the FLUORIDES, the methods described § 98, *d*, 4 and 5, are the safest under all circumstances.

Compounds in which all the more frequently occurring acids and bases, metals and metalloids, are supposed to be present.

A. 1. SUBSTANCES SOLUBLE IN WATER. DETECTION OF ACIDS AND METALLOIDS.

II. *Presence of Organic Acids.*

§ 124.

1. CHROMIC ACID, ARSENIOUS, and ARSENIC ACID, have already been detected when testing for the bases; concerning the distinction of arsenious from arsenic acid, compare § 93, additions and remarks.

2. Hydrochloric acid is added to a portion of the solution. The formation of a precipitate, which, upon being heated on a platinum plate volatilizes partly or totally, emitting the characteristic odour of BENZOIC ACID, indicates the presence of this acid. Effervescence, upon the addition of the hydrochloric acid, may be caused by the presence of CARBONIC ACID, or by that of SULPHURETTED HYDROGEN. (Vide § 108, 2.)

3. Ammonia is added to a portion of the solution, till the latter manifests a feebly alkaline reaction; the solution is then filtered, if necessary, and chloride of barium added.

Should hydrochloric acid have produced a precipitate in the original solution, the filtrate of this ought to be used for this experiment.

a. NO PRECIPITATE IS FORMED. Absence of sulphuric acid, phosphoric acid, chromic acid, boracic acid, arsenic acid, arsenious acid, silicic acid, oxalic acid, tartaric acid, citric acid; these may, therefore, be disregarded in the further course of examination. What we have stated at § 123, 2, *a*, (note,) applies also to the last six of these acids.

b. A PRECIPITATE IS FORMED. Hydrochloric acid is added.

α. The precipitate redissolves: Absence of sulphuric acid.

β. A residue remains: SULPHURIC ACID.

4. Nitrate of silver is added to a portion of the solution, which must first be EXACTLY neutralized with nitric acid, if alkaline, and with ammonia, if acid.

a. No precipitate is formed: absence of phosphoric acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, citric acid; these may, therefore, be disregarded in the further course of examination.

b. A PRECIPITATE IS FORMED.

α. It is whitish or yellow. A portion of the fluid, together with the precipitate suspended therein, is boiled. Complete and rapid reduction indicates FORMIC ACID. Protonitrate of mercury is used as a conclusive test, § 104, *b*, bearing in mind the remarks which will be found at the end of this number, (4.) The rest of the precipitate is treated with nitric acid. If it is redissolved, neither CHLORINE, nor IODINE, nor CYANOGEN, are present; but if the precipitate does not completely redissolve in nitric acid, the residue is tested for these salt radicals, as § 123, 3, *b*, *β*, directs.

β. The precipitate produced by nitrate of silver is purple: CHROMIC ACID. Should arsenic acid be present, acetate of lead is added, or (as a conclusive test, to a fresh portion of the solution) the formation of a yellow precipitate proves the presence of CHROMIC ACID. CHLORINE, IODINE, and CYANOGEN, may also be present in the silver precipitate: test for these salt radicals as § 123, 3, *b*, directs.

In the presence of chromic acid, formic acid cannot be detected with certainty, by the reduction of silver and mercury. In this case there remains no other means of its certain detection, except distilling the compound under examination, with the addition of some sulphuric acid. The distillate is saturated with soda, and then tested with perchloride of iron, (which chromic acid tinges blood-red,) and with nitrate of silver. (Compare § 104, *b*.)

5. If chloride of barium and nitrate of silver have given rise to the formation of precipitates, test for PHOSPHORIC ACID, as directed § 123, 5, and for SILICIC ACID as directed § 99, *b*, 2.

6. A portion of the solid substance under examination (or, if in solution—(should the latter be acid, it must first be saturated with potash)—the residue obtained by evaporating the solution to dryness) is drenched with alcohol in a small tube, concentrated sulphuric acid to the extent of about one-third of the volume of the alcohol, and the mixture heated to the boiling point. If any odour of acetic ether is emitted—which, in many instances, may be clearly detected upon agitating the mixture, whilst cooling or when cold—ACETIC ACID is present. The contents of the tube are poured into a small crucible, heated, and ignited. If the flame is green, BORACIC acid is present.

7. A portion of the fluid is rendered feebly alkaline by the addition of ammonia, filtered, if necessary, and chloride of calcium added. If the solution was neutral, some sal ammoniac must be added before the addition of chloride of calcium.

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER THE LAPSE OF SOME TIME. Absence of oxalic acid and tartaric acid; pass over to 8.

b. A PRECIPITATE IS FORMED IMMEDIATELY, OR AFTER THE LAPSE OF A FEW MINUTES. The solution is filtered off from this precipitate, and the filtrate further tested as 8 directs.

The precipitate is washed, digested, and agitated with somewhat dilute solution of potash in excess, without the aid of heat, filtered, and the filtrate boiled for some time. If a precipitate is formed which disappears again, on cooling, tartaric acid is present.

Solution of gypsum is added to a portion of the original solution, which, if acid, must first be made neutral by the addition of ammonia. The formation of a precipitate, which does not disappear upon the addition of acetic acid, but is dissolved by hydrochloric acid, indicates OXALIC ACID.

8. The fluid in which chloride of calcium has produced no precipitate, or that which has been filtered off from the precipitate formed—(in which latter case some more chloride of calcium is added)—is mixed with alcohol.

a. NO PRECIPITATE IS FORMED. Absence of citric acid and of malic acid. Pass over to 9.

b. A PRECIPITATE IS FORMED. The solution is filtered off and the filtrate treated as 9 directs. The precipitate is washed with alcohol, and (being left on the filter) dissolved in the least possible quantity of dilute hydrochloric acid. Ammonia is then added to this latter filtrate, till it manifests a feebly alkaline reaction, and heat applied to the boiling point, at which it must be kept for some time.

α. THE FILTRATE REMAINS CLEAR. Absence of citric acid. Presence of MALIC ACID; alcohol is again added to the fluid, and the lime precipitate which is formed, heated to redness, as a conclusive test for malic acid; the reaction with acetate of lead is moreover resorted to as a confirmatory proof, § 102, *e*, 5.

β. A HEAVY, WHITE PRECIPITATE IS FORMED. Presence of CITRIC ACID. The solution is filtered whilst boiling, and the filtrate tested for malic acid, as described at α.

9. Perchloride of iron is added to the filtrate of 8, *b*, or to the fluid, in which no precipitate has been formed, on mixing with alcohol, (§ 128, 8, *a*,) after having previously expelled the alcohol by heat, and after having exactly neutralized with hydrochloric acid. If no light brown flocculent precipitate is formed, neither succinic acid nor benzoic acid are present; if a precipitate of this kind is formed, and no benzoic acid has been detected during the previous examination, (§ 124, 2,) this consists of SUCCINIC ACID. But if benzoic acid was present, the solution is filtered off, and the precipitate washed and then digested with ammonia in excess, filtered, the filtrate evaporated to dryness, and the benzoate of ammonia dissolved out of it by alcohol; the succinate of ammonia remains undissolved. This succinate is dissolved in water, and both solutions are tested with perchloride of iron.

10. Test for NITRIC ACID as directed § 123.

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids, are supposed to be present.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID AND IN NITRIC ACID. DETECTION OF THE ACIDS AND METALLOIDS.

I. *Absence of Organic Acids.*

§ 125.

In examining these compounds we must look for all the acids occurring at § 123, with the exception of chloric acid. Cyanogen compounds are not examined after this method: compare § 128.

1. What we have stated at § 111, 2, with regard to ARSENIOUS and ARSENIC ACID, HYDROSULPHURIC ACID and CHROMIC ACID, applies also to this paragraph.

2. A portion of the substance is boiled with nitric acid, and the solution filtered, should any residue remain.

a. Effervescence takes place; this may be caused by the presence of CARBONIC ACID, or by that of NITRIC OXIDE GAS; the former may be detected as § 99, *a*, directs, the latter usually indicates the presence of a sulphur compound.

b. Violet vapours escape, which impart a blue tint to starch: IODINE.

3. Nitrate of silver is added to a portion of the nitric solution.

a. NO PRECIPITATE IS FORMED: pass over to 4, for no chlorine is present.

b. A PRECIPITATE IS FORMED. The solution is filtered off, and the precipitate washed, and digested with ammonia; if it redissolves completely or partly, CHLORINE is present.

4. A portion of the substance under examination is boiled with hydrochloric acid, and the solution filtered, if necessary. A portion of the solution or filtrate is mixed with chloride of barium. The formation of a precipitate indicates SULPHURIC ACID.

5. Another portion of the hydrochloric solution is tested for NITRIC ACID, with indigo and protosulphate of iron. (Vide § 123, 4.) In many cases it will already have been detected by the deflagration on charcoal before the blowpipe.

6. If the experiment, § 125, 2, *b*, has not yet indicated the presence of iodine, a portion of the substance under ex-

amination is heated with concentrated sulphuric acid. If any IODINE compound be present, violet vapours will be evolved, which impart a blue tint to starch. (Compare § 100, *c*, 6.)

7. Test for BORACIC ACID by treating a portion of the substance to be examined with sulphuric acid and alcohol. (Vide § 98, *b*, 5.)

8. The fluid of § 119, *a*, (in which phosphate of soda produces no precipitate,) or that of § 119, 1, (in which carbonate of ammonia produces no precipitate,) or—(should carbonate of ammonia have produced a precipitate in it)—the filtrate of the same (§ 119, 2,) (vide § 121,) are tested for PHOSPHORIC ACID and OXALIC ACID, as directed § 123, 5, and 9. (Oxalic acid, when combined with barytes, strontian, or lime, will have been detected already, in testing for the bases; the same applies to phosphoric acid when combined with magnesia.)

9. Test for SILICIC ACID as § 99, *b*, 3, directs. With regard to the more rarely occurring BROMINE and FLUORINE compounds, we refer to the remarks made at the end of § 123.

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids, are supposed to be present.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, AND IN NITRIC ACID. DETECTION OF THE ACIDS AND METALLOIDS.

II. *Presence of Organic Acids.*

§ 126.

1. Test for CARBONIC ACID, ARSENIC ACID, ARSENIOUS ACID, SULPHURIC A[illegible] NITRIC ACID, BORACIC ACID, CHROMIC ACID, SILICIC [illegible]D, CHLORINE, IODINE, and SULPHUR, as directed at § 125; for ACETIC ACID as stated at § 124, 6. CYANOGEN compounds are not examined after this method: compare § 128.

2. A portion of the compound under examination is dis-

solved in hydrochloric acid, and the solution filtered, should any residue remain, (which latter is tested for BENZOIC ACID, as directed at § 124, 2.) The filtrate is mixed with solution of carbonate of potash, and the mixture boiled for some time. The fluid is filtered off from the precipitate formed, and the filtrate saturated with dilute hydrochloric acid, and tested for PHOSPHORIC ACID and OXALIC ACID, as directed at § 123, 5, and 9; and for TARTARIC ACID, CITRIC ACID, MALIC ACID, SUCCINIC ACID and BENZOIC ACID, exactly as directed at § 124, 7, 8, and 9.

Compounds in which all the more frequently occurring bases, acids, metals, and metalloids, are supposed to be present.

B. SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE BOTH IN WATER AND IN HYDROCHLORIC ACID. DETECTION OF THE BASES, ACIDS, AND METALLOIDS.

§ 127.

The following substances and combinations belong to this class:

SULPHATE OF BARYTES, SULPHATE OF STRONTIAN, SULPHATE OF LIME, CHLORIDE OF SILVER, CHLORIDE OF LEAD, SULPHATE OF LEAD, SULPHURET OF MERCURY, BISULPHURET OF MERCURY, PROTOCHLORIDE OF MERCURY, SOME OF THE FERROCYANIDES, SEVERAL SULPHURETS, SILICIC ACID, SULPHUR and CARBON.

Besides these, a few acid arseniates belong to this class; they are, however, as rarely occurring in the analyses of those mixtures and compounds important in pharmacy, manufacture, arts, and trades, as the insoluble modification of oxide of chromium, or as roasted peroxide of tin, or as fluoride of calcium. Of these latter less frequently occurring substances, we purpose to [illegible] separately.

For the insoluble cyanides, vide § 128.

A. THE RESIDUE IS WHITE. It may in that case contain SULPHATE OF BARYTES, SULPHATE OF STRONTIAN, SULPHATE OF LIME, SULPHATE OF LEAD, CHLORIDE OF LEAD, CHLORIDE OF SILVER, PROTOCHLORIDE OF MERCURY, SILICIC ACID, SULPHUR.

No attention need be paid to the presence of sulphate of lime, if this substance has already been detected in the aqueous solution. The same remark applies to the lead compounds: we may disregard these, if the previous examination has not already proved their presence.

1. A small portion of the substance under examination is heated upon a platinum plate, and flame allowed to play on it. If any odour of sulphurous acid is emitted, SULPHUR is present. If no residue remains, sulphur alone is present. If the heat applied was very intense, protochloride of mercury may have volatilized. The sensible properties of the residue will show whether this is to be apprehended.

2. Hydrosulphuret of ammonia is added to a very small portion of the substance under examination.

a. It remains white. Pass over to § 127, 3, for no metallic compounds are present.

b. It becomes black. This proves with certainty the presence of a metallic salt, either protochloride of mercury, chloride of silver, chloride of lead, or sulphate of lead. Moreover, all the other compounds enumerated under A, may be present. The method of the further operation varies according to whether lead is present or not.

The following preliminary experiment is made in order to ascertain which method ought to be adopted.

A small portion of the substance is mixed with carbonate of soda, and exposed to the reducing flame of the blow-pipe. The production of a metallic grain, (which oxidizes in the oxidizing flame,) attended with a yellow incrustation of the charcoal, indicates lead.

α. THIS PRELIMINARY EXAMINATION INDICATES THE PRESENCE OF LEAD IN THE WHITE PRECIPITATE.

aa. The largest half of the residue (which, if moist, must first be dried) is fused with three parts of dry carbonate of soda and three parts of cyanide of potassium, in a small crucible, over a spirit-lamp. The mass fuses easily; it is maintained in a state of fusion for some time. After cooling, it is boiled with water, filtered, and the residue very carefully washed. The greater portion of the filtrate is supersaturated with hydrochloric acid, and a portion of this solution tested with chloride of barium. The formation of a precipitate indicates the presence of a SULPHATE. (Should a precipitate (silicic acid) be formed, upon supersaturating the filtrate with hydrochloric acid, the fluid must be diluted and filtered, and then tested for sulphuric acid.) The rest of the solution (supersaturated with hydrochloric acid) is evaporated to dryness and the residue treated with water. If a residue remains, this consists of SILICIC ACID. The formation of a clear glass, when fused with carbonate of soda in the blow-pipe flame, is a conclusive proof of the presence of silicic acid. The rest of the filtrate, which has not been mixed with hydrochloric acid, is acidified with nitric acid, boiled until it emits no longer any odour of hydrochloric acid, and nitrate of silver added; the formation of a precipitate of chloride of silver denotes that the residue, insoluble in water and hydrochloric acid, contains a CHLORIDE, (provided always, the reagents be free from chlorine, and the residue completely washed.) The residue obtained upon treating the fused mass with water, and which has been very carefully washed, (vide supra,) is treated with acetic acid; if it partly dissolves in this acid with effervescence, the presence of sulphates of the alkaline earths is certain. If no effervescence takes place, it proves the absence of the sulphates of the alkaline earths; the residue is therefore treated with nitric acid, and the solution treated as follows. If effervescence has taken place, a portion of the acetic solution is tested with sulphuretted hydrogen. If a black precipitate is formed, (sulphuret of lead,) the lead is removed in the same manner from the entire acetic solution, and the filtrate (which, if necessary, is concentrated by evaporation) treated as § 119 directs, beginning at 2, *a*. If the test portion of the acetic solution remains unaltered upon being treated with sulphuretted hydrogen, the rest of the solution is directly tested as directed, § 119, 2, *a*. The residue, which has remained on treating with the acetic acid, is treated with nitric acid, and a small portion of the solution is then tested with sulphuric acid for lead, (after having removed the excess of acid by evaporation;) the rest strongly diluted with water, and then tested for SILVER, with hydrochloric acid. If nitric acid leaves a residue, this consists of undissolved silicic acid, or incompletely decomposed sulphate of the alkaline earths.

bb. Half of the remainder of the residue is boiled with carbonate of potash. If its white colour change into gray or black, PROTOCHLORIDE OF MERCURY is present. As a confirmatory test the other half is heated in a small glass tube, together with dry carbonate of soda. (Vide § 90, *b*, 7.)

β. THE PRELIMINARY EXAMINATION PROVES THE ABSSNCE OF LEAD, IN THE WHITE PRECIPITATE. The entire entire residue is drenched and digested for some time, with hydrosulphuret of ammonia, the solution filtered, and the filtrate tested for chlorine, as *aa* directs. The precipitate is washed and boiled with nitric acid.

aa. The precipitate dissolves with the exception of the separated sulphur. CHLORIDE OF SILVER alone is present. To assure ourselves, we test the nitric solution for silver, with hydrochloric acid. To prove the presence of chlorine, the filtrate of § 127, A, 2, *β*, is supersaturated with nitric acid, and boiled, in order to expel the sulphuretted hydrogen. The fluid is then filtered from the sulphur which has separated, and tested with nitrate of silver.

bb. A residue remains besides the separated sulphur.

αα. This residue is black: MERCURY. The fluid is filtered from the residue, and the filtrate tested for silver, with hydrochloric acid: the residue is heated with aqua regia. If it is completely redissolved, with the exception of the separated sulphur, the investigation may be considered at an end, the absence of the sulphates of the alkaline earths and that of silicic acid being proved; if a white residue remains, this is washed and treated as § 127, A, 3, directs. The solution in aqua regia is tested with polished copper or with protochloride of tin to assure ourselves of the presence of mercury, (vide § 117, 2.) The chlorine, which must be present, is detected in the filtrate of β, as *aa* directs.

ββ. THE RESIDUE IS NOT BLACK: absence of mercury. For the further operation vide 3.

3. This residue, or, in the case of § 127, A, 2, *a*, the original residue is fused in a platinum crucible,* over a spirit lamp with a double draught of air, together with four parts of carbonate of potash and soda; the fused mass is soaked in water, boiled, filtered, and the residue (if any remain) washed until chloride of barium no longer produces any precipitate in the water which runs off. (This water must not be added to the filtrate. The residue is treated as 4 directs. The filtrate is supersaturated with hydrochloric acid, and a portion of it tested with chloride of barium; the formation of a precipitate indicates the presence of SULPHATES OF THE ALKALINE EARTHS. The rest of the filtrate is evaporated to dryness and then treated with water; if any residue remains, this consists of SILICIC ACID.

4. The residue remaining upon boiling the fused mass with water, (vide 3,) indicates SULPHATES OF THE ALKALINE EARTHS. It is carefully washed and then treated with hydrochloric acid. It is a certain proof of the presence of sulphates of the alkaline earths, if it dissolves partly or totally, and with effervescence in

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* A porcelain crucible may be substituted for a platinum crucible, in which case, six parts of a mixture of equal parts of dry carbonate of soda and cyanide of potassium must be employed, instead of the carbonate of potash and soda; the method in the text is however the best.

this menstruum. The hydrochloric solution is tested as § 119 directs, beginning at 2, *a*. If a residue remains upon treating with hydrochloric acid, this consists of silicic acid or of a sulphate of the alkaline earths which is not yet completely decomposed.

B. THE RESIDUE IS NOT WHITE. Even its colour will in that case enable us to draw some conclusions (cinnibar, sulphuret of arsenic.)

1. Test for SULPHUR as § 127, A, 1, directs.

2. The greater part of the residue is treated with aqua regia and boiled; the solution is filtered whilst still hot, and should any residue remain, besides the separated sulphur, this is once more boiled with water, filtered, and this second filtrate added to the first. The filtrate is then evaporated nearly to dryness, redissolved in some water, and one portion of the solution tested for LEAD, with sulphuric acid, another portion for MERCURY by means of polished copper. (If a hydrochloric solution has been employed in testing for bases, (§ 106,) the solution in aqua regia must be tested for metals, in the usual way, as various other sulphurets, insoluble or sparingly soluble in hydrochloric acid, might be present.)

3. If aqua regia has left any residue undissolved besides sulphur, which may have separated, this residue is carefully washed. If a compound of lead has been present, this rinsing process is conducted with hot water and continued until the filtrate is no longer blackened by hydrosulphuret of ammonia.

a. THE RESIDUE IS WHITE: a portion of it is tested with hydrosulphuret of ammonia.

α. *It becomes black.* The entire residue is digested with hydrosulphuret of ammonia, and the further operation conducted exactly as § 127, A, 2, *b*, β, directs.

β. *It remains white.* The residue is treated as directed § 127, A, 3.

b. THE RESIDUE INSOLUBLE IN AQUA REGIA, IS BLACK; this indicates the presence of carbon in some form. If it is totally consumed over a lamp, or in the blowpipe flame, nothing besides carbon is present; but if a residue remains, or if the combustion is not complete, (carburet of iron graphyte,) we must look moreover for CHLORIDE OF SILVER, SULPHATES OF THE ALKALINE EARTHS and SILICIC ACID; the residue in that case, is treated as § 127, B, 3, *a*, *α*, directs. Of acids and electro-negative substances CHLORINE and SULPHURIC ACID alone can be present besides those already mentioned. To assure ouselves whether they are present or not, what remains of the residue insoluble in hydrochloric acid is digested with hydrosulphuret of ammonia, super-saturated, filtered, and one-half of the filtrate boiled with hydrochloric acid, the other half with nitric acid; both solutions are filtered and the hydrochloric fluid is tested with chloride of barium for sulphuric acid, the nitric fluid with nitrate of silver for chlorine.

The insoluble PEROXIDE OF TIN and OXIDE OF CHROMIUM may be detected before the blow-pipe. Peroxide of tin, when mixed with carbonate of soda and cyanide of potassium, and exposed on charcoal to the reducing flame of the blow-pipe, yields a soft metallic grain, without incrustation of the support. Oxide of chromium, which is, moreover, distinguished by its green colour, is treated with microcosmic salt, as stated § 87, *b*, 5, or it is fused together with carbonate of soda and nitre, (vide § 87, *b*, 4.) The arsenic acid of the insoluble ARSENIATES is detected before the blow-pipe or by means of reduction in a glass tube. (Vide § 94, *d.*) To enable us to test for the bases, these insoluble arseniates must first be decomposed by means of concentrated sulphuric acid. FLUORIDE OF CALCIUM is decomposed by concentrated sulphuric acid, in a platinum crucible: the fluorine is detected by its property of etching glass; the lime remains as sulphate of lime. There are still several other compounds which are rendered insoluble in acids by being heated to redness; but it would exceed the limits of this work, to treat of them all.

§ 128.

SPECIAL METHOD FOR THE DECOMPOSITION OF INSOLUBLE CYANIDES, FERROCYANIDES, &C.*

Since in treating these compounds according to the usual method, fallacious phenomena frequently occur, and since moreover their solution in acids frequently succeeds but imperfectly, it is advisable to pursue the following method, in their analysis. The residue which has been freed by water from, all soluble substances is boiled with solution of carbonate of potash.

a. COMPLETE DECOMPOSITION TAKES PLACE, which is easily detected by the change of colour and the rapid deposition of the separated pure or carbonated oxides; the solution is filtered and the residue washed. This residue may contain all the bases, which were contained in the substance under examination as compounds insoluble in water. For the determination of these bases, the residue is treated exactly as § 106, A, 2, directs. A portion of the filtrate is tested for CYANOGEN, by mixing it with hydrochloric acid, till the reaction becomes strongly acid, and then adding solution of the double proto- and per-chloride of iron; if cyanogen be present, Prussian blue precipitates. For the detection of the other acids, the rest of the filtrate is treated as § 124 directs. This filtrate may, moreover, possibly contain all the cobalt, all the iron of the substance under examination, besides chromium and manganese, since the combinations of their cyanides with other cyanogen compounds, on boiling with alkalies, are decomposed in such a manner as to cause the separation of insoluble oxides, whilst the cobalticyanide of potassium, ferrocyanide of potassium, &c., remain in solution. These metals must not be disregarded. To detect them, a portion of the fluid is mixed with nitric acid greatly in excess, the mixture evaporated to dryness and the residue fused;

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* The student is advised to read the additional remarks to § 128, contained in the second chapter, previous to entering upon this method of analysis.

should the quantity of the nitre formed not be sufficient, some must be added whilst fusing the residue. The metals, with the exception of chromium, remain as oxides, and are separated and detected according to the methods given above. The chromium is obtained as soluble chromate of potash.

b. NO COMPLETE DECOMPOSITION TAKES PLACE: caustic potash is added and the mixture boiled. Should any residue remain, this is filtered, after the previous addition of some water, and then dissolved and treated as § 106, A, 2, directs. The alkaline filtrate is saturated with sulphuretted hydrogen. If any precipitate be formed, this is again filtered, dissolved in nitric acid, and the solution treated as § 114, III. directs. The filtrated liquor is slightly acidified with hydrochloric acid and sulphuretted hydrogen added should it appear necessary. If a precipitate be formed, this is treated as § 116 directs. The filtrate is tested for cyanogen and the other electro-negative bodies, and acids, and for cobalt, iron, manganese, and chromium, as § 128, *a*, directs. (When fusing the residue with nitre, according to the method laid down in § 128, *a*, (vide this section from the words, "These metals must not be disregarded," to the end,) besides the oxides, alumina is obtained, if any be present; this must be borne in mind.)

§ 129.

GENERAL RULES FOR THE DETECTION OF INORGANIC SUBSTANCES; IN CASES WHERE ORGANIC SUBSTANCES ARE PRESENT, WHICH BY THEIR COLOUR, CONSISTENCE, OR OTHER PROPERTIES, IMPEDE THE APPLICATION OF THE REAGENTS, OR RENDER THE PHENOMENA OBSCURE.

We have already stated in our introductory remarks, that cases of this kind are so manifold, that it is impossible to lay down a determinate method for every especial case; we must, therefore, content ourselves with giving only such methods as are applicable in *most* cases, and leaving it to the judgment of the operator to adopt those modifications which he may deem necessary.

1. THE SUBSTANCE DISSOLVES IN WATER, BUT IS OF A DARK COLOUR OR HAS A SLIMY CONSISTENCE.

a. One part of the solution is boiled with hydrochloric acid, and chlorate of potash gradually added till the fluid has become discoloured and limpid; the solution is then heated until all odour of chlorine has disappeared, diluted with water, and filtered. The filtrate is treated after the usual method, beginning at § 115°.

b. Another portion of the solution is boiled for some time with nitric acid, filtered, and the filtrate tested for silver, potash, and hydrochloric acid. This kind of treatment is frequently preferable to all others in such cases where the destruction of the colouring, slimy matters, &c., succeeds well by means of nitric acid.

2. *The body does not dissolve in boiling water, or dissolves only in part.* The solution is filtered, and the filtrate treated either as § 114 directs, or, if it be necessary to destroy the colouring matters which it may contain in admixture, as directed § 129, 1. If it is impossible to filter the solution, the further operation must be conducted as stated § 129, 2, *c.* The nature of the residue may be various.

a. IT IS GREASY. The fatty matters are removed by means of ether, and should any residue remain, this is treated as § 106 directs.

b. IT IS RESINOUS. Alcohol is employed instead of ether, or a mixture of both liquids is used.

c. IT IS OF ANOTHER NATURE, e. g. organic fibrine, &c. The residue insoluble in water is dried, and the greater part of it rubbed together with from three to four parts of pure nitre; the mixture is gradually deflagrated in a red hot crucible. The residue is treated as § 106, A, directs. Another part is boiled with aqua regia, the solution filtered and the filtrate tested for mercury. The rest is tested for ammonia, as § 122 directs.

§ 130.

IV. CONFIRMATORY EXPERIMENTS.

When the various bases, acids, and electro-negative bodies, present in the substance under examination have been detected, it is, in many cases, *advisable*, in others absolutely *necessary*, to verify our conclusions. In many cases this is easily accomplished, since certain substances have such characteristic reactions that their presence or absence may at once be determined, although many other substances are present at the same time. But many substances have not such characteristic reactions, in which cases we must satisfy ourselves by a strict and minute examination, and by varying our processes, determine whether the phenomena usually indicating the presence of a substance, do not proceed from extraneous causes.

Thus ammonia may be erroneously supposed to be present in a substance, whilst it is in fact derived from the atmosphere of the laboratory, &c.

In the course of this work we have pointed out those reactions which may be sought as confirmatory proofs, and the precautions necessary to secure the purity of our reagents.

CHAPTER II.

EXPLANATORY NOTES AND ADDITIONS TO THE PRACTICAL COURSE.

I. REMARKS ON THE PRELIMINARY EXAMINATION.

§ 105.

THE sensible qualities of bodies, as I before remarked, may often enable us at once to deduce certain general conclusions, as to their nature, at least negatively. Thus, a white powder cannot be cinnabar, a light flocculent body cannot be a compound of lead, &c. But the student must beware of forming opinions prematurely, respecting the nature of a body from its sensible properties only, lest it give rise to such preconceptions as may lead him to draw fallacious conclusions from the reactions which manifest themselves afterwards in the course of the real examination.

In the examination of bodies, at a high temperature, small glass tubes may be often advantageously substituted for a metallic spoon, since they enable us to observe any substance which may volatilize in the process; but as a new tube is needed in every experiment, the metallic spoons may serve in ordinary practice.

With respect to the blow-pipe examination, the student must avoid drawing positive conclusions until he has acquired a certain degree of experience, from practice; a slight incrustation may not imply the presence of a metal, nor his inability to effect a reduction or to produce a colour by solution of cobalt, the *absence* of a substance sought. The blow-pipe phenomena are, indeed, in most cases unerring, but they are easily modified by adventitious circumstances.

The preliminary examination is in no case to be passed over by the student.

II. ADDITIONAL REMARKS UPON SOLUTION, &C.

§ 106.

There is some difficulty in determining the limits of the two classes of bodies, soluble and insoluble, since these terms are but relative, and we use the phrases *easily*, and *sparingly*, or *difficultly soluble*; and, indeed, these two classes merge into each other. Sulphate of lime which is soluble in four hundred and sixty-one parts of water might perhaps serve as a limit between these two classes, since it may still be distinctly detected in aqueous solutions by means of the very susceptible reagents which we possess for lime and sulphuric acid.

When examining an aqueous fluid by evaporating a few drops of it upon a platinum plate, there remains sometimes a very minute residue, which leaves us in doubt as to the nature of the substance; in this case the fluid must, 1st, be tested with litmus papers; 2d, one drop of solution of chloride of barium added to a portion of it; and, lastly, some carbonate of potash added to another portion. If these tests produce no alteration, it is unnecessary to examine it further for acids or bases. We may, in such cases, feel certain, that the substance of which the residue remaining upon evaporation consists, will be better detected amongst the bodies insoluble in water, since both the acids and bases, which principally form sparingly soluble compounds, are sensibly indicated by the above-mentioned tests.

If water has dissolved any portion of the substance under examination, the student will always do well to examine separately this solution for acids and bases, as this will permit him to detect the nature of the compound under examination with greater facility, and, moreover, will render his conclusions the safer, which advantages will counterbalance the disadvantage of meeting sometimes with the same substance in the aqueous and in the acid solution.

The following substances are insoluble in water, but soluble in hydrochloric acid or in nitric acid, (with some exceptions,) the phosphates, arseniates, arsenites, borates, carbonates, and oxalates of the earths and metals; and also several tartrates, citrates, malates, benzoates, and succinates, the oxides and sulphurets of the heavy metals, alumina, magnesia, many metallic iodides and cyanides, &c. Nearly all of these compounds are decomposed, if not by dilute, yet by boiling concentrated hydrochloric acid, (for the exceptions vide § 127,) but this decomposition gives rise to the formation of insoluble compounds when oxide of silver is present, and of sparingly soluble compounds in the presence of protoxide of mercury and lead. This is not the case with nitric acid, and thus we often effect a complete solution by its means in cases where hydrochloric acid has left a residue. But nitric acid, besides the substances insoluble in simple acids, leaves also oxide of antimony, peroxide of tin, peroxide of lead, &c. undissolved, whilst it dissolves many other substances more or less completely. When, therefore, the compound under examination is not completely dissolved by nitric acid, (with the exception of sulphur, which may have separated,) we must in the course of analysis again have recourse to the hydrochloric solution, in order to assign exact limits in some measure to the third class of substances, viz. those bodies which are insoluble in water and simple acids.

With regard to the solution of pure metals or alloys, we must remark, that white precipitates frequently are formed upon boiling with nitric acid, though no tin or antimony be present. Inexperienced students often confound these precipitates with the oxides of these two metals, although their external appearance is quite different. These precipitates consist of nitrates sparingly soluble in the nitric acid present, but of easy solution in water. Consequently, before we can pronounce these precipitates to consist of tin or antimony, we must previously ascertain whether they are soluble in water.

III. ADDITIONAL REMARKS UPON THE REAL EXAMINATION.

From § 107 *to* § 129.

A. GENERAL SURVEY AND EXPLANATION OF THE ANALYTICAL COURSE.

a. DETECTION OF THE BASES.

We have divided the bases into six groups, (vide Chapter III. Part I.) and explained the method of detecting and isolating the individual bases. These objects we have kept in view in the practical course, and as a correct apprehension of this is of primary importance, we subjoin a brief explanation of the grounds of our division,—a key as it were, to the analytical course of study, so far as those bases are concerned. The general reagents which we employ in the course of analysis to divide the bases into principal groups, are HYDROCHLORIC ACID, SULPHURETTED HYDROGEN, HYDROSULPHURET OF AMMONIA, and CARBONATE OF AMMONIA; this is also the order of succession in which they are employed. Hydrosulphuret of ammonia performs a *double* part.

Let us suppose we have in solution all the bases, arsenious acid, and phosphate of lime, (which latter may serve as a type for the salts of the alkaline earths, soluble in acids, and precipitated by ammonia, unaltered.)

Chlorine forms insoluble compounds with silver and mercury alone; chloride of lead is sparingly soluble in water. The insoluble protochloride of mercury corresponds with the protoxide of mercury. If, therefore, we add to our solution

1. *Hydrochloric acid*, we remove from the solution the metallic oxides of the first section of the fifth group, viz. the OXIDE OF SILVER and the PROTOXIDE OF MERCURY. A portion of the LEAD, also, may, perhaps, precipitate as chloride of lead, should the solution be concentrated; this is, however, immaterial, as a sufficient quantity of the lead remains in solution as to admit of its detection afterwards.

Sulphuretted hydrogen precipitates the oxides of the fifth and sixth group completely from solutions containing a free mineral acid, as both the affinity which the metallic radicals of these oxides have for sulphur, and that which hydrogen possesses for oxygen, are so powerful as to overcome the affinity between the metal and oxygen, together with that between the oxide and a strong acid, EVEN THOUGH THE ACID BE PRESENT IN EXCESS. But none of the other bases are precipitated under those circumstances, the bases of the first, second, and third group forming no sulphur compounds insoluble in water; those of the fourth group are not precipitated, because the affinity which their metallic radicals possess for sulphur, together with that manifested by hydrogen for oxygen, are not sufficiently powerful to overcome that of the metal for oxygen, and of the oxide for a strong acid, IF THE LATTER IS NOT PRESENT IN EXCESS.

If, therefore, after the removal of oxide of silver and of p toxide of mercury, by means of hydrochloric acid, we add to our solution, (which still contains free hydrochloric acid)

2, *Sulphuretted hydrogen:* we remove from it the rest of the oxides of the fifth, together with those of the sixth group, viz. OXIDE OF LEAD, PEROXIDE OF MERCURY, OXIDE OF COPPER, OXIDE OF BISMUTH, OXIDE OF CADMIUM, PEROXIDE OF GOLD, PEROXIDE OF PLATINUM, PROTOXIDE OF TIN,

PEROXIDE OF TIN, 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, e. g. peroxide of iron, chromic acid, &c.

The sulphurets corresponding with the oxides of the sixth group have the property of combining with electro-positive metallic sulphurets (the sulphurets of the alkali metals) forming sulphur salts soluble in water, whilst the sulphurets corresponding with the oxides of the fifth group do not possess this property. If, therefore, we treat all the sulphurets precipitated by sulphuretted hydrogen from acid solution, with

3. *Hydrosulphuret of ammonia*, or *sulphuret of potassium*, the bisulphurets of mercury, lead, copper, bismuth, and cadmium will remain undissolved, whilst the other bisulphurets are dissolved as the double SULPHURETS OF GOLD, PLATINUM, ANTIMONY, TIN, ARSENIC, and ammonium or potassium, and from this solution they are precipitated upon the addition of an acid, either unaltered, or having acquired a higher degree of sulphuration, by receiving sulphur from the hydrosulphuret of ammonia, (sulphuret of tin.) In this process the acid decomposes the sulphur salt formed. The sulphur base (hydrosulphuret of ammonia or sulphuret of potassium) is decomposed at the expense of the constituents of decomposed water, into an oxygen base (ammonia or potash) and sulphuretted hydrogen; the former combines with the acid added, the latter escapes, and the liberated electro-negative sulphur precipitates. (If the acid is an hydracid, its radical combines with the ammonium and its hydrogen with the sulphur.) Sulphur precipitates at the same time, the hydrosulphuret of ammonia always containing sulphur in excess. This sulphur renders the colour of the precipitated sulphurets lighter, which must be always borne in mind, when determining their nature.

Of the oxides still in solution, the alkalies, the alkaline earths, alumina and oxide of chromium have remained so, because their sulphur compounds are soluble in water, or because their salts are not at all affected by sulphuretted hydrogen; the oxides of the fourth group would have been precipitated by sulphuretted hydrogen, had not the free acid present prevented their precipitation, as their corresponding sulphur compounds are insoluble in water. If, therefore, this free acid be removed, i. e. if the solution be made alkaline and sulphuretted hydrogen added, or if, what answers both purposes at once,

4. *Hydrosulphuret of ammonia* be added to the solution, the sulphurets corresponding with the oxides of the fourth group are precipitated, viz.: SULPHURET OF IRON, SULPHURET OF MANGANESE, SULPHURET OF COBALT, SULPHURET OF NICKEL, and SULPHURET OF ZINC, and at the same time, ALUMINA, OXIDE OF CHROMIUM, and PHOSPHATE OF LIME, are precipitated, the affinity which the ammonia possesses for the acid of the salt of oxide of chromium or of alumina, or for the acid which keeps the phosphate of lime in solution, causing decomposition of the water and subsequently formation of oxide of ammonium and of sulphuretted hydrogen. The former combines with the acid, the latter escapes, incapable of entering into combination with the oxides deprived of their acids or with the phosphate of lime,—the oxides and the limesalt precipitate. We have now remaining in solution only the alkaline earths and the alkalies. The neutral carbonates of the former are insoluble in water, whilst those of the latter are soluble. If, therefore, we add

5. *Carbonate of ammonia* and apply heat, in order to decompose acid carbonates which may, peradventure, have been formed, all the alkaline earths ought to precipitate. This is, however, the case only as regards BARYTES, STRONTIAN, and LIME; of magnesia we know that, owing to its disposition of forming double compounds with ammoniacal salts, it precipitates only in part, or, not at all, in presence of another ammoniacal salt. To avoid this uncertainty, sal ammoniac is added previous to the addition of carbonate of ammonia, in order completely to prevent the precipitation of magnesia.

We have now still in solution, magnesia and the alkalies; of the presence of magnesia we may assure ourselves by means of phosphate of soda and ammonia; but for its separation we pursue a different way, since the presence of phosphoric acid would impede the further progress of the analysis. The process which we employ is based either upon magnesia being insoluble in its pure state or as a carbonate. The substance under examination is heated to redness in order to expel the ammoniacal salts, and the magnesia is then either precipitated by means of barytes whilst the alkalies remain in solution; or the substance is heated to redness, with the addition of sulphuric acid, and the sulphates formed are by decomposition with acetate of barytes, converted into acetates, and these, by the application of a red heat, into carbonates; upon treating these latter with water, carbonate of magnesia remains, whilst the alkaline carbonates are dissolved. A fresh specimen must, of course, be employed for the detection of ammonia.

b. DETECTION OF THE ACIDS.

Previous to entering upon the examination for acids and electro-negative substances, we must first consider which of these bodies may and which of them *cannot* be present according to the detected bases, and accordingly to the solubility of the substances under examination; thus we shall avoid making unnecessary experiments. A table useful for this purpose, will be found in the appendix. The general reagents employed for the detection of acids are, for the inorganic acids, CHLORIDE OF BARIUM and NITRATE OF SILVER; for the organic acids, CHLORIDE OF CALCIUM and PERCHLORIDE OF IRON. It is, therefore, indispensable, first to assure ourselves whether we have to operate upon a substance containing inorganic acids alone, or organic acids alone, or both together. When examining for bases, the general reagents serve for the real separation of the various groups of bases from each other; in the examination for acids, we only use them to assure ourselves of the presence or absence of the acids belonging to the different groups.

Let us suppose we have in an aqueous solution all the acids we have treated of in the present work, combined, for instance, with soda.

Barytes form insoluble compounds with sulphuric acid, phosphoric acid, arsenious acid, arsenic acid, carbonic acid, silicic acid, boracic acid, chromic acid, oxalic acid, tartaric acid, and citric acid; these compounds are soluble in hydrochloric acid, with the exception of sulphate of barytes. If, therefore, to a portion of our neutral or neutralized solution, we add

1. *Chloride of barium*, the presence of at least one of these acids will immediately become manifest. Upon treating the precipitate formed with hydrochloric acid, the presence of sulphuric acid will be detected, as all the salts of barytes are soluble in this menstruum, with the exception of the sulphate. When sulphate of barytes is present, the reaction with chloride of barium does not enable us to detect all the other acids enumerated with safety. For upon filtering the hydrochloric solution of the precipitates and supersaturating with ammonia, the borate, tartrate, citrate, &c. of barytes do not precipitate again, being kept in solution by the sal ammoniac formed. Chloride of barium, therefore, cannot be employed to separate the individual acids from each other, and thus is of no use for their individual detection, except for that of sulphuric acid. It is, however, of great importance as a reagent, since the non-formation of a precipitate in neutral or alkaline solutions, upon its application proves at once the absence of a considerable number of acids.

Silver forms compounds insoluble in water, with chlorine, iodine, bromine and cyanogen; and oxide of silver, with phosphoric acid, arsenious acid, arsenic acid, boracic acid, chromic acid, silicic acid, oxalic acid, tartaric acid, and citric acid. All these compounds are soluble in ammonia, with the exception of iodide of silver, and in nitric acid, with the exception of iodide, chloride, bromide, and cyanide of silver. If, therefore, we add to our solution (which must be completely neutral,)

2. *Nitrate of silver*, we detect immediately the presence of one or several of the acids enumerated; chromic acid, arsenic acid, and several other acids, the silver salts of which are coloured, may even be individually detected with a certain degree of safety, by the colour of their precipitates. If we add nitric acid to the precipitate, we detect the presence of the haloid compounds, as these remain undissolved, whilst the oxide salts are dissolved. The complete separation and individual detection of those acids which form insoluble compounds with oxides of silver, are prevented by the same cause which renders the

individual detection of acids by chloride of barium unsafe. For the ammoniacal salt formed prevents the reprecipitation by ammonia, of several salts of silver, from the acid solution; nitrate of silver serves us, therefore, besides detecting chlorine, iodine, bromine, and cyanogen, and indicating chromic acid, &c., especially to prove at once the absence of many acids, if it produces no precipitate in neutral solutions. The behaviour of solutions under examination with chloride of barium and with nitrate of silver, therefore, points out at once what course we have further to pursue in our investigation. Thus, for instance, if chloride of barium has produced a precipitate, whilst we have obtained none by nitrate of silver, it is not necessary to test for phosphoric acid, chromic acid, boracic acid, silicic acid, arsenious acid, arsenic acid, oxalic acid, tartaric acid, and citric acid, provided always that the solution does not already contain ammoniacal salts. The same is the case if we obtain a precipitate by nitrate of silver, but none by chloride of barium. Returning to our first supposition, viz., that all acids are present in the compound under examination, we have thus detected CHLORINE, BROMINE, IODINE, and CYANOGEN, (for their separation and individual detection, vide § 100,) as well as SULPHURIC ACID, and we have reason further to test for all the other acids precipitated by these two reagents. Their detection is based upon the results of special experiments, which have already been explained in the course of the present work: the same applies to the other inorganic acids, and thus also to nitric acid and chloric acid.

Of the organic acids, oxalic acid, tartaric acid, and paratartaric acid, are precipitated by chloride of calcium, from aqueous solutions, at a low temperature, even in the presence of sal ammoniac; but the precipitation of citrate of lime is prevented by the presence of ammoniacal salts, and takes place only upon boiling or upon mixing the solution with alcohol; the latter means is also employed for the separation of oxalic lime from aqueous solutions. If, therefore, we add to our solution,

3. *Chloride of calcium* and sal ammoniac, OXALIC ACID, TARTARIC ACID, and PARATARTARIC ACID are precipitated, but the lime-salts of several inorganic acids, which have not yet been separated, precipitate at the same time (phos-

phate of lime, for instance.) We must, therefore, select, for the individual detection of the precipitated organic acids, such reactions only as do not admit the possibility of confounding the organic acids with the inorganic acids precipitated at the same time. For the detection of oxalic acid we thus select solution of gypsum, with the addition of acetic acid, (§ 98, *c*, 4,) for the detection of tartaric and paratartaric acid; we treat the precipitate produced by chloride of calcium, with solution of potash, since the lime-salts of these two acids alone dissolve in this menstruum, at a low temperature, whilst all the other insoluble lime-salts remain undissolved.

Of the organic acids we have now still in solution citric acid and malic acid, succinic acid and benzoic acid, acetic acid and formic acid. CITRIC ACID and MALIC ACID precipitate upon alcohol being added to the fluid filtered off from the oxalate, tartrate, &c., of lime, and which contains still chloride of calcium in excess. Sulphate and borate of lime always precipitate together with the malate and citrate of lime, if sulphuric acid and boracic acid are present; we must, therefore, carefully guard against confounding the lime precipitates of these acids with those of citric acid and malic acid. The alcohol is then removed by evaporation, and

4. *Perchloride of iron* added; this precipitates SUCCINIC ACID and BENZOIC ACID in combination with peroxide of iron, whilst FORMIC ACID and ACETIC ACID remain in solution. The methods for the further separation of the groups and the reactions whereupon the detection of the individual acids depends, have already been described.

B. SPECIAL AND ADDITIONAL REMARKS UPON THE SYSTEMATIC COURSE OF ANALYSIS.

§ 114.

We have at the beginning of § 114, given the instruction to mix neutral or acid aqueous solutions with hydrochloric acid. This acid must be added drop by drop. If no precipitate is formed, a few drops are sufficient; if a precipitate is formed, the acid must be added until the precipitate ceases to increase and the fluid has acquired a distinct acid reaction. The addition of a large proportion of hydrochloric acid is not only unnecessary, but injurious. The precipitate produced by hydrochloric acid in neutral or acid solutions may consist of chloride of silver, protochloride of mercury, chloride of lead, and a basic salt of antimony. The two latter substances redissolve upon diluting and heating the acid fluid, and thus the non-solution of the precipitate upon the application of these processes, is an indication of the probable presence of chloride of silver or protochloride of mercury. Should compounds of antimony or bismuth be present, this dilution with water will separate from them insoluble basic salts in a state of most minute division; these must be redissolved by the addition of hydrochloric acid, before we can draw any correct conclusion from the remaining or disappearing of the precipitate produced by hydrochloric acid. If we have to operate upon an alkaline solution, the hydrochloric acid must be added, until the fluid manifests a strong acid reaction. A great excess of the acid must, however, be avoided. The substance which causes the alkaline reaction of the fluid, is neutralized by the hydrochloric acid, and the bodies combined with it, or dissolved in it, separate. If the alkali present was in a free state, oxide of zinc, for instance, alumina, &c., may be precipitated. But these redissolve in an excess of the hydrochloric acid, whilst chloride of silver, if present, will not redissolve, and chloride of lead only sparingly. If a metallic sulphur salt be the cause of the alkaline reaction, the electro-negative sulphuret (e. g. sulphuret of antimony) will precipitate, on the addition of the hydrochloric acid; whilst the electro-positive sulphuret, (e. g. sulphuret of sodium) will form chloride of sodium, and sulphuretted hydrogen, with the constituents of hydrochloric acid. If an alkaline carbonate, or an alkaline sulphuret, be the cause of the alkaline reaction, carbonic acid or sulphuretted hydrogen will escape. All these phenomena ought to be carefully observed, for they not merely point out the presence of the relative substance, but also exclude entire series of substances from the further examination.

§ 115.

We have already had occasion to remark, that upon adding a reagent (e. g. sulphuretted hydrogen) to a fluid under examination, a precipitate may or may not ensue. If a precipitate is formed, this may be, *a*, white, *b*, yellow, *c*, orange, *d*, brown or black. Every one of these various cases is a different answer given to the question put by means of the reagent, and every answer has a different meaning. An accurate distinction of the individual case is, therefore, indispensable. Any error here must prevent the student from obtaining correct results.

The colour of the precipitate is almost invariably pointed out as a criterion in the systematic course of analysis. We may presume that a darker precipitate will sometimes conceal one of a lighter colour, and thus, e. g. that yellow sulphuret of arsenic may be present, invisible in a precipitate of black sulphuret of mercury; and so we may also conclude that no dark precipitate can be contained in a light-coloured one, e. g. no black precipitate in a white. These conclusions cannot, however, always be drawn with the same degree of safety, all colours not contrasting so pointedly with each other as black and white ; but many of them rather merging into each other, e. g. yellow and orange. Whenever the colour of the precipitate admits of any doubt as to its nature, it is always advisable to pursue that course which the darker of the colours in question indicates, since in this regard has been had to all the metals which can possibly have precipitated, whilst in the other the metallic precipitates of darker colour are disregarded. The safer way is always to be preferred, although it may be the more protracted.

A judicious distribution and economy of time is especially to be studied in the practice of analysis ; many of the operations may be carried on simultaneously, which the student will readily perceive and arrange for himself.

In such cases, where we have before us only metallic oxides of the sixth group, (e. g. oxide of antimony,) and oxides of the fourth group, (e. g. the oxides of iron,) it is not necessary for their separation to precipitate them from acidified solutions by means of sulphuretted hydrogen, but we may at once add hydrosulphuret of ammonia in excess to the neutralized solution. The sulphuret of iron, &c., will then be obtained in a precipitate, whilst the antimony, &c., will remain in solution, from which, upon the addition of an acid, it will immediately precipitate a sulphuret of antimony. This method has the advantage of rendering the fluid less dilute than when sulphuretted hydrogen is employed, and moreover of facilitating and accelerating the operation.

§ 116.

When digesting the precipitates produced by sulphuretted hydrogen from acid solutions, with hydrosulphuret of ammonia, it is indispensable to apply this latter reagent in a correct proportion. A small quantity is generally sufficient, but if sulphuret of tin be present, a somewhat larger amount must be employed. Inexperienced students, however, use so much of it, that, upon the addition of an acid, sulphur precipitates to such an amount that the colour of the metallic sulphuret, which precipitates at the same time, is quite obscured and concealed by it. The separation and individual detection of oxide of antimony, peroxide of tin, and arsenic, is not very easy if all three oxides have been precipitated as sulphurets. Inexperienced students will find it difficult safely to detect and separate them before the blow-pipe. Of the many methods applicable for the distinction of these three metals, that given at § 116 has been proved the safest by experience. If sulphuret of arsenic, sulphuret of antimony, and sulphuret of tin, are deflagrated with nitre in excess, and carbonate of soda, the metals and the sulphur oxidize at the expense of the oxygen of the nitric acid: we have, therefore, in the fused mass alkaline arseniate, antimoniate, sulphate, and stannate, besides excess of nitre and carbonate of soda. On treating with water, the alkaline sulphate and arseniate are dissolved; the alkaline antimoniate is decomposed; an insoluble acid salt remains, whilst a small amount of antimonic acid is dissolved in the form of a basic salt. A portion of the peroxide of tin also dissolves in the carbonated alkali present. If boiling water is employed, the amount of the dissolved antimonic acid and peroxide of tin is not inconsiderable, whilst it is but minute in cold water; the latter is, therefore, preferable to boiling water in this operation. If the alkaline solution obtained is then saturated with nitric acid, and heat applied, the dissolved peroxide of tin and antimonic acid precipitate; but this precipitate is never free from arsenic. This will show how carefully we ought to avoid getting much peroxide of tin or antimonic acid in solution. In the fluid saturated with nitric acid, or slightly acidified, filtered off from the precipitate formed, we have now still arseniated and sulphated alkali. One portion of this fluid is tested, as stated § 116, with solution of silver and ammonia, and another portion with solution of lead. Since the fluid must be perfectly neutral to render the arseniate of silver visible, and since it is not always easy to hit upon the exact neutralization point, the fluid, after the addition of the solution of silver, is covered with a layer of dilute ammonia. This is the easiest method of producing a precipitate when but small quantities of arsenic are present. On the precipitation with solution of acetate of lead, we obtain a mixture of sulphate and arseniate of oxide of lead. The presence of the sulphate of lead renders the quantity of the precipitate greater, and thus its collection and testing before the blow-pipe more easy; it, moreover, increases the bulk of the button obtained. Though by means of these reactions the presence of arsenic may be proved beyond doubt, yet the production of metallic crusts is the safest test.

If the residue remaining upon treating the deflagrated mass with water, and which is to be examined for tin and antimony, be not carefully washed, and thus freed from all the nitre still adhering to it, previous to fusing with cyanide of potassium, explosions will take place, (§ 101, *a*, 3,) whereby not only the test specimens are thrown off, but the operator himself may meet with some injury.

§ 117.

If the sulphurets of the second section of the fifth group are heated to the boiling point with nitric acid, lead, bismuth, copper, and cadmium, oxidize at the expense of a portion of the nitric acid, which decomposes into nitric oxide and oxygen, the sulphur separates, and the oxides formed combine with another portion of the nitric acid, forming soluble nitrates. Sulphuret of mercury is not decomposed by nitric acid, provided no chloride be present at the same time, owing to imperfect rinsing. Ammonia decomposes all the metallic nitrate dissolved. But the oxides of lead and bismuth are insoluble in an excess of ammonia, whilst those of cadmium and copper are dissolved by this reagent. Ammonia, therefore, affords us a means of testing the solution for the presence of the oxides of lead and bismuth, as well as of precipitating and separating them from it. The presence of oxide of copper is also detected by this reagent; the ammonia-nitrate of copper, which is formed upon its addition to the fluid under examination, imparting a blue colour to the fluid. The causes whereupon the further separation and detection of the four metals in question depends, have already been sufficiently explained at § 91, (recapitulation and remarks.) With regard to the detection of bismuth, it must be remarked, that it never succeeds if the excess of acid present is not as slight as possible; this is best attained in the manner described § 117. But if the operator evaporates only nearly to dryness, so much acid frequently remains present, that the separation of a basic salt cannot be accomplished.

Besides the method given at § 91, (recapitulation and remarks,) and at § 117, for the distinction of cadmium, copper, lead, and bismuth, the following method also leads with great safety to the desired end. Carbonate of potash is added to the nitric solution as long as any precipitation takes place; solution of cyanide of potassium in excess is then added, and heat applied. Lead and bismuth are hereby completely separated as carbonates, whilst copper and cadmium are obtained in solution as the double cyanides of copper and potassium, and cadmium and potassium. Lead and bismuth may then easily be separated by means of sulphuric acid; copper and cadmium, by adding to the solution of their cyanides in cyanide of potassium) sulphuretted hydrogen in excess, and applying heat; some more cyanide of potassium must then be added to redissolve the sulphuret of copper, which, peradventure, may also have precipitated. A yellow precipitate of sulphuret of cadmium, insoluble in cyanide of potassium, indicates cadmium. The fluid is filtered off, and hydrochloric acid added to the filtrate; the formation of a black precipitate of sulphuret of copper indicates copper. The presence of mercury is indeed already proved by a black residue remaining, upon heating the sulphurets with nitric acid. A more minute examination of any residue remaining upon boiling with nitric acid, is, however, necessary, always provided this residue be not pure yellow sulphur, which in most cases floats on the surface of the fluid. The reasons for this further examination are the following: separated sulphur frequently envelops small particles of the other black sulphurets, and for this reason appears black here and there. Sulphuret of mercury, moreover, may, under certain circumstances, lose its black colour, and the precipitate in that case be confounded with sulphate of lead, (into which substance a portion of the sulphuret of lead present is in most cases converted,) or with pertoxide of tin, (which may have been formed by the action of nitric acid upon sulphuret of tin present, and not completely removed by hydrosulphuret of ammonia. The test with polished copper is the most convenient, and yields the quickest result. It must, however, be remarked, that errors occur more frequently, when employing this test, than when we select the reaction with protochloride of tin. When employing the latter reagent, we must especially assure ourselves of its being still undecomposed, and of the solution of mercury containing no nitric acid. If after the method described, the protoxide of mercury has first been separated by hydrochloric acid, and a precipitate of sulphuret of mercury is formed, upon the addition of sulphuretted hydrogen, this corresponds always with the peroxide and perchloride, &c. of mercury. If we have to operate upon an aqueous solution, or a solution in very dilute hydrochloric acid, it existed as such in the original substance. But when we have a nitric solution before us, it may have originally existed as protoxide, and subsequently acquired a higher degree of oxidation.

§ 118.

The precipitate produced by hydrosulphuret of ammonia, may (as we have already stated, page 259) consist of sulphurets, of oxides, and of the phosphates of the alkaline earths, phosphate of alumina, oxalate of lime (barytes and strontian.) The borates of the alkaline earths and the oxalate of magnesia would, moreover, be precipitated, but they remain in solution, owing to the sal ammoniac formed in the fluid or added to it. Upon dissolving the precipitate in hydrochloric acid, or in aqua regia, the metallic sulphurets and the hydrated oxides are converted into soluble chlorides, whilst the phosphates and oxalates dissolve without decomposition. If to this acid solution, ammonia is added, the phosphates and oxalates are re-precipitated, and, together with them, alumina, oxide of chromium, and peroxide of iron fall down, as these do not (like the oxides of manganese, nickel, cobalt, and zinc) form soluble double compounds with ammoniacal salts. This precipitation by ammonia, in presence of sal ammoniac, is the base whereon the further distinction and individual detection of the substances enumerated depends. At this result we may also arrive by merely adding sal ammoniac and ammonia in excess to the fluid filtered from the precipitate produced by sulphuretted hydrogen, after having expelled the excess of sulphuretted hydrogen by boiling, and converted the iron which, peradventure, may be present, into peroxide of iron, by heating with nitric acid. We obtain thus, of course, the peroxide of iron, the alumina, oxide of chromium, and the phosphates, &c., of the alkaline earths alone in the precipitate, whilst the manganese, cobalt, nickel, and zinc, are contained in the fluid which runs off, and may then be precipitated by means of hydrosulphuret of ammonia. Under certain circumstances this method is preferable to the first, and may then be employed with advantage ; but in general it requires more time than the other. With regard to the further detection of nickel, cobalt, manganese, and zinc, we have nothing to add to § 118, 2, except that ammoniacal salts must not be present, if the separation of these four metals from each other is to succeed after the method described at § 118, 2. But as the separation of manganese, nickel, &c., from iron, &c., depends upon the presence of ammoniacal salts, these must be removed either by evaporating the solution and heating the residue to redness, or by precipitating these four metals again by hydrosulphuret of ammonia, (which latter method generally is preferable to the former.) The precipitate of the metallic sulphurets must, of course, be carefully washed. The separation of the peroxide of iron, and of the phosphates and oxalates of the alkaline earths from alumina and oxide of chromium rests upon the solubility of the latter and the insolubility of the former compounds, in caustic potash; and that of peroxide of iron from the salts of the alkaline earths, upon the circumstance that the precipitation of the former is prevented by adding tartaric acid to the acid solution, previous to the addition of ammonia, which is not the case with the latter. (Vide recap. and rem. to § 88.)

§ 127.

The third class of substances also has no strictly definable limits, as the solubility or insolubility of several compounds belonging to it, depends very much upon the quantity and concentration of the acid and the time of boiling. Besides the difficultly soluble substances enumerated, we must especially look for many metallic sulphurets and iodides, which also only dissolve after some time in concentrated hydrochloric acid, at a high temperature. If a substance is dissolved in nitric acid after long boiling, we must not conclude that protochloride of mercury is absent, since this substance, as we have already stated, is converted in this process into pernitrate of mercury and perchloride of mercury, and is thus dissolved.

Chloride of silver, protochloride of mercury, and chloride of lead may have been present in the original compound as such, or may have been formed upon treating with hydrochloric acid. The presence of chloride of lead has in that case already been detected in the aqueous solution; of the original presence of the two other substances we may assure ourselves in the following manner. The substance insoluble in water is treated with dilute nitric acid. All the salts of protoxide of mercury and oxide of silver present are thereby dissolved, whilst the chlorides enumerated above remain undissolved together with iodide of silver; they are separated by means of ammonia, which at the same time allows us to detect the protochloride of mercury.

The decomposition of the sulphates of the alkaline earths may be effected also in the humid way by boiling them for some time with solution of carbonate of potash. But the fusion with the carbonate of potash and soda, yields far safer results, and leads quickly to the desired end, when operating upon small quantities. This method has, moreover, the advantage of leading to the safe detection of the presence of silicic acid.

The sulphates of the alkaline earths are decomposed by the alkaline carbonates in such a manner as to give rise to the formation of carbonates of the alkaline earths and of sulphates of the alkalies. If the precipitate of the former be not carefully washed, previously to its solution in hydrochloric acid, sulphates of the alkaline earths will again be formed by the action of the sulphated alkali still adhering to the precipitate; this would render the experiment very unsafe at the least, since, for instance, all the barytes dissolved might precipitate again.

Carbon has been connected with this third class, since it occurs sometimes in the course of examinations, and thus may become a great obstacle to the progress of the inexperienced student, if not prepared for its presence. Graphites is distinguished from the other forms of carbon by its difficult combustion before the blow-pipe, and its non-combustion in a platinum spoon; besides the iron, which it generally contains in admixture, indicates its presence.

§ 128.

The analysis of cyanogen compounds is not very easy in certain cases, and sometimes it is indeed extremely difficult to ascertain whether we have a cyanide before us or not. If, however, the phenomena which the substance under examination manifests, when heated to redness (§ 105, A, I., 2, *f*,) be carefully observed, and also whether upon boiling with hydrochloric acid any odour of hydrocyanic acid manifests itself, (§ 106, A, 2,) the presence or absence of a cyanide will generally not long be doubtful.

It must above all be borne in mind that the insoluble cyanogen compounds occurring in pharmacy, &c., belong to two quite different classes. They are either SIMPLE CY-

ANIDES, or compounds of metals with ferrocyanogen, or with some other similar compound radical.

All the simple cyanides are decomposed by boiling with concentrated hydrochloric acid, into metallic chlorides and hydrocyanic acid. Their analysis, therefore, is never difficult. The ferrocyanides, &c., however, (to which the method given § 128 indeed exclusively refers,) undergo by acids such complicated decompositions that their analysis in this manner does not easily succeed. Their decomposition by alkalies is far more simple; these precipitate the metal combined with the ferrocyanide, &c., as oxide, by yielding their oxygen to it, and combining in their metallic state with the compound radicals, forming soluble ferrocyanide of potassium, &c. The method given at § 128 endeavours first to effect a decomposition of this kind by means of CARBONATE OF POTASH. If this succeeds, we have the advantage of obtaining the oxides as a precipitate, which circumstance renders their further analysis simple; if it does not succeed, we must have recourse to CAUSTIC POTASH. But in an excess of caustic potash, several oxides are soluble, such as oxide of lead, oxide of zinc, &c. If, therefore, e. g. the double ferrocyanide of zinc and potassium, be boiled with caustic potash, it will completely dissolve in that menstruum. Were we to add an acid to this solution, we should re-obtain our original precipitate of the double ferrocyanide of zinc and potassium, and our experiment thus would be of no avail. To prevent this, we transmit sulphuretted hydrogen through the solution. All the heavy metals dissolved as oxides in the potash solution are thereby converted into sulphurets. Those of them which are insoluble in potash, such as sulphuret of lead, sulphuret of zinc, &c., precipitate, whilst those soluble in alkaline sulphurets, such as sulphuret of tin, sulphuret of antimony, &c., remain in solution, and precipitate only upon the addition of an acid.

The cyanogen is always contained in the liquid filtered from the precipitated oxides or sulphurets, as ferrocyanide, &c., of potassium, (provided always the compound before us has a double compound of cyanogen radicals.) From most of them (ferrocyanide, ferricyanide, chromicyanide, and manganocyanide of potassium) the cyanogen partly separates as hydrocyanic acid, upon boiling this solution with sulphuric acid, and may thus be easily detected. But the cobalticyanide of potassium is not decomposed by sulphuric acid, and this renders it difficult DIRECTLY to prove the presence of cyanogen in this double compound. Upon fusion with nitre, all these double compounds are decomposed, cobalticyanide of potassium not excepted. They must previous to this operation be treated with an excess of nitric acid, and then concentrated by evaporation, or else explosions will ensue. Caution in this operation is highly advisable. If we merely propose to detect the bases present in simple or double cyanides, it is in most cases sufficient either to heat the substance to redness for some time by itself, or better still, to fuse it together with the carbonates of potash and soda. By this process the metals are obtained either in their metallic state, or combined with carbon. If the compound has been fused together with the carbonated alkalies, we obtain in the dross, cyanate of potassium, if this substance has not been converted into cyanate of potash, owing to the adventitious presence of reducible oxides. (Vide § 100, *d*, 1.)

APPENDIX TO PART SECOND.

I.

GENERAL SCHEME FOR A JUDICIOUS ARRANGEMENT OF THE SUCCESSION IN WHICH SUBSTANCES OUGHT TO BE ANALYZED.

It is not a matter of indifference whether the student, in analyzing for the sake of practice, follow no rule or order whatever in the selection of substances to be examined, or whether, on the contrary, his investigations and experiments follow a definite system. Many ways may lead to the desired end, but one of them invariably will prove the shortest. I will, therefore, here point out a system which experience has shown will lead safely and rapidly to the object in view.

Let the student take one hundred compounds, distributed according to the following scheme, and the successful examination of these will be amply sufficient to enable him to attain the desired degree of skill in practical analysis. When analyzing for the sake of practice only, the student must above all things possess the means of verifying the results obtained by his experiments. The compounds to be examined ought, therefore, to be mixed by a friend who knows their exact composition.

A. *From* 1 *to* 20.

Aqueous solutions of simple salts: e. g. sulphate of soda, sulphate of lime, chloride of copper, &c.;—for the acquisition of the method to be pursued in the analysis of substances soluble in water, and which contain but one base. In these investigations it is only intended to ascertain which base is present in the fluid under examination, without regard to the detection of the acid; it is not necessary to prove that no other base is present, besides the one detected.

B. *From* 21 *to* 50.

SALTS, &c., (CONTAINING ONE BASE AND ONE ACID,) IN A SOLID FORM, as powder: e. g. carbonate of barytes, borate of soda, phosphate of lime, arsenious acid, chloride of sodium, tartar, acetate of copper, sulphate of barytes, chloride of lead, &c;—to learn how to convert a solid substance to a state which admits of its examination, (solution, or fluxing,) how to detect ONE metallic oxide, even though the substance under examination be NOT soluble in water, and how to prove the presence of ONE acid. Base and acid must be detected; it is not necessary to prove that no other constituents, &c. are present.

C. *From* 51 *to* 70.

AQUEOUS OR ACID SOLUTIONS OF SEVERAL BASES;—to acquire the method of separating and distinguishing several metallic oxides. It is necessary to prove that no other bases are present besides those detected. No regard is paid to the acids.

I. From No. 51 to 60. To acquire the method of separating the metallic oxides into the principal groups. The solutions contain, therefore, e. g. potash, lime, and lead;—copper, iron, and arsenic;—barytes, antimony, bismuth, and potash, &c.

II. From No. 61 to 70. To acquire the method of detecting side by side the individual bases belonging to the same group. The solutions contain, e. g. potash, soda, and ammonia;—zinc, manganese, and nickel;—copper, mercury, and lead;—antimony, tin, arsenic, &c.

D. *From* 71 *to* 80.

AQUEOUS SOLUTIONS CONTAINING SEVERAL ACIDS, EITHER IN THEIR FREE OR IN THEIR COMBINED STATE, e. g. sulphuric acid, phosphoric acid, and boracic acid;—carbonic acid, sulphuretted hydrogen, and hydrocyanic acid; tartaric acid, citric acid, and malic acid;—chlorine, iodine, and bromine;—nitric acid, hydrochloric acid, and oxalic acid;—to acquire the method of detecting several acids contained in the same compound. It is necessary to prove that no other acids are present besides those detected. The bases are disregarded.

E. *From* 81 *to* 100.

ALLOYS, MINERALS, AND MIXED SUBSTANCES OF EVERY DESCRIPTION;—for further practice, and to prove that the student has attained the object he had in view when entering upon these experimental examinations. All the constituents of a substance under examination must be detected; the nature of the substance must be examined.

II.

TABLE

OF THE

MORE FREQUENTLY OCCURRING FORMS AND COMBINATIONS OF THE SUBSTANCES CONSIDERED IN THE PRESENT WORK,

WITH ESPECIAL REGARD TO THE CLASSES TO WHICH THEY BELONG,

ACCORDING TO THEIR VARIOUS DEGREES OF SOLUBILITY

IN WATER, IN HYDROCHLORIC ACID, OR IN NITRIC ACID.

PRELIMINARY REMARKS.

THE various classes to which compound substances belong according to the division specified at § 106, are expressed by figures. Thus 1 or I means a substance soluble in water; 2 or II a substance insoluble in water, but soluble in hydrochloric acid, or nitric acid; 3 or III a substance insoluble both in water and acids. The Roman figures denote officinal and more frequently occurring compounds, whilst the Arabian figures indicate less frequently occurring compounds. For those substances standing as it were, on the limits between the various classes, the figures of the classes in question are jointly expressed: thus 1—2 signifies a substance difficultly soluble in water, but soluble in hydrochloric acid or nitric acid; 1—3 a body difficultly soluble in water and the solubility of which is not increased by the addition of acids; and 2—3 a substance insoluble in water and difficultly soluble in hydrochloric acid and in nitric acid; wherever the relation of a substance to hydrochloric acid is different from that to nitric acid, this is stated in the notes.

The haloid salts and sulphur compounds will be found in the columns of the protoxide and peroxide. Most of the salts given are neutral, the basic and acid and double salts are mentioned in the notes; the small figures placed near the corresponding neutral or simple salts, refer to these. Cyanogen, chloric acid, citric acid, malic acid, benzoic acid, succinic acid, and formic acid, are of more frequent occurrence only in combination with a few bases, and have, therefore, not been admitted into the table. The most frequently occurring combinations of these substances are: cyanide of potassium I, ferrocyanide of potassium I, ferricyanide of potassium I, sesqui-ferrocyanide of potassium (Prussian blue) III, ferrocyanide of zinc and potassium II—III, chlorate of potash I, the alkaline citrates I, the alkaline malates I, permalate of iron I, the alkaline benzoates I, the alkaline succinates I, and the alkaline formiates I.

A TABLE OF THE VARIOUS FORMS

	KO	NaO	NH_4O	BaO	SrO	CaO	MgO	Al_2O_3	MnO	FeO	Fe_2O_3	CoO	NiO	ZnO
	I	I	I	I	1	I–II	II	II	II	II	II	II	II	
S	I	I	I	I	I	I–II	2		II	II	II	[15]	[16]	II
Cl	I	I	I[12]	I	I	I	I	1	I	I	I[12]	1	I	1
J	I	1	I	1	1	1	I		1	1	1			1
SO_3	I[1]	I	I[13]	III	III	I–III	I	I[1·13]	I	I	I	I	I	I
NO_5	I	I	I	I	I	I	1	1	I	1	I	I	I	1
PO_5	1	I[10]	I[10]	2	2	II[14]	2	2	2	2	II	2	2	2
CO_2	I[2]	I[11]	I	II	II	II	II		II	2		2		II
C_2O_3	I[3]	1	I	2	2	II	2	2	2	1–2	1–2	2	2	2
BO_3	I[4]	I[4]	1	2	2	2	2	2	2	2	2	2	2	2
$\bar{A}$	I	I	I	I	1	1	1	I		1	1	I	1	I
$\bar{T}$	I[5-9]	I[7]	I[6]	2	2	II	1–2	1	1–2	1–2	I[8]	I		2
AsO_5	I	1	1	2	2	2	2	2	2	2	2	2	2	3
AsO_3	I	1	1	2	1	2				2		2	2	
CrO_3	I	1	1	2	2	1	1	2	1		1	2	1	

NOTES.

1. Sulphate of potash and alumina I.
2. Bicarbonate of potash I.
3. Binoxalate of potash I.
4. Tartarized borax I.
5. Bitartrate of potash I.
6. Tartrate of potash and ammonia I.
7. Tartrate of potash and soda I.
8. Tartrate of potash and peroxide of iron I.
9. Tartrate of antimony and potash I.
10. Phosphate of soda and ammonia I.
11. Bicarbonate of soda I.
12. Chloride of iron and ammonium I.
13. Sulphate of ammonia and alumina I.
14. Basic phosphate of lime II.
15. Sulphuret of cobalt is easily decomposed by nitric acid, but very difficultly by hydrochloric acid. This substance is not officinal.

	CdO	PbO	SnO	SnO_2	BiO	CuO	Hg_2O	HgO	AgO	PtO_2	AuO_3	SbO_3	Cr_2O_3
	2	2[18]	2	2 & 3	2	II[22]	II	II	2	2		[35]	II & III
S	2	2	[20]	[20]	2	[23]	III	III	[30]	3		II[36]	
Cl	1	I–III	I	1	1	I[24]	II–III	I[28]	III	I[31-33]	I[34]	I[37]	I
J	1	II	2				II	II	3				
SO_3	I	I	1	1	1	I[25]	1–2	I[29]	I–III	1		2	I
NO_5	1	I			I[21]	I	I[27]	I	I	1			I
PO_5	2	2				2	2	2	2				2
CO_2	2	II			2	II	2	2	2				
C_2O_3	2	II	2		2	2	2	2	2			1–2	1
BO_3	1–2	2	2		2	2	1		2				2
$\overline{A}$	1	I[19]	1	1	1	I[26]	1–2	1	I			1	1
$\overline{T}$	1–2	II	1–2		2	1	1-2	2	2			I[38]	1
AsO_5		2			2	2	2	2	2			2	1
AsO_3		2				II	2	2	2			2	
CrO_3		II–III	2		2	2	2	1–2	2			2	2

16. The same applies to sulphuret of nickel.

17. The same applies to sulphuret of zinc.

18. Minium is converted by hydrochloric acid into chloride of lead, by nitric acid into an oxide soluble in an excess of the acid and into brown peroxide of lead, insoluble in nitric acid.

19. Basic acetate of lead I.

20. Sulphuret and bisulphuret of tin are decomposed and dissolved by hydrochloric acid, whilst they are converted into insoluble oxides by nitric acid in excess. Sublimed bisulphuret of tin dissolves only in aqua regia.

21. Basic nitrate of bismuth II.

22. Ammoniacal oxide of copper I.

23. Sulphuret of copper is difficultly decomposed by hydrochloric acid, but with facility by nitric acid.

24. Chloride of copper and ammonium 1.

25. Sulphate of copper and ammonia 1.

26. Basic acetate of copper, soluble partially in water, and completely in acids.

27. Basic protonitrate of mercury and ammonia II.
28. Basic chloride of mercury and ammonium II.
29. Basic persulphate of mercury II.
30. Sulphuret of silver soluble only in nitric acid.
31. Sulphuret of platinum is not affected by hydrochloric acid; boiling nitric acid converts it into a soluble sulphate of platinum.
32. Chloride of platinum and potassium 1—3.
33. Chloride of platinum and ammonium 1—3.
34. Chloride of gold and sodium I.
35. Oxide of antimony soluble in hydrochloric acid, but not in nitric acid.
36. Sulphuret of antimony and calcium 1—2.
37. Basic chloride of antimony II.
38. Tartrate of antimony and potash I.

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